

American Chemical Society
Division of Colloid and Surface Chemistry
ABSTRACTS

228th ACS National Meeting

Philadelphia, PA
August 22-26, 2004

R. Nagarajan, Program Chair

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- **Catalysis by Metal Oxides: Comparison Between Bulk Mixed Oxides, Supported Oxides, Oxide Clusters, Organometallic Oxides and Oxide Single Crystals**
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DIVISION OF COLLOID AND SURFACE CHEMISTRY

1. MULTISCALE CHALLENGE OF MACROMOLECULAR COMPLEXES: FROM ION CHANNELS TO VIRUSES. *Rob Phillips, Applied Physics, California Institute of Technology, 1200 E. California Blvd, CA 91125, phillips@aero.caltech.edu*

Many of the most intriguing biological structures within cells are assemblies of various components such as nucleic acids, proteins and lipids. This talk will describe two case studies: one involving the life cycle of bacterial viruses and the other of which involves the action of membrane-bound proteins whose function is dictated by tension in the surrounding membrane. In particular, I will illustrate how continuum models can be exploited to produce a predictive description of these systems, in the first case treating DNA as a one-dimensional elastic rod and in the second, treating lipid-bilayer membranes as an elastic sheet. It will be argued that though such models provide a useful starting point for describing macromolecular complexes, there remain outstanding atomic-scale effects such as sequence-dependent elasticity of DNA and residue-specific properties of proteins which have experimental consequences and are one of the central "multiscale" challenges in thinking about biological macromolecular assemblies.

2. THERMALLY ACTIVATED FLEXIBILITY IN BIOPOLYMERS. *Philip C Nelson, Physics, University of Pennsylvania, David Rittenhouse Lab, 209 S 33d St, Philadelphia, PA 19104, Fax: 215-898-2010, nelson@physics.upenn.edu*

Recent experiments have measured a rate of spontaneous looping in short DNA fragments that is orders of magnitude greater than the prediction of fluctuating elastic rod models (the wormlike chain and its successors). Generalizations of the wormlike chain model that include fixed, sequence-dependent kinks also appear to be unable to explain the new results. Instead, the experiments strongly suggest that DNA can transiently develop sharp kinks, not accounted for by the linear rod elasticity assumed in existing models. The question then arises as to why the elastic-rod models have given such a good account of other experiments on DNA, for example, single-molecule force-extension curves. We formulate two simple models of DNA with thermally-activated, flexible tracts, and show that these models can allow a significant population of such tracts while still fitting available force-extension data.

3. THEORY OF POLYMORPHISM IN BACTERIAL FLAGELLA. *Thomas R. Powers and Srikanth Srigriraju, Division of Engineering, Brown University, Box D, Providence, RI 02912, Fax: 401-863-9009, Thomas_Powers@brown.edu*

Escherichia coli and *Salmonella* swim using several flagella, each of which consists of a rotary motor, a universal joint known as the hook, and a helical filament which acts as a propeller. The filament is normally left-handed in the absence of external stress, but undergoes mechanical phase transitions to other helical states ("polymorphs") in response to external torque. The filament is made of identical flagellin protein subunits which are organized into eleven protofilaments which wind around the filament. We develop an effective theory in which the flagellin subunits and their connections along the protofilaments are modelled with a double-well potential. A helical spring represents the other connections of the subunits, and introduces a twist-stretch coupling and an element of frustration in our model. We solve for the ground states and the phase diagram for filament shapes.

4. ACTIN SELF-ASSEMBLY AND LISTERIA MOTILITY. *Andrea J. Liu, Ajay Gopinathan, Jennifer Schwarz, and Kun Chun Lee, Dept. of Chemistry and Biochemistry, UCLA, 405 Hilgard Ave, Los Angeles, CA 90095, Fax: 310-267-0319, liu@chem.ucla.edu*

The bacterial pathogen *Listeria monocytogenes* hijacks the actin machinery of the host cell in order to move through it to infect neighboring cells. Polystyrene

beads coated with the protein ActA have been shown to use actin polymerization to move through actin-rich cytoplasmic extracts, much as *L. cytogenes* moves through cells. The Theriot group has measured the mean speed of the beads as a function of bead size, and has found that there is a maximum in the mean speed at a size similar to that of the bacterium. Previous theories of the propulsion mechanism predict either a monotonic increase or monotonic decrease in mean speed as a function of bead size. We present a simple Brownian ratchet model for actin-based propulsion that yields a maximum in the mean speed with quantitatively reasonable predictions for the mean speed as a function of bead size.

5. PROBING THE ELECTRONIC STRUCTURE AND CHEMICAL BONDING OF METAL OXIDE CLUSTERS USING PHOTOELECTRON SPECTROSCOPY. *Lai Sheng Wang, Department of Physics, Washington State University, 2710 University Drive, Richland, WA 99352, Fax: 509-376-6066, ls.wang@pnl.gov*

I will present our effort to elucidate the electronic structure and chemical bonding of metal oxide clusters using photoelectron spectroscopy and theoretical calculations. One key advantage of cluster studies is the flexibility to create clusters with any stoichiometry. I will show that metal oxide clusters with fixed numbers of metal atoms exhibit a behavior of sequential oxidation up to the maximum oxidation state of the metal atoms. For oxygen-rich clusters, O₂ unit begins to appear as per- or super-oxide. Comparison between photoelectron spectra and theoretical calculations will be used to provide detailed information about the structures and chemical bonding of oxide clusters. This information is the prerequisite to understanding the chemical reactivities of the clusters and providing insight into catalytic mechanisms of metal oxide materials. Preliminary studies on the electronic structure of polyoxometalate anions in the gas phase using electrospray and photoelectron spectroscopy will also be discussed.

6. REACTIVITY OF THE OXYGEN SITES IN THE V₂O₅-TiO₂ (ANATASE) CATALYST: A PERIODIC DFT STUDY. *M. Calatayud, Laboratoire de Chimie Théorique, Université P. et M. Curie, 4, PI Jussieu, 75252 Paris, France, Fax: +33144274117, calatayu@lct.jussieu.fr, and Christian Minot, Laboratoire de Chimie Théorique, University Pierre et Marie Curie, Paris VI, case 137, 4, place jussieu, Paris cedex 05 75252, France, Fax: 33-1-44-27-41-17, minot@lct.jussieu.fr*

Supported metal-oxide catalysts are widely used in industrial processes. They consist of two-dimensional metal oxide layers like vanadia deposited on a metal oxide support (titania, alumina, silica). The oxide/support interaction plays a major role in the catalytic reaction but little is known on the structure at an atomic level. Evolution of the computational techniques makes now available the construction of realistic surface models. In this work we will study the structure of V₂O₅/TiO₂ catalyst by means of periodic GGA calculations with the VASP program. We propose a model for dimeric V₂O₅ units deposited on the (100) and (001) surfaces of anatase TiO₂. We will investigate the reactivity of the different oxygen sites present at the interface. According to our results, the V-O-Ti oxygen atoms would be the most reactive ones, while the vanadyl V=O atoms would not be as reactive as proposed in the literature.

7. TD-DFT ANALYSIS OF THE ELECTRONIC SPECTRA OF TI-CONTAINING CATALYSTS. *M. C. Capel-Sanchez, Victor A. de la Pena-O'Shea, Gema Blanco-Brieva, Jose M. Campos-Martin, and Jose L. G. Fierro, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie, s/n, Madrid E-28049, Spain, Fax: +34-91-585-4760, mcapel@icp.csic.es*

Ti-containing catalysts (TS-1, Ti-, Ti ordered mesoporous silica, Ti-xerogels and Ti/SiO₂) exhibit high efficiency and molecular selectivity in oxidation reactions with H₂O₂ under mild conditions. Although there is a large body of

current agreement that the active site is titanium in tetrahedral coordination, there is still a considerable debate over the type of species present in the catalysts. One of the most useful tools to study the titanium environment is the UV-Vis spectroscopy. The electronic spectra of Ti-containing catalysts show absorption associated with the ligand metal charge transfer from the oxygen to the TiIV ion: $Ti4+O2- \rightarrow Ti3+O-$. Our work revealed a correlation between the Ti sites coordination showed by experimental UV-vis and photo-physical properties calculated using Time-Dependent Density Functional Theory (TD-DFT). This finding makes the TD-DFT methodology an excellent tool to generate and interpret the electronic spectra of isolated atoms in the surface of heteroatom-containing inorganic substrates.

8. PHYSICO-CHEMICAL INTERACTIONS BETWEEN TRANSITION METAL OXIDES AND NOBLE METAL CLUSTERS: PROMOTER EFFECTS IN SUPPORTED METAL CATALYSIS.

Bert M. Weckhuysen and **Fernando Morales**, *Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Sorbonnelaan 16, Utrecht 3508 TB, Netherlands, Fax: +31-30-2511027, b.m.weckhuysen@chem.uu.nl*

The performances of supported metal catalysts are often enhanced by the addition of the correct amounts of metal oxides and the specific preparation method. In this presentation, we will discuss the effect of the addition of MnO₂ on the electronic properties of TiO₂-supported Co particles active in Fischer-Tropsch catalysis. TEM-EELS provides information on the exact location of the Mn oxide phase, whereas soft X-ray absorption spectroscopy monitors the surface electronic properties of the supported Co particles.

9. EXPLORING THE CATALYTIC PROPERTIES OF MCM-41 THROUGH THE REDUCTION OF METHYL VIologen BY SULFIDE IONS.

Yan Ting Liao, *Department of Chemistry, College of The City University of New York, New York, NY 10031, Fax: 00, Yanting_liao@yahoo.com, Ling Zang, Chemistry and Biochemistry, Southern Illinois University, and Daniel L. Akins, Department of Chemistry and The Center for Analysis of Structures and Interfaces, The City College of the City University of New York*

Methyl viologen in the presence of mesoporous MCM-41 and sulfide ions is found to experience, at room temperature, a spontaneous catalytic reduction to methyl viologen radical (MV^{•+}). Various control experiments, including passivation of the external surface and modification of the internal surface of MCM-41, indicate that the catalytic reduction occurs principally within the pores of MCM-41. The source of the sulfide ions can be either an added salt or sulfide ions at the surface of an occluded sulfide nanoparticle. The present system offers a means for the spontaneous formation of methyl viologen radicals, allowing for spectroscopic study of this widely used charge transfer partner. Also, the catalytic reaction that occurs provides a means to determine the presence and location of sulfide nanoparticles synthesized within or outside the pores of mesoporous materials.

10. γ -ALUMINA SUPPORTED Na_2CO_3 , K_2CO_3 , AND CuO FOR FLUE GAS DESULFURIZATION.

D. E. Jiang¹, **Biying Zhao**², and **Youchang Xie**². (1) *Department of Chemistry and Biochemistry, University of California, Los Angeles, Box 951569, Los Angeles, CA 90095-1569, Fax: 310-267-0319, djiang@chem.ucla.edu*, (2) *Institute of Physical Chemistry, Peking University*

The removal of SO₂ from flue gas is an important environment issue. Conventional processes employ non-regenerable wet lime-limestone system to absorb SO₂ and the resulting plaster usually ends up as landfill. New promising technology using regenerable adsorbents can recover sulfur as more valuable products such as sulfuric acid. Here we investigate γ -alumina supported Na₂CO₃, K₂CO₃, and CuO as regenerable adsorbents for SO₂ removal from air. We use γ -alumina because its pore size and shape can be easily tuned. We prepare all the adsorbents based on the principle of spontaneous monolayer dispersion of oxides or salts on high-surface-area supports. We characterize them with XRD, BET, and XPS, and measure their capacities to adsorb SO₂ by breakthrough curves. We find an excellent correlation between the maximum adsorption capacity of SO₂ and the monolayer loading of Na₂CO₃, K₂CO₃, or CuO on γ -alumina.

11. ADSORPTION OF H₂S ONTO ACTIVATED CARBON FIBERS UNDER DRY AND ANOXIC CONDITIONS.

Wenguo Feng¹, **Xue Feng**², **Eric Borguet**³, and **Radisav Vidic**¹. (1) *Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, PA 15260, wef3@pitt.edu*, (2) *Department of Chemistry, University of Pittsburgh*, (3) *Chemistry Department and Surface Science Center, University of Pittsburgh*

Adsorption of hydrogen sulfide on activated carbon fibers (ACFs) was studied using a fixed bed reactor under dry and anoxic conditions. Adsorption/desorption of H₂S onto/from three ACF samples after different pre-treatment (oxidation with pure oxygen or heat treatment at 900 °C) were investigated. The surface area and pore size distribution of ACFs before and after treatment were analyzed using N₂ adsorption. H₂S adsorption amount increased with an increase in pore volume and/or surface area. Both oxidation with pure oxygen and heat treatment slightly improved the adsorption capacity. On the other hand, oxidation with HNO₃ resulted in a significant increase in the adsorption capacity. In all cases, a certain amount of hydrogen sulfide was irreversibly adsorbed onto the carbon surface (could not be desorbed in a pure nitrogen flow). This finding is supported both by H₂S breakthrough studies and by sulfur analysis of ACF samples before and after desorption in nitrogen. The irreversible adsorption was much more pronounced at 150 °C than at room temperature. Temperature programmed desorption (TPD) showed peaks around 200-300 °C, indicating strong interactions between the sulfur compounds and the carbon surface. FTIR study also showed the existence of sulfur species of higher valence, such as -SO₃H group.

12. CATALYTIC PROPERTIES OF ACTIVATED CARBON SURFACE IN THE PROCESS OF ADSORPTION/OXIDATION OF METHYL MERCAPTAN.

Svetlana Bashkova¹, **Andrey Bagreev**², and **Teresa J. Bandoz**². (1) *Chemistry, Graduate School of City University of New York, 138th Street and Convent Ave, New York, NY 10031, Fax: 212-650-6107, sbashkova@yahoo.com*, (2) *Chemistry, City College of New York*

Activated carbons of different origins were used as adsorbents of methyl mercaptan (MM). Before the MM breakthrough capacity tests were carried out the surface of carbons was characterized from the point of view its chemistry (Boehm titration) and porosity (adsorption of nitrogen at its boiling point). The results showed that the ability of carbon to adsorb methyl mercaptan depends strongly on its surface chemistry, particularly on the presence of basic oxygen-containing groups and ash content. Catalytic effect of one metal, iron, was studied in more details. It was found that introduction of iron enhances the removal capacity significantly as a result of electron transfer reaction in which thiolate ion is oxidized to dimethyl disulfide (DMDS). This reaction involves likely the reduction of iron sites, which are regenerated after further exposure to oxygen. DMDS as a main reaction product is strongly adsorbed in small pores. Water is required for the formation of DMDS since it facilitates dissociation of MM. That dissociation occurs in water film when pH of the local system is greater than apparent pK_a of MM in the confined pore space.

13. DIFFUSION OF VOLATILE ORGANIC MATERIALS IN A NATURAL ZEOLITE.

Billur Sakintuna, **Enis Fakiođlu**, and **Yuda Yurum**, *Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul 34956, Turkey, Fax: 90-216-4839550, billur@su.sabanciuniv.edu*

In most phenomena occurring to molecules in zeolites, diffusion plays an essential role. Although literature contains some theoretical values, there is lack of experimental data about diffusion of volatile organic materials in zeolites. The diffusion coefficients of methanol, ethanol, propanol and pyridine into the porous structure of Turkish Manisa G6rdes zeolite at 24-30°C were measured, using Fick's law. Organic material uptake of the zeolite samples was recorded in an adiabatic set up until a constant weight was attained. The diffusion coefficients of methanol measured from the slope of graphs of Mt /M versus t /2 were 4.0095x10⁻¹⁴ m²/s and 4.6560x10⁻¹⁴ m²/s respectively at 24°C and 30°C. for the consecutive steps during the diffusion process. Activation energies calculated for different temperatures were 11.06 and 18.25 kJ/mol respectively for ethanol and methanol.

14. EFFECT OF SURFACE SPECIES ON THE RATE OF HYDROGEN SORPTION INTO NANOSTRUCTURED PALLADIUM. *Jan Marwan, Département de Chimie, Université de Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal, QC H3C 3P8, Canada, Jan_Marwan@yahoo.ca, and Philip N. Bartlett, School of Chemistry, University of Southampton*

Mesoporous metals with regular nanoarchitectures can be prepared using chemical or electrochemical reduction of a metal salt dissolved in the aqueous domains of a lyotropic liquid crystalline phase. In this approach the metal is formed from the lyotropic phase of a non-ionic surfactant (typically between 30 and 60 wt%) and an aqueous solution of the appropriate metal salt. The resulting H1-e metals are "casts" of the particular lyotropic phase used so that it is possible to produce mesoporous metals with different pore topologies and with different pore and wall thicknesses depending on the choice of surfactant and template solution composition. H1-e metal films have very high surface area (in excess of 10^6 cm²/cm³) and were found to be useful as catalysts in chemical sensors, batteries and fuel cells. In Pd films deposited from the hexagonal lyotropic liquid crystalline phase the Pd walls between the pores are only a few nanometres thick. Consequently the diffusion of hydrogen atoms into Pd bulk is not the rate-limiting step. Studies of the hydrogen region of the resulting H1-e Pd films in 1 M sulphuric acid reveal well resolved peaks associated to the hydrogen adsorption and absorption process which can be readily distinguished due to the thin walls of the nanostructure and the high surface area. Cyclic voltammetric measurements indicate that the absorption process takes place without passing through the adsorbed state so that hydrogen diffuses directly into Pd bulk. This process speeds up when the formation of adsorbed hydrogen is suppressed by the coverage with crystal violet or Pt. The permeation of hydrogen into the Pd metal lattice then occurs with fast kinetics. We suggest that strongly adsorbed hydrogen on the Pd surface acts as a blocking layer for the absorption of hydrogen into the Pd lattice.

15. ETHYLMETHYLAMINE ADSORPTION ON ACTIVATED CARBONS: ROLE OF SURFACE CHEMISTRY. *Yehya A. Elsayed, Department of Chemistry, City College of the City University of New York, 138 Street & Convent Avenue, Marshak Bldg., J1024, New York, NY 10031, Fax: 212-650-6107, yehya1975@hotmail.com, and Teresa J. Bandosz, Chemistry, City College of New York*

Samples of activated carbons of various origins were used in this study. The initial samples were modified by oxidation with nitric acid or by impregnation with urea followed by heat treatment. The modifications were done to introduce oxygen and nitrogen containing groups to the carbon matrix. The surface of the carbon samples was characterized using sorption of nitrogen, Boehm and potentiometric titrations, and thermal analysis. Ethylmethylamine adsorption isotherms from aqueous solution were measured at 299 K. The results showed that the amount of ethylmethylamine adsorbed on all carbons at high concentration is dependent on the total number of surface groups whereas at low concentration it is governed by the number of acidic groups. This indicates that hydrogen bonding and/or specific acid-base interactions play an important role in the process of ethylmethylamine adsorption on activated carbons.

16. KINETICS OF PROTEIN ADSORPTION: MULTISCALE MOLECULAR APPROACH. *Igal Szleifer, Department of Chemistry, Purdue University, 1383 Brown Building, West Lafayette, IN 47907, Fax: 765-494-0239, igal@purdue.edu*

Protein adsorption is a challenging fundamental problem due to the interplay between electrostatic, van der Waals, steric and solvation interactions that results in very large competing energy scales and very long time scales. In this talk we present a theoretical approach aimed at understanding the kinetics and thermodynamics of protein adsorption. We will concentrate our attention to the application of the theory to understand the role of grafted polymers as surface modifiers to control protein adsorption. The theoretical approach is aimed at integrating the time and length scales from atomistic to the meso and macroscopic scales necessary to describe protein adsorption isotherms and the kinetics of protein adsorption. The molecular theory enables the systematic study of the equilibrium and kinetics of protein adsorption. The basic idea of the kinetic approach is the separation of time scales into fast and slow motions and then averaging over the fast degrees of freedom to be able to study the slow moving proteins. From the results of the complex simulations we find the rate

determining step and build a modified kinetic approach that enables the systematic study of adsorption and desorption of proteins. The last part of the presentation will be used to demonstrate how the theory can be applied to design surface modifiers that can trap proteins. We will show how to control the rate of protein desorption from an electrode surface, by combining the proper molecular architecture of grafted polymers and the applied electrostatic potential on the electrode. Finally, we will describe the limitations of the theory and the directions that we are taking to improve it.

17. PROBABILISTIC DESIGN OF FOLDING HETEROPOLYMERS. *Jeffery G. Saven, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, Fax: 215-573-2112, saven@sas.upenn.edu*

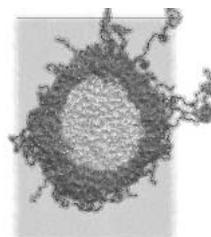
Proteins are the most well known example of folding heteropolymers: chain molecules that reversibly self-organize to form well-determined three-dimensional structures. Theoretical methods will be presented for the design and study of such polymers, and the experimental characterization of designed folding heteropolymers will also be discussed.

18. RESOLUTION FOCUSING IN SIMULATIONS OF MOLECULAR LIQUIDS. *Cameron F. Abrams, Department of Chemical Engineering, Drexel University, 3141 Chestnut St., Philadelphia, PA 19104, Fax: 215-895-5837, cfa22@drexel.edu*

We discuss a technique to simulate, using molecular dynamics (MD), a liquid in a sample volume which is divided into subvolumes of different resolutions. The case study we consider is liquid methane, which in region I is represented as a fully atomistic 5-center model (a), and in region II as a coarse-grained super-atom (c). Molecule trajectories may cross the I-II boundary, and each crossing results in either an a→c or c→a mapping event. We describe algorithms (1) to handle the transfer of momentum and energy upon mapping, and (2) to construct proper coarse-grained interaction potentials. We consider both planar and spherical boundaries. By describing how to "focus in" on a region of interest in an otherwise coarse-grained liquid to see atomic-level detail, it is hoped that this preliminary work will contribute to multiscale modeling efforts aimed at understanding the role of atomic detail in the behavior of more complex fluids.

19. SELF ASSEMBLY AND PROPERTIES OF DIBLOCK COPOLYMERS VIA COARSE GRAIN MOLECULAR DYNAMICS. *Goundla Srinivas, department of Chemistry, Center for Molecular Modeling, Department of Chemistry, University of Pennsylvania, 231S, 34th Street, Philadelphia, PA 19104, srini@cmm.upenn.edu, Dennis Discher, School of Engineering and Applied Science, University of Pennsylvania, and Michael L. Klein, Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania*

Block copolymer amphiphiles have recently been observed to assemble into vesicles and other morphologies long known for lipids but with remarkably different properties. Coarse grain molecular dynamics (CG-MD) is used herein to elaborate the structures and properties of diblock copolymer assemblies in water. By varying the hydrophilic/hydrophobic ratio of the copolymer in line with experiment, the bilayer, cylindrical, and spherical micelle morphologies spontaneously assemble. Varying the molecular weight (MW) with hydrophilic/hydrophobic ratio appropriate to a bilayer yields a hydrophobic core thickness that scales as a random coil polymer, in agreement with experiment, for large MW. The extent of hydrophobic-segment overlap in the core increases nonlinearly with MW, indicative of chain entanglements and consistent with the reported dramatic decrease in lateral mobility in polymer vesicles. Calculated trends with MW agree with experiment, demonstrating that CG-MD simulations provide a rational design tool for diblock copolymer assemblies.



20. COARSE-GRAIN MOLECULAR DYNAMICS STUDY OF INTERACTIONS BETWEEN TRANSMEMBRANE NANOTUBES. *Steve O. Nielsen¹, Bernd Ensing², Preston B. Moore³, and Michael L. Klein¹.* (1) Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104-6323, Fax: 215-573-6233, snielsen@cmm.upenn.edu, (2) Department of Chemistry, University of Pennsylvania, (3) Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia

A generic nanotube functionalized with hydrophilic termini can insert into a biomembrane, forming a nanopore. The direct and membrane-mediated interactions between these nanopores can lead to their aggregation and has implications for the design of synthetic channels and antibiotics. The role of hydrophobic/hydrophilic matching is examined in this context. Specifically, the loss of stability due to the hydrophobic/hydrophilic mismatch is quantified by measuring the free energy of the meniscus. Then, an attempt is made to relate this free energy to the aggregation propensity.

21. ENTROPICALLY DRIVEN HELIX FORMATION. *Yehuda Snir, Physics and Astronomy, University of Pennsylvania, DRL, 209 S 33rd St, Philadelphia, PA 19104, ysnir@student.physics.upenn.edu, and Randall D. Kamien, Department of Physics and Astronomy, University of Pennsylvania*

We model the entropically driven self-assembly of a long polymer chain in the presence of noninteracting spherical colloids. The polymer is forced to bend due to the thermodynamic interaction with the colloids. By modeling the polymer as a long, semi-flexible tube we calculate the equilibrium shape of the tube that minimizes its depletion volume. We find that the minimal shape of the tube is a helix of radius and pitch that weakly depends on colloid size for small colloids.

22. MODIFICATIONS ON V-O SURFACE: STUDIES BY AB INITIO DFT METHOD. *Malgorzata Witko, Renata Tokarz-Sobieraj, and Robert Grybos, PAS, Institute of Catalysis and Surface Chemistry, ul. Niezapominajek 8, Cracow 30239, Poland, Fax: 48124251923, ncwitko@cyf-kr.edu.pl*

In the course of any catalytic reaction a number of different products can be obtained and the role of the catalyst is to accelerate only one path that leads to the desired product. Often a small modification of the catalyst composition alters its catalytic properties to such an extent that the direction of the reaction is changed and a new product is formed. Influence of different modifications (formation of surface species, creation of surface vacancies, dopant and support effects, addition of other element) on the electronic properties of the catalyst will be discussed on an example of V2O5 surface. Surface species facilitate formation of surface vacancy, local defect and dopant create new energy levels, which are chemically active, support acts as an electron reservoir fixing the Fermi level and/or allows for the formation of catalytically active structures not found in crystalline V2O5, whereas the additional third element (Mg, P) changes the nucleophilicity of surface oxygen.

23. MECHANISTIC STUDIES OF THE REACTION OF ORGANOSULFUR COMPOUNDS ON METAL OXIDE SINGLE CRYSTAL SURFACES. *John M. Vohs and Barr Halevi, Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 220 S. 33rd street, Philadelphia, PA 19104-6393, vohs@seas.upenn.edu*

The interaction of SO₂, H₂S and organosulfur compounds, such as thiols and disulfides, with metal oxide surfaces is an increasingly important area of heterogeneous catalysis. For example, catalytic hydrodesulfurization using oxide or sulfide-based catalysts is used for the removal of sulfur from hydrocarbon feedstocks and metal oxide catalysts are used in the synthesis of thiols and alkylsulfides. While these examples illustrate the importance of the reactions of sulfur containing compounds on oxide surfaces, the mechanisms of these reactions are generally not well understood. In an effort to develop structure-activity relationships for the reaction of organosulfur compounds on oxides we have recently started to investigate the interaction of thiols and disulfides with metal oxide single crystal surfaces. Our experimental approach is similar to that which has been used previously to study the mechanism of selective oxidation reactions on oxide surfaces and makes use of TPD of probe molecules to measure reaction kinetics and energetics and surface sensitive spectroscopic

probes such as XPS and HREELS to identify stable surface intermediates. In this talk we will present our most recent results for the reaction of methane and ethane thiols on the (0001) and (000-1) surface of ZnO.

24. SELECTIVE OXIDATION OF METHANETHIOL AND ISOPROPANETHIOL: ACTIVE SITES AND REACTION PATHWAYS. *Hanjing Tian, Department of Chemical Engineering, Lehigh University, 7 Sinclair 120, Lehigh University, Bethlehem, PA 18015, Fax: 610-758-6555, hat2@lehigh.edu, and I. E. Wachs, Department of Chemical Engineering, Lehigh University*

Methanethiol and isopropanethiol oxidation under steady-state condition have been investigated. Five standard catalysts: Al2O3 (pure acidic sites), 11.5%K2O/Al2O3 (pure basic sites), 20%V2O5/Al2O3, (acidic and redox sites), 11.5%K2O-20%V2O5/Al2O3 (basic and redox sites) and 20%V2O5/Al2O5 (pure redox sites) were studied. The Lewis acidic surface sites exclusively yielded disulfide and H2O. The surface basic sites were not selective and produced disulfide and COx. The surface redox sites were selectively formed oxygenates, and SO2. Thus, only surface acidic and surface redox sites were found to be selective for thiol oxidation to disulfides and oxygenates, respectively. The formation of disulfides revealed that the surface intermediates during thiol oxidation are present as surface alkane thiolates, CH3S* and (CH3)2CHS*, and the S-H bond is cleaved upon adsorption. In the presence of labile surface oxygen, the alkane thiolate intermediates were converted to surface alkoxides, CH3O* and (CH3)CH2O*, by S-O exchange, which is as same intermediate as alcohol oxidation.

25. NO OXIDATION CATALYSIS: ALTERNATIVES TO PRECIOUS METALS. *Peter J. Schmitz¹, Robert J. Kudla², Andrew R. Drews¹, Dairene Uy¹, Ann E. Chen³, Erica P. Murray¹, Christian C. Goralski Jr.², Charlotte K. Lowe-Ma¹, and William F. Schneider¹.* (1) Physical and Environmental Science Department, Ford Motor Company, MD3083, SRL, P.O. Box 2053, Dearborn, MI 48121-2053, Fax: 313-322-7044, pschmit1@ford.com, (2) Chemical Engineering Department, Ford Motor Company, (3) Material Science Department, Ford Motor Company

The development of catalysts and control strategies for lean-burn gasoline and diesel technologies continues to be a primary driver for automotive catalysis research. These lean technologies offer inherently better fuel economy but are beset by challenges related to NOx and particulate removal. Most NOx and particulate remediation strategies depend on the use of an oxidation catalyst to convert NO to NO2, a function traditionally accomplished using Pt-based catalysts. Attractive alternatives include supported base-metal oxides given their low cost and stability in a lean environment. Previous attempts to employ oxide catalysts for stoichiometric gasoline applications were inhibited by their tendency for thermal deactivation and sulfur poisoning. However, advances in fuel formulations coupled with the low operating temperatures of both lean-burn gasoline and diesel suggest that they may yet prove viable. The work to be presented focuses on the use of a high throughput approach for providing a systematic evaluation of the synthesis and NO oxidation screening of supported Pt and base-metal oxide systems. We propose an approach that deemphasizes simple acceleration of the development and optimization process, and instead concentrates on the establishment of a comprehensive understanding of NO oxidation catalysis as a means of advancing system design and optimization.

26. INFLUENCE OF STRUCTURE ON THE PERFORMANCE OF CU/ZRO2 METHANOL SYNTHESIS CATALYSTS. *Michael D. Rhodes, Konstantin Pokrovski, and Alexis T. Bell, Chemical Sciences Division, Lawrence Berkeley National Laboratory, and Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462, mrhodes@berkeley.edu*

Cu/ZrO2 exhibits particularly high activity for methanol synthesis from both CO and CO2. In-situ infrared spectroscopy studies demonstrate that Cu/ZrO2 operates in a bifunctionally. Zirconia adsorbs CO/CO2, and all carbon-containing intermediates, whereas Cu particles adsorb H2 dissociatively and provide a source of H atoms to the zirconia via spillover. The present study has examined the influence of zirconia phase and Cu loading, as well as the effects of introducing Ce into the ZrO2 lattice, on catalyst activity and selectivity for methanol synthesis from CO/H2. For a fixed Cu dispersion, catalysts prepared using monoclinic zirconia were 5-6 times more active than those prepared using tetragonal zirconia. Substitution of Ce into the ZrO2 lattice produced a further

twofold increase in activity. All increases in activity were accompanied by an increase in selectivity. Enhanced methanol synthesis activity is attributable to an increase in concentration of mildly acidic Zr-OH groups and an enhanced CO adsorption capacity.

27.

HIGH SURFACE AREA, MESOPOROUS FIBERS FOR REMOVAL OF ORGANICS FROM WATER. *Zhongren Yue¹, James Economy¹, Kishore Rajagopalan², Gary Bordson², and Marv Piwoni².* (1) Department of Materials Science & Engineering, University of Illinois, 1304 W. Green St., Urbana, IL 61801, Fax: 217-333-2736, yue@staff.uiuc.edu, jeconomy@staff.uiuc.edu, (2) Illinois Waste Management and Research Center

High surface area, mesoporous materials were prepared for the removal of organic from water. Cellulose or polyacrylonitrile (PAN) were dissolved in 66 wt% of ZnCl₂. Fiber glass was dip-coated into these solutions then heat stabilized in air, activated in N₂ at a temperature lower than 600°C. The resulting materials displayed high BET surface area, for example, cellulose-based material made at 400°C has a BET surface area between 2000-3000 m²/g. The pore size distributions can be controlled by the temperatures of heat stabilization and activation. The peak value of mesopore size is 20 Å to 40 Å. This material shows an enhanced adsorption capacity to humic acid from water. Furthermore, the low temperature activation results in a high content of oxygen-containing functional groups for cellulose-based material and nitrogen-containing groups for PAN-based material. These functional groups along with high surface area are expected to improve the adsorption of polar organics (such as MTBE and humic acid) in water.

28.

HYDRATION STRUCTURE OF RBBR NANOSOLUTION CONFINED IN CARBON MICROPORES. *Takahiro Ohkubo¹, Hirofumi Kanoh², Hideki Sakai¹, Masahiko Abe¹, and Katsumi Kaneko².* (1) Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan, Fax: 81-4-7122-1442, (2) Department of Chemistry, Faculty of Science, Chiba University

Understanding the electrolytic solution confined in nanospaces (nanosolution; NSN) is indispensable to develop the energy capacitor systems and to provide carrier mechanism of ions in biochemical systems. We revealed the structural anomalies of hydration structure of NSN of RbBr confined in nanospaces of pitch-based activated carbon fibers (ACFs) with EXAFS technique. The structural information around a Rb ion shows that the distance between a Rb ion and a water molecule decreases in smaller nanospaces, indicating the strong compression effect in narrower nanospaces. On the other hand, the structure around a Br ion shows the strong dehydration effect stemming from the cluster-mediate ordering of water molecules in hydrophobic nanospaces. Hence, NSN cannot form the hydration structure similar to the bulk solution. Also the pore width governs the special structure of NSN.

29.

NANOPOROUS STRUCTURES FOR METAL ION DETECTION. *Nancy N. Kariuki, Jin Luo, Li Han, Mathew M. Maye, Tanya Menard, Asif Hassan, and Chuan Jian Zhong,* Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6000, nkariuki@binghamton.edu

Nanostructured thin films with tunable nanoporous structures have potential applications in monitoring and removal of heavy metals from the environment. In this presentation, we will describe a three-dimensional ligand framework that was formed by hydrogen-bonding mediated assembly of gold nanoparticles capped with alkanethiolate shell using carboxylic acid-functionalized alkyl thiols as the mediating or linking agents. The assemblies exhibit nanoporous structures with open frameworks in which void space forms channels with the nanometer sized cores defining its size and the shell structures defining the chemical specificity of the channels. The interfacial fluxes of a series of metal or complex ions and their redox reactivities at the nanoporous thin films have been characterized using electrochemical and FTIR techniques. It is shown that the nanostructure has the capability of molecular recognition for metal ion detection, and the interfacial mass fluxes are reversible. Implications of the results to the design of nanocomposite membranes for chemical/biological sensing will also be discussed.

30.

REMOVAL OF TRACE AMOUNTS OF ATRAZINE FROM WATER USING POROUS CARBONS COATED ON A FIBERGLASS SUBSTRATE. *Zhongren Yue¹, James Economy¹, Kishore Rajagopalan², Gary Bordson², and Marv Piwoni².* (1) Department of Materials Science & Engineering, University of Illinois, 1304 W. Green St., Urbana, IL 61801, Fax: 217-333-2736, yue@staff.uiuc.edu, jeconomy@staff.uiuc.edu, (2) Illinois Waste Management and Research Center

A new generation of low cost, high surface area porous materials has been developed for removal of trace atrazine from water. These porous materials were prepared by coating fiber glass assemblies with a polymeric solution (such as, phenolic resin, polyacrylonitrile (PAN) or polyvinyl alcohol (PVA)) along with a chemical activation agent such as ZnCl₂ or H₃PO₄, then stabilization and heat treatment in N₂ or air at 300-500°C. The isotherm data confirm that chemically activated carbon coated on fiberglass displays a higher adsorption capacity for atrazine than commercially available GAC, primarily because the chemically activated carbon materials have an increased pore size as well as higher surface areas. The breakthrough tests show that a filter made from chemically activated porous materials is at least eight times more effective than commercially available GAC filter to remove the atrazine to below current EPA standards and far more effective in the range below one part-per-billion. The filter can be regenerated under modest conditions, and shows a better competitive adsorption of atrazine in presence of 5000 ppb of humic acid.

31.

HIGH SURFACE-AREA ALUMINA OXIDE-SUPPORTED MANGANESE OXIDE BY COLLOIDAL PRECIPITATION. *Jose M. Bermudez, Wan Y. Shih, and Wei Heng Shih,* Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street. Drexel University, Materials. LeBow 344, Philadelphia, PA 19104, jose.bermudez@drexel.edu

Catalytic oxides are used in the automotive industry for abatement of pollutants. It is necessary to improve the performance of catalytic converters by increasing the surface area and preventing the reactions between the catalytic oxides and the support (alumina) at high temperatures. Alumina-supported manganese oxide was prepared by a colloidal precipitation method to vary the morphology of the manganese oxide in the presence of alumina. The specific surface area of the manganese oxide-alumina mixture was shown to be higher than those of aluminum oxide and manganese oxide alone. In addition, the specific surface area of the manganese hydroxide-aluminum hydroxide mixture could be increased by heat treatment at 500°C, possibly due to the breakup of the hydroxides during the phase transformation to oxides. Scanning electron microscopy was used to illustrate the morphological changes.

32.

SYNTHESIS AND CHARACTERIZATION OF CLAY-BASED MATERIALS FOR THE DESALINATION OF BRACKISH WATERS. *Jason D. Pless¹, Mark L. F. Phillips¹, Robert S. Maxwell², and Tina M. Nenoff¹.* (1) Chemical and Biological Technologies, Sandia National Laboratories, P.O. Box 5800, 0734, Albuquerque, NM 87185-0734, Fax: 505-844-1840, (2) Lawrence Livermore National Laboratory

High ion-exchange capacity oxides were studied for use in desalination processes. Permutite exhibits a cation exchange capacity between 1.7 to 2.7 milliequivalents of H⁺ per gram, depending on the dopant amount. Structure/property relationships of the materials were studied using NMR, FTIR, XRD, BET and ion exchange capacity. Hydrotalcite (HTC) exhibits an anion exchange capacity between 2.0 and 3.2 milliequivalents of OH⁻, depending upon the synthesis technique. The combination of permutite and HTC leads to a very energy efficient desalination process, with minimal negative environmental effect, resulting in far-reaching impact with the desalination of brackish ground waters or produced waters. These materials can be regenerated or disposed after use. The current desalination processes of distillation and reverse osmosis suffer from the high energy required for pumping, and costs associated with membrane fouling.

Sandia is a multiprogram laboratory operated by Sandia Corporation, Lockheed Martin Company, for US DOE's NNSA, Contract DE-AC04-94-AL85000.

33.

RHEOLOGY OF SINGLE-WALLED CARBON NANOTUBES/PMMA

NANOCOMPOSITES. *Karen I. Winey, Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, PA 19104, Fax: 215-573-2128, winey@lrsm.upenn.edu*

We examine the effects of nanotube loading, nanotube dispersion and alignment, and molecular weight of the polymer on the rheological behavior of SWNT/poly(methyl methacrylate) (PMMA) nanocomposites. Composites were prepared using our coagulation method and Raman imaging used to evaluate dispersion. As nanotube loading increases, the storage shear modulus (G') increases significantly at low frequencies. At nanotube loading higher than 0.2wt%, the terminal rheological behavior disappears and the dependence of G on ω at low frequency is weak, which is indicative of a transition from liquid-like to solid-like viscoelastic behavior and the formation of a nanotube network. A power law relation is used to determine the threshold of the rheological percolation, 0.12%, which is comparable to the percolation threshold of electrical conductivity, 0.39%. Finally, our results show that more nanotube alignment, worse nanotube dispersion, and shorter polymer chains reduce the solid-like response of these SWNT/PMMA nanocomposites. Support from ONR and NSF-MRSEC.

34.

FRACTURE PROPERTIES OF CNT-SOY OIL BASED COMPOSITES.

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Carbon nanotubes (CNTs) with their impressive mechanical properties, should prove to be excellent reinforcement material. CNTs have also been shown to increase fracture toughness. Dispersions were made with 1wt% unpurified CNTs in acrylated epoxidized soy oil (AESO) and styrene, from which CNT composites have previously been made. However, no improvements in fracture properties were seen. Using SEM, aggregates containing both CNTs and soot impurities, on the scale of 1-2 μm , were seen on the fracture plane. AESO and soy oil were found to purify CNT/carbon soot mixtures by holding small amounts of CNT in solution while the majority of the carbon soot settles out. These purified CNTs, when dispersed in AESO/styrene polymer resulted in composites in which no aggregation occurred and showed improved fracture properties.

35.

NEMATIC NANOTUBE GELS.

Mohammad F. Islam, Ahmed M. Alsayed, Zvonimir Dogic, Jian Zhang, Tom C. Lubensky, and Arjun G. Yodh, Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, islam@physics.upenn.edu

We report the creation of nematic nanotube gels containing large domains of oriented, half-micron-long, single-wall carbon nanotubes (SWNTs). We make them by homogeneously dispersing surfactant coated SWNTs at low concentration in an N-isopropyl acrylamide gel and then inducing a volume-compression transition. These gels exhibit hallmark properties of a nematic: birefringence, anisotropy in optical absorption, and disclination defects. We also investigate the isotropic-to-nematic (I-N) transition of these gels, and we describe the physical properties of their ensuing nematic state, including a novel buckling of sample walls. Finally, we provide a simple model to explain our observations. This work has been partially supported by the NSF through the MRSEC Grant DMR 00-79909 and DMR-0203378 and by NASA, Grant NAG8-2172.

36.

CONDUCTIVITY OF SINGLE WALL CARBON NANOTUBE IN EPOXY

COMPOSITES. *Jay M. Kikkawa, Mohammad F. Islam, Arjun G. Yodh, and Mateusz Bryning, Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, kikkawa@physics.upenn.edu, mbryning@student.physics.upenn.edu*

Aggregation and rope formation of single wall carbon nanotubes (SWNTs) play a key role in determining the electrical properties of SWNT-composite systems. We have developed a procedure for incorporating SWNTs into an epoxy matrix that allows us to control the dispersion of nanotubes from homogeneous to diffuse agglomerates to dense aggregates. Direct current conductivity measurements and images from optical and scanning electron microscopes show that if the nanotubes are allowed to form agglomerates/aggregates in the epoxy matrix,

then the nanotubes form conductive network at a very low concentration (~ 0.006 vol%). On the other hand, a homogeneous dispersion of nanotubes in the epoxy matrix leads to a higher percolation threshold (0.01 vol%). We will discuss the percolation behavior of nanotubes with existing models of non-interacting and interacting rods. This work has been partially supported by the NSF through the MRSEC grant DMR 00-79909, DMR-0203378, by DARPA through grant WP00-30-066, and by NASA through grant NAG8-2172.

37.

MELTING OF LAMELLAR PHASES IN TEMPERATURE SENSITIVE

COLLOID-POLYMER SUSPENSIONS. *Ahmed M. Alsayed, Zvonimir Dogic, and Arjun G. Yodh, Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, sinan@student.physics.upenn.edu*

We investigate the behavior of a novel suspension composed of rod-like fd virus and thermosensitive polymer Poly(N-isopropylacrylamide) whose phase diagram is temperature and concentration dependent. The system exhibits a rich variety of stable and metastable phases, and, more importantly, provides a unique opportunity to directly observe melting of lamellar phases and single lamellae. Typically lamellar phases swell with increasing temperature before melting into the nematic phase. The highly swollen lamellae can even be superheated as a result of topological nucleation barriers that slow formation of nematic phases. Using optical forces we prepare metastable nematic and multilayer structures starting from a single colloidal membrane, and then observe the system evolve back into a single membrane.

38.

VISCOELASTICITY OF ATTRACTIVE RIGID ROD NETWORKS.

Lawrence A. Hough, Arjun G. Yodh, and Mohammad F. Islam, Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, hough@sas.upenn.edu

We report the viscoelastic properties of an attractive rigid rod system composed of aqueous suspensions of surfactant stabilized single wall carbon nanotubes. The onset of elasticity occurs at a characteristic volume fraction of the stabilized nanotubes, and is interpreted as a rigidity percolation transition. A percolation exponent is obtained from the dependence of the viscoelastic storage modulus on rod volume fraction. This exponent agrees with simulations of associating rods connected by bonds that are freely jointed, but resist stretching. In the non-linear viscoelastic regime, yielding is observed in concentrated nanotube suspensions. In addition, the non-linear viscoelastic properties can be scaled onto a master curve using novel scaling relations that depend on the microscopic topology of the network.

39.

METHANOL REACTIONS OVER OXIDIZED RE SURFACES: INFLUENCE OF SURFACE STRUCTURE AND OXIDATION STATES.

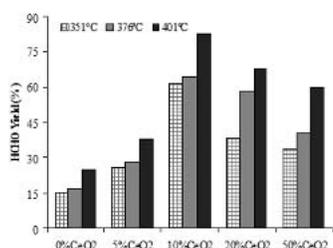
Ally S. Y. Chan, Wenhua Chen, Hao Wang, and Theodore E. Madey, Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, Piscataway, NJ 08854, Fax: 732-445-4991, allychan@physics.rutgers.edu

We report on the fabrication, characterization, and reactivity towards methanol, of oxidized Re surfaces prepared with different morphologies and surface oxidation states. Using a morphologically-unstable planar Re(12-31) substrate, we find that nanometer-scale 'sawtooth' facets develop when the surface is pre-covered with oxygen and annealed, thus providing a suitable template to investigate structure-reactivity relationships in methanol reactions. Partial oxidation of methanol to CH₂O and CO occurs on the planar and nano-faceted Re surfaces, while no reaction is observed from the thin-film oxide. Notably, the selectivity towards partial oxidation products is not affected by morphological differences between the planar and nano-faceted surfaces. However, the activity of the oxidized surfaces decreases progressively in the order: planar O/Re > faceted O/Re > thin-film oxide/Re. The inertness of the thin-film oxide is attributed to the formation of low oxidation state Re oxides on this surface, while the different activities of the planar and nano-faceted surfaces may be due to changes in local geometrical structure. We discuss these results in the context of the catalytic oxidation of methanol to methylal [CH₂(CH₃O)₂] over Re oxide catalysts.

40.

ROLE OF CERIUM ON THE CATALYTIC BEHAVIOR OF SILICA-SUPPORTED MOFEO CATALYSTS FOR METHANOL OXIDATION. *Ana Paula Vieira Soares and Manuel Farinha Portela, Instituto Superior Técnico, Technical University of Lisbon, ICEMS-UQUIMAF-GRECAT, Av Rovisco Pais, Torre Sul, s/n, Lisboa 1049-001, Portugal, Fax: 351 21 8499242, apsoares@popsrv.ist.utl.pt*

Supported MoFeO catalysts for the oxidation of methanol have been prepared using commercial SiO₂ (60m²/g) modified by deposition of CeO₂. The catalytic behavior during methanol oxidation showed that the catalysts with CeO₂/SiO₂ supports are much more active and selective than those supported over silica. The sample without Ce produces mostly dimethoxymethane (DMM) instead of formaldehyde. Additionally Ce appears to attenuate Mo loss during reaction. In order to identify the active phase samples without Fe were also prepared. Catalytic performances are discussed on the basis of the presence of iron and cerium molybdates. A synergy effect between ferric and cerium molybdates is considered. The role of Fe for Mo based supported catalysts is questioned. Previous results and the above presented seem to point that Mo based supported catalysts for selective oxidation of methanol do not need Fe. The iron can be replaced by other elements with oxidant character such as Ce or P.



41.

METHANOL OXIDATION OVER ACIDIC SUPPORTED WO₃ CATALYSTS. *Tae Jin Kim and Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, 7 Asa Drive, Bethlehem, PA 18015, Fax: 00, tj4@lehigh.edu*

The molecular structures of the WO₃ on three supports, Al₂O₃, TiO₂, and Nb₂O₅, catalysts have been investigated by combining two techniques, one is temperature programmed surface reaction (TPSR) and the other is visible Raman spectroscopy. The absence of crystalline WO₃ particles was confirmed by Raman spectroscopy, and further showed that the supported tungsten oxide phase were 100% dispersed on all three supports. These supported WO₃ catalysts exclusively possess surface acidic characteristics. Supported metal oxide catalysts generally exhibit a "ligand effect" in this case the selective oxidation of methanol to dimethyl ether (DME). This "ligand effect" generally results in orders of magnitude variations in the turnover frequency (TOF). For the supported WO₃ catalysts, it was found that the products are DME, CO, CO₂, MeOH, H₂O, and HCHO and DMM are trace products. The methanol oxidation results demonstrated that the TOF values are related to the electronegativity of the support. The TOF for supported tungsten oxide catalysts decreases in the following order: Al₂O₃ > Nb₂O₅ > TiO₂.

42.

HIGHLY DISPERSED AMORPHOUS TUNGSTEN OXIDE ON ZIRCONIA FOR N-PENTANE ISOMERIZATION. *William V. Knowles¹, Elizabeth I. Ross², Israel E. Wachs², and Michael S. Wong³. (1) Department of Chemical Engineering, Rice University, 6100 Main St., MS-362, Houston, TX 77251-1892, Fax: 713-348-5478, wvk@rice.edu, (2) Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, (3) Department of Chemical Engineering and Department of Chemistry, Rice University*

Tungstated zirconia (WO_x-ZrO₂) catalysts were prepared via conventional incipient wetness impregnation, coprecipitation, supramolecular templating of nanoparticles, and sol-gel methods at 5-50 W atoms/nm² to probe the surface structure/reactivity relationship for n-pentane isomerization. Previous literature studies have demonstrated maximum isomerization rates for intermediate atomic tungsten surface densities (5-8 W/nm²), a value that is consistent with the reported rate maxima of ~7-8 W/nm² for the acid-catalyzed reactions of

o-xylene isomerization and 2-butanol dehydration. These intermediate surface densities are proposed to maximize the amount of polytungstate species, which become the active sites after in situ reduction under H₂-rich reaction conditions. Postulating a similar structure-property relationship for n-pentane isomerization, we pursued multiple catalyst preparation methods to increase the population of amorphous polytungstate species relative to isolated WO_x and crystalline WO₃ domains, as determined by x-ray diffraction and Raman spectroscopy. Tungsten oxide supported on ZrO₂ nanoparticles were stabilized as polytungstate species at surface densities as high as 11.0 W/nm², while remaining thermally stable at 600 °C. Activity results confirm that such nanoparticle-supported tungsten oxides are enhanced for n-pentane isomerization compared to conventionally prepared tungstated zirconia at the same WO₃ weight loading.

43.

NATURE OF SURFACE ACIDIC SITES IN MIXED METAL OXIDE CATALYSTS.

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This study was conducted using model supported metal oxides to investigate the formation of surface acidic sites for the supported TiO₂/SiO₂ catalytic system. The model supported metal oxide catalysts contained 100% dispersed surface TiO_x on the SiO₂ support and was molecularly characterized by in situ Raman and XANES. At low surface coverage, the surface titania species possess TiO₄ coordination and are isolated. At monolayer coverage, the surface titania species possess TiO₅ coordination and are polymerized (presence of bridging Ti-O-Ti bonds). IR ammonia adsorption studies were employed to detect the presence of surface Bronsted and Lewis acid sites. At low coverage of titania on SiO₂, only a weak IR band at ~1630 cm⁻¹ corresponding to chemisorbed NH₃ on a surface Lewis acid site was present and no surface Bronsted acid sites due to chemisorbed NH₄⁺ at ~1450 cm⁻¹ could be detected. At monolayer surface TiO_x/SiO₂ coverage, some surface Bronsted acid sites were found to coexist with the surface Lewis acid sites (probably associated with the bridging Ti-O-Ti bonds of the surface TiO₅ species). The chemical properties of the surface TiO_x/SiO₂ species were molecularly probed by CH₃OH-TPSR spectroscopy and steady-state CH₃OH oxidation studies. Below monolayer surface titania coverage, only reaction products originating from surface TiO_x redox sites were formed. At monolayer surface coverage, a minor amount of reaction products originating from the surface Bronsted acid sites was also present in addition to the reaction products originating from the surface TiO_x redox sites. Thus, the isolated surface TiO₄ species exclusively possess surface redox characteristics and the polymerized surface TiO₅ species predominately also possess surface redox properties as well as a minor amount of Bronsted acidity. These new insights are being employed to develop a new fundamental model for surface Bronsted and Lewis acid sites in mixed metal oxide catalysts.

44.

MECHANISTIC STUDY OF DIMETHYL ETHER PRODUCTION. *Naa Larteakor Quarcoo, Acopian Engineering Center, Chemical Engineering Department, Lafayette College, Easton, PA 18042, tavakoli@lafayette.edu, Javad Tavakoli, Chemical Engineering, Lafayette College, and Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University*

The US Environmental Protection Agency has issued guidelines for diesel engine emissions in heavy duty vehicles scheduled to take effect in 2006. These regulations are meant to control the emission of particulate matter, oxides of nitrogen and non-methane hydrocarbons. The new regulations obligate vehicle manufacturers to either install exhaust emission controls or use a reformulated fuel to ensure compliance. A growing interest has focused on the latter in recent years.

It has been reported that the addition of oxygenates to diesel fuel such as dimethyl ether (DME), could control/reduce soot precursors significantly. The rising demand for DME has prompted development and examination of new technologies for its production. Methanol oxidation over alumina supported metal oxide catalysts such as WO₃/Al₂O₃, Ta₂O₅/Al₂O₃, TiO₂/Al₂O₃, and FeO/Al₂O₃ has been reported as alternatives. This paper investigates the reaction mechanisms of DME formation on alumina supported metal oxides during methanol oxidation.

45. ADSORPTION CHARACTERIZATION OF ORGANIC SURFACES SUPPORTED ON MINERAL PARTICLES. *Alexander Fadeev, Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079, fadeeval@shu.edu*

Characterization of surface modified minerals (porous and/or high-surface area powders) is important for their application as fillers, pigments, adsorbents and catalysts. This work investigates the vapor phase adsorption of nitrogen on different organic surfaces supported on silica, titania and other metal oxides. Thermodynamic data of adsorption (isosteric heats of adsorption, C constant of the BET equation) are used to characterize the surface energy of the materials. The changes of surface energy of solid supported surfaces depending on the nature of the organic groups and their concentration on the surface are discussed.

46. USING INVERSE GAS CHROMATOGRAPHY TO MEASURE CARBON FIBER-POLYMER INTERACTION STRENGTHS. *Daniel J Burnett, Surface Measurement Systems, 2222 South 12th Street, Suite D, Allentown, PA 18103, Fax: 910-798-0334, burnett@smsna.com, and Frank Thielmann, Surface Measurement Systems Ltd*

The quality and performance of carbon fiber composites depends strongly on the interaction of the two components at the interface. Those interactions are typically described as adhesion or cohesion phenomena, which depend on the material's surface energy. Surface energies were measured by Inverse Gas Chromatography (IGC), which has become a popular alternative to contact angle techniques due to its high sensitivity and reproducibility. In this study a series of carbon fibers with different surface modifications have been investigated by IGC as well as various polymers used for surface coatings. The results obtained for the individual components have been applied to calculate fiber-polymer interactions. A novel route for the determination of dispersive and specific interactions based on a modified van Oss approach has been used. This allows for more accurate predictions of the interaction between the fiber and polymer. The calculated adhesion values correlated with mechanical properties of the different composites.

47. EXAMINATION OF POLAR SURFACE ENERGETICS OF CALCIUM CARBONATES BY INVERSE GAS CHROMATOGRAPHY. *D. Steven Keller and Philip Luner, Empire State Paper Research Institute, SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, Fax: 315-470-6945, dskeller@syr.edu*

Inverse gas chromatography used to investigate the polar surface energetics of natural and synthetic calcium carbonates. The weak Lewis basicity of the double bond in the 1-alkenes was used to assess the acidity of a Chalk and a precipitated calcium carbonate (PCC) (key materials in papermaking coatings and fillers). Both samples were found to have increased interaction due to the acidic sites. Based on the difference in free energy of adsorption for the alkenes and alkanes, the interaction attributed to the double bond for the two CaCO₃ samples were found to be quite similar. Dehydration of the samples increases this interaction suggesting the uncovering or generation of acidic sites at the surface. The probe chain length had a more significant affect on the interactions with the Chalk than the PCC. This may result from differences in the basic sites on the surfaces, or in microstructure. Lengthening of the alkene chain tended to reduce the interaction of the π bond. The enthalpy of interaction of the π bond was determined for the PCC. However, the strong interaction of the alkenes with the Chalk preconditioned at or above 200°C resulted in indefinitely long retention times, preventing comparative enthalpies of interaction from being determined.

48. LIQUID WETTING OF ROLLED SILK AND NYLON TEXTILES FOR SURFACE FREE ENERGY CHARACTERIZATION. *Irene F. Karsten, Conservation Processes and Materials Research, Canadian Conservation Institute, 1030 Innes Road, Ottawa, ON K1A 0M5, Canada, Fax: 613-998-4721, irene_karsten@pch.gc.ca, Nancy Kerr, Department of Human Ecology, University of Alberta, and Zhenghe Xu, Department of Chemical and Materials Engineering, University of Alberta*

The surface free energy components of silk and nylon textiles were determined using the Washburn technique but with rolled fabric specimens instead of fibers or flat fabric specimens. Rolled strips of fabric were attached to the edge of an

aluminum cylinder, which was clamped to a Krüss K12 tensiometer. Sorption graphs for water, formamide, 1-bromonaphthalene, and hexadecane were produced. Rolling the fine, flexible fabrics stiffened them sufficiently to provide good contact with liquid surfaces, and increased the mass of liquid absorbed, permitting easier sorption measurement. Water wicked into rolled nylon specimens but not flat ones. Sorption was characterized by two wetting periods: the first almost instantaneous, the second much slower. The slope for the second period, having more data points, was used in the Washburn equation for the calculation of contact angles. Surface free energy values, calculated using the van Oss-Chaudhury-Good approach, were comparable to those found in the literature.

49. SPREADING AND ADHESION OF ASA ON CELLULOSE, STARCH AND HYDROPHILIC AND HYDROPHOBIC SiO₂ MODEL SURFACES. *Per Stenius, Janne Laine, Susanna Ylisuvalo, and Juha Lindfors, Laboratory of Forest Products Chemistry, Helsinki University of Technology, Vuorimiehentie 1 A, P.O.Box 6300, 02015 Espoo, Finland, Fax: 358-(0)9-4514259, Per.Stenius@hut.fi, juha.lindfors@hut.fi*

Spreading kinetics and adhesion of liquid alkenyl succinic anhydride (ASA) on cellulose, starch and hydrophilic and hydrophobic SiO₂ model surfaces has been studied. The experiments were performed with contact angle measurement apparatus both in air and in aqueous environment. ASA spreads fairly well on all the studied surfaces in air, but in aqueous environment spreading only occurs in the case of hydrophobic surface. On hydrophilic surfaces the contact angle remains in 150° - 170° in water. The work of adhesion of ASA was 50 - 60 mJ/m² on all the studied surfaces in air. In water the work of adhesion on hydrophobic surface was 20 mJ/m², but only approximately 1 mJ/m² on the hydrophilic surfaces. As a result of the study, it can be concluded that for avoiding the adhesion of ASA on process equipment, maintaining aqueous environment and using hydrophilic surfaces is essential.

50. SURFACE CHARACTERISATION OF MECHANICAL FIBRES BY CONTACT ANGLE MEASUREMENTS USING WILHELMY TECHNIQUE. *Krista Koljonen and Per Stenius, Laboratory of Forest Products Chemistry, Helsinki University of Technology, Vuorimiehentie 1 A, P.O.Box 6300, 02015 Espoo, Finland, Fax: +358-9-4514259, Krista.Koljonen@hut.fi*

The effects of water washing, dichloromethane extraction, dithionite and peroxide bleaching, alkaline and ozone treatment on the surface energies of Norwegian spruce (*Picea abies*) pressure groundwood (PGW), thermomechanical (TMP) and chemithermomechanical (CTMP) pulps were evaluated by contact angle measurements on single fibres.

Water, ethylene glycol and α -bromonaphthalene were used as wetting liquids. Lifshitz-van der Waals (LW), acid (A) and base (B) components of surface energy were calculated using the Good-van Oss approach using acid/base values for the liquids proposed by Della Volpe and Siboni. The fibres were predominantly basic relative to water. Basicity increased after extraction, ozone treatment, sulphonation and sulphonation followed by peroxide bleaching.

LW and AB contributions to the adhesion (W_a) of water or ethylene glycol to the fibres were evaluated. W_a^{AB} increased after all treatments, whereas W_a^{LW} remained constant.

It is concluded that the increased hydrophilicity of mechanical fibres resulting from different chemical treatments and removal of extractives is primarily due to increased surface basicity.

51. RODS AND TEMPERATURE-SENSITIVE POLYMERS IN SUSPENSIONS AND GELS. *Arjun G. Yodh, Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, yodh@physics.upenn.edu*

I will discuss recent experiments from my lab which probe the behavior of biopolymers in nematic suspensions of rods, and the phases of rods (e.g. fd-virus, carbon nanotubes) in NIPA polymer suspensions and gels. The temperature sensitivity of NIPA polymer enables us to convert lyotropic suspensions into 'thermotropic' suspensions, and in this way we were able to study melting of lamellar phases into nematic phases with optical microscopy.

This work was done in collaboration with Mohammad Islam, Zvonimir Dogic,

Jian Zhang, Ahmed Alsayed, Andy Lau, Dennis Discher, Paul Janmey, Tom Lubensky, Randy Kamien, H. Aranda-Espinoza, and P. Dalhaimer.

52.

STRUCTURES AND PROPERTIES OF SUPRAMOLECULAR ASSEMBLED NANOCOMPOSITES: FULLERENE-BASED SURFACTANTS CONFINED IN POLY(DIMETHYLSILOXANE) MATRICES. *Shuiqin Zhou and Jianying Ouyang, Department of Chemistry, Graduate Center and College of Staten Island, City University of New York, 2800 Victory Blvd, Staten Island, NY 10314, Fax: 718-982-3910, zhoush@postbox.csi.cuny.edu*

Multihydroxylated [60]fullerene (fullerenol) surfactants were complexed with the amino end-functionalized poly(dimethylsiloxane) (PDMS) in tetrahydrofuran. Light scattering results reveal that the size and size distribution of the fullerenol-PDMS complexes depend on the ratios of components and total concentrations. Small angle X-ray scattering (SAXS) results indicate that the increase of fullerenol content in the nanocomposites increases the size of fullerenol nanodomains. This novel structural feature results in superior thermal and thermal mechanical stability, severely suppressed crystalline phase, elastic mechanical response, and unique dielectric properties of the nanocomposites, e.g., high content of fullerenol increases the permittivity but dramatically decreases the loss factor. SAXS results indicate that the complexation of multiaminofullerene surfactants of 1-(4-Methyl)-piperazinylfullerene (MPF) with carboxylic acid side-functionalized PDMS produces different structures of nanocomposites. The increase of MPF content in the nanocomposites decreases the interdomain distance and increases the number density of fullerene aggregates, which results in compromised dielectric properties of the nanocomposites.

53.

EXTENT OF INTERFACIAL INTERACTIONS BETWEEN METAL NANOCLUSTERS AND POLYMERS IN NANOCOMPOSITES. *Rina Tannenbaum, Georgia Institute of Technology, School of Materials Science and Engineering, 771 Ferst Drive, Atlanta, GA 30332, Fax: 404-894-9140, rina.tannenbaum@mse.gatech.edu*

The properties of nanocomposites are dominated by the large interfacial area created when nanoparticles are embedded in a polymer matrix. A strong interaction between the polymer and the nanoparticles will result in a flat configuration of the polymer on the surface of the nanoparticles, and a compact interface. On the other hand, a weak interaction will result in the extension of the polymer chains into the bulk polymer matrix, creating a diffuse interface. The experimental determination and theoretical analysis of the thickness of the polymer layer adsorbed on nanoparticles will help to elucidate the effectiveness of the polymer adsorption and ultimately relate the required characteristics of the interface to the optimal mechanical properties of the nanocomposite. This work examines the properties of the interface between metal oxide nanoparticles embedded in poly(methyl methacrylate) (PMMA) and in polystyrene (PS) matrices, two polymers having functional groups with different reactivities. Preliminary results indicate that the interfacial region created between the metal oxide particles and PMMA is denser and more compact than that created with PS, due to the strong adsorption of PMMA on the surface of the metal oxide particles.

54.

MOBILE NANOPARTICLES IN POLYMER BLEND FILMS: WETTING AND PHASE SEPARATION BEHAVIOR. *Russell J. Composto and Hyun Joong Chung, Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, PA 19104/6272, Fax: 215-573-2128, composto@lrs.m.upenn.edu*

Polymer films containing nanoparticles (NP) are of technological interest because fillers can alter the mechanical, electrical and optical properties. Here, we present the first systematic experimental study of phase separation dynamics in thin films containing mobile NP. Thin films (650nm) of PMMA:SAN (50:50) containing silica NP (~22nm) was chosen as a model system. Initially, the NP are homogeneously dispersed, as confirmed by TEM and RBS. Upon annealing, NP initially segregate towards the surface and substrate, coinciding with the wetting of PMMA. This observation along with TEM images strongly suggests that the NP partition into the PMMA phase. During the intermediate stage, the lateral correlation length \times scales as $t^{1/3}$, for blends with 0, 2 wt.% and 5 wt.

% NP. However, \times grows more slowly as the NP concentration increases. These results are consistent with a coalescence model using an enhanced viscosity of PMMA due to the NP.

55.

NANOCLAY FILLED BIO-BASED ELASTOMERS: SYNTHESIS AND CHARACTERIZATION. *Lin Zhu and Richard P. Wool, Department of Chemical Engineering, University of Delaware, Academy Street, Newark, DE 19716, Fax: 302-831-1048, zhul@che.udel.edu*

A new bio based elastomer synthesized from soybean oil was filled with nanoclays to generate an elastic nanocomposite. Nanoclays modified with different organic functional groups were dispersed into an acrylated oleic methyl ester matrix. X ray diffraction and transmission electron microscopy analysis were used to characterize the degree of the exfoliation and confirm the formation of the nanocomposites. The morphology varies from fully exfoliated to intercalated structure with different types of clay and clay concentrations. Tensile strength and elongation were both enhanced and the glass transition temperature was decreased. The properties of the material were related to the degree of the exfoliation. The network structure was studied by the swelling test as well as the dynamic mechanical test. Rheology tests showed the formation of a percolated filler network. The effects of the nanoclay on the macroscopic and microscopic properties were explored.

56.

RHEOLOGICAL PROPERTIES OF COMPLEX FLUIDS FORMED BY GUM ARABIC AND BOVINE SERUM ALBUMIN (BSA). *Jooyoung Lee and Qingrong Huang, Department of Food Science, Rutgers, The State University of New Jersey, 65 Dudley Rd., New Brunswick, NJ 08901, Fax: 732-932-6776, jooylee@rci.rutgers.edu*

The interactions between polysaccharides and proteins determine the final structure, texture, and stability of the food materials. At certain pH, the mixture of polysaccharide and protein may undergo two types of phase separation: (1) the solid-liquid phase separation called precipitation; and (2) the liquid-liquid phase separation called coacervation. Complex fluids formed by proteins and oppositely charged polysaccharides provide excellent model systems to study the coacervation phenomenon, which is believed to result from weak attractive and nonspecific interactions such as electrostatic, van der Waals, hydrophobic interactions, or hydrogen bonding between proteins and polysaccharides. Coacervates have already been widely used in cosmetic formulations, microencapsulation of food ingredients, enzymes, cells, and pharmaceuticals. Although the coacervation phenomenon was found more than 50 years ago, many questions still remain unanswered for these unique complex fluids. In this paper, we carried out systematic rheological studies of complexes formed by BSA and gum arabic, a hydrocolloid that is commonly used as emulsifier and film-former in the beverage industry to stabilize flavors and essential oils. The effects of pH, ionic strength, and the ratio of BSA and gum arabic on the viscoelastic properties BSA/gum arabic complexes will be discussed.

57.

THE COUPLING OF MOLECULAR ASYMMETRY TO INTERFACE STRUCTURE IN MIKTOARM COPOLYMER MELTS. *Gregory Grason, Physics and Astronomy, University of Pennsylvania, DRL, 209 S 33rd St, Philadelphia, PA 19104, grason@student.physics.upenn.edu, and Randall D. Kamien, Department of Physics and Astronomy, University of Pennsylvania*

Using strong-segregation theory (SST) and self-consistent field theory (SCFT) techniques we investigate the phase behavior of AB_n miktoarm copolymer melts. In particular, we examine how the molecular asymmetry stabilizes morphologies with highly curved interfaces. While SST calculations ignoring micelle lattice symmetry tend to overestimate this effect for asymmetric molecules, our modified SST calculation and SCFT results are in strong agreement with experiments on PI-PS miktoarm copolymer melts. In addition, we report the stability of a new cubic phase of one-component block copolymer melts, with Pm3n symmetry. This phase, the A15 phase of spherical micelles, is a stable phase for melts of AB_n copolymers for $n \geq 2$. We interpret the relative stability of the sphere phases in terms of well-studied, geometric moments of the candidate sphere lattices.

58.

SURFACE COMPOSITION OF SUPPORTED AND BULK MIXED METAL OXIDE CATALYSTS: NEW INSIGHT FROM ION SCATTERING SPECTROSCOPIC STUDIES. *Wolfgang Gruenert¹, Laura Briand², Olga P. Tkachenko³, Nikolai N. Tolkachev³, and Israel E. Wachs⁴.* (1) Laboratory of Industrial Chemistry, Ruhr University Bochum, Universitaetsstrasse 150, Bochum D-44780, Germany, Fax: +49 234 321 4115, w.gruenert@techchem.rub.de, (2) Centro de Investigación y Desarrollo en Ciencias Aplicadas, UNLP, (3) N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, (4) Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University

Supported and bulk V (Mo) oxide catalysts and bulk vanadate and molybdate mixed metal oxide compounds have been investigated by Ion Scattering Spectroscopy (ISS). A new methodology has been applied to make sure that oxide-oxide interactions are fully developed in the samples studied. ISS results for several supported catalysts with V(Mo) content corresponding to the theoretical monolayer capacity (e.g. V₂O₅/ZrO₂, MoO₃/TiO₂) prove that the supports are covered by close-packed monolayers of V (Mo) surface oxide species, which confirms earlier conclusions drawn on the basis of Raman spectroscopy. For several bulk vanadates and molybdates (e.g. AlVO₄, ZrV₂O₇, BiVO₄, Ce₈Mo₁₂O₄₉) a strong surface enrichment of V(Mo) was observed by ISS, which reveals a striking analogy between the surface compositions of supported catalysts and bulk mixed metal oxide systems and confirms recent conclusions from work with chemical probes. Consequences for future investigations with mixed-oxide catalysts will be discussed.

59.

PREPARATION OF NOVEL VANADIUM PHOSPHORUS OXIDE CATALYSTS USING HIGH TEMPERATURE CRYSTALLISATION. *Wen Sheng Dong, Jonathan K. Bartley, and Graham J. Hutchings, Department of Chemistry, Cardiff University, PO Box 912, Cardiff CF10 3TB, United Kingdom, Fax: ++29 2087 4030, DongW@cf.ac.uk*

Vanadium phosphorus oxide catalysts have been widely studied for the selective oxidation of butane to maleic anhydride. The catalytic performance depends on the method of preparation of the precursor, VOHPO₄·0.5H₂O. As the transformation of the precursor to the final catalyst is topotactic, the morphology of the precursor is of crucial importance in determining the eventual catalyst morphology and the performance following activation. Typically VOHPO₄·0.5H₂O is synthesised under reflux conditions in either water or isobutanol, so that the reaction temperature is *circa* 100°C. Few studies have focused on the use of elevated temperatures or pressures. In this study we have synthesised vanadium phosphate materials in an autoclave at 100-400°C and 1-150 bar. Under these conditions the product is dependent on the reaction temperature and pressure, giving rise to new vanadium phosphorous oxide phases that are active for butane oxidation or can be transformed into well known phases.

60.

TRANSIENT STUDIES ON THE ROLE OF OXYGEN ACTIVATION IN THE PARTIAL OXIDATION OF METHANE OVER ZrO₂-BASED CATALYSTS. *J.J. Zhu, J.G. van Ommen, and L. Lefferts, Faculty of Science & Technology, Catalytic Processes and Materials, University of Twente, PO Box 217, Enschede 7500 AE, Netherlands, Fax: 00, l.lefferts@utwente.nl, l.lefferts@utwente.nl*

In this work, CPOM over ZrO₂-based oxide catalysts is studied by transient experiments, such as pulse, step-change and temperature-programmed experiments. ¹⁸O isotopic exchange between gas phase oxygen and the oxide catalyst is investigated under reaction conditions for CPOM. Interestingly, the oxidation products (CO, CO₂, H₂O and H₂) do not contain any ¹⁸O, after pulsing a mixture of CH₄ and ¹⁸O₂ (2:1) over YSZ catalysts in the temperature window between 500°C and 900°C. This indicates that methane is oxidized by lattice oxygen of the catalysts. The consumed oxygen is restored by gas phase oxygen via oxygen exchange with the oxide. Surface oxygen vacancies are characterized by temperature-programmed desorption of N₂O. The role of oxygen vacancies in both the surface and the bulk on the activation of oxygen is explored. Interaction between gas phase oxygen and intrinsic oxygen vacancies in ZrO₂ and oxygen vacancies generated by doping Y₂O₃ in ZrO₂ is discussed in detail. The composition of both the surface layer and the bulk of the catalysts are characterized by X-ray fluorescence (XRF) and low energy ion scattering

(LEIS) respectively. The catalytic performance is very sensitive to segregation of extremely low-level contaminations like earth alkali oxides. The effect of traces of contaminations on the catalytic performance is discussed as well.

61.

HIGHLY REACTIVE OXYGEN SPECIES ON VANADIA ALUMINA CATALYSTS AS DETERMINED BY MULTI-TRACK: RELEVANCE FOR STEADY STATE ACTIVITY AND ROLE OF FE-CONTAMINATION IN ALUMINA. *Guido Mul¹, S. J. Khatib², Bart van der Linden¹, Miguel A. Banares³, and Jacob A. Moulijn¹.* (1) Reactor and Catalysis Engineering, Delft University of Technology, Julianalaan 136, Delft 2628 BL, Netherlands, Fax: 00-31-15-2785006, G.Mul@tnw.tudelft.nl, (2) Institute of Catalysis and Petrochemistry, CSIC, (3) CSIC-Institute of Catalysis

Vanadia/alumina based catalysts have attracted many people active in the field of heterogeneous oxidation catalysis, e.g. because of good performance in oxidative dehydrogenation (ODH) of propane. In the present contribution the use of Multi-Track (an advanced TAP reactor) to determine the amount of highly reactive oxygen species (i.e. not the oxygen associated with the oxide itself) on these catalysts is evaluated. It will be shown that using so-called pump-probe experiments (in which the exposure of the catalyst to O₂ and CO, respectively, is delayed by 1 second), and varying the pulse size of CO, can be used to quantify the amount of reactive oxygen present on the catalytic surface (see Figure). Following the results presented in the fall meeting in New York last year, a correlation between the amount of reactive oxygen thus determined, and the steady state conversion of several vanadia/alumina catalysts in CO oxidation is discussed. Furthermore, contaminations in the alumina support are shown to affect the amount of highly reactive oxygen species. Specifically the role of Fe in the applied alumina is illustrated on the basis of Fe-doped vanadia/alumina catalysts.

62.

IN SITU STUDIES OF THE MARS VAN KREVELEN MECHANISM IN HYDROCARBON OXIDATION. *Mark A. Barteau, D Wang, and Lisa Lopez, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, Fax: 302-831-8201, barteau@che.udel.edu*

Conventional wisdom has held that metal oxide-catalyzed selective oxidations follow the Mars van Krevelen mechanism. The organic reactant is oxidized by lattice oxide ions at the surface; these are replenished by dioxygen dissociation with surface and solid state diffusion to reoxidize surface sites. Studies using a flow microbalance reactor to examine butane oxidation by vanadyl pyrophosphate catalysts have quantitatively determined the kinetics of catalyst reduction and reoxidation in the Mars van Krevelen scheme. Comparisons with the steady-state rate demonstrate that oxygen removal from the lattice is too slow to account for the overall reaction rate. The Mars van Krevelen mechanism using catalyst lattice oxygen can account for only about 5% of the total oxidation activity. Previous isotope exchange studies suggest that VPO catalysts for butane oxidation and Bi-Mo oxide catalysts for propene oxidation utilize lattice oxygen to much different extents, providing useful tests of microbalance-based mechanistic studies.

63.

INKJET PRINT QUALITY AND PAPER-INK INTERACTION. *Shigenori Kuga, Huihong Yuan, and Toshiharu Enomae, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan, Fax: +81-3-5684-0299, skuga@sbp.fpa.u-tokyo.ac.jp*

Automatic scanning absorptometry (ASA; computerized Bristow's measurement) was applied to analysis of correlation between print quality and liquid penetration into inkjet media. Liquid absorption profile in 10-5000 millisecond range was recorded for various combinations of paper and liquid including actual jet inks. While water absorptivity was remarkably faster for IJ papers than for regular paper, ink liquids showed wide variety in absorption behavior according to ink-solvent composition and nature of paper surface. Differences between dye ink and pigment ink were noted in absorptivity and dot properties. While IJ grade papers give generally superior color quality to uncoated paper, one type of defect, i. e. banding in color gradation, was more notable on IJ grade coated surface. Cause of this anomaly is discussed based on characteristics in ink absorption and dot characteristics.

64.

SURFACE ENERGY OF COATED BLEACH BOARD. *Ali R. Bashey, Specialty Minerals Research Center, 9 Highland Avenue, Bethlehem, PA 18017, Ali.Bashey@Mineralstech.com, and Nigel D. Sanders, Discovery Research, Specialty Minerals Research Center*

The energetics of coated paper surfaces may be important to understanding phenomena critical to the use of coated paper.

Measuring contact angles of coated paper is a complex task due to lack of surface uniformity, fiber swelling and porosity. The objective of our study was to develop a statistically sound method for measuring contact angles and applying the technique to a controlled sample group. We are interested in determining the significance of surface energy and whether it can be used as a predictor of coated paper performance.

Contact angle measurements were taken with three probe liquids and applied to the van Oss equation. Statistical analyses of the data were examined to determine the significance of sample comparisons. Methods were developed to reduce the variance of the contact angle measurements and increase the confidence of sample treatment factor evaluations. Also presented in this study are complementary surface compositional data measured by XPS.

65.

ULTRASONIC SYSTEMS FOR LIQUID ABSORPTION MEASUREMENTS. *Jerzy Skowronski, G. Gruener, and W. de Groot, IGT Testing Systems, Inc, 3322 Tennyson Dr, Florence, SC 29501-7385, JerzySkowronski@aol.com*

The novel ultrasonic analyzer is presented as a tool to deal with print mottle problem. The new tester is designed to measure the uniformity of liquid absorption by paper at very short contact time between paper and testing printing liquids. Paper and paperboard up to 600 g/m² can be tested with a resolution of 25 dpi. Such resolution is achieved due to the use of ultrasonic multi-sensor comprised of 32 horizontally arranged mini-sensor elements of surface area measured 1 mm² each. New tester was used for uncoated paper like newsprint and SC papers as well as coated papers and paperboards. Test liquids such as water, acid oil or fountain solution were used to meet the specific objectives. Testing time can be reduced to minutes comparing to hours needed for performing the visual rating. Test gives not only the accuracy but also points out the problem.

66.

CATIONIZATION OF CELLULOSE BY POLYALLYLAMINE. *Min Wu, Makoto Tanaka, and Shigenori Kuga, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan, Fax: +81-3-5684-0299, wumin@sbp.jp.a.u-tokyo.ac.jp, skuga@sbp.jp.a.u-tokyo.ac.jp*

Cationization of cellulosic materials was achieved by chemically binding polyallylamine by varied treatment conditions. Cellulose was partially oxidized by aqueous sodium periodate, and resulting aldehyde groups served as binding sites for polyallylamine (MW 60000, 5000 and 1000) via Schiff base formation followed by reduction stabilization. Degree of cationization could be controlled by the degree of oxidation and the type of polyallylamine used. The effect of cationization for adsorbent uses was demonstrated for various proteins as adsorbates. Influence of cellulose morphology was examined for native cotton, alkali-treated cotton (cellulose II), and regenerated cellulose gel (chromatography packing). The latter two showed greater adsorption capacities, presumably because of improved accessibility for large molecules.

67.

STUDIES ON USING PROTEINS AS WET STRENGTH ADDITIVES OF PAPER. *Xin Li, Department of Chemical Engineering, McMaster Center for Pulp and Paper Research, McMaster University, 1280 Main Street west, lixin@mcmaster.ca, and Robert Pelton, McMaster Pulp and Paper Centre, McMaster University, 1280 Main St. West, Fax: 905-528-5114, peltonrh@mcmaster.ca*

Wet strength is one of the most important paper properties. Polymeric resins have been used as wet strength additives to paper products. However, conventional wet strength resins have been criticized because they release formaldehyde or contribute to AOX emissions and cause difficulties on paper recycling. Therefore, an attractive alternative is to find out one or more kinds of renewable

and biodegradable biopolymers to replace the traditional resins. In the present research, we investigated the wet peel strengths of 20 proteins with oxidized (OCM) and non-oxidized cellulose membrane, and the results showed that proteins containing high -NH₂ group improved the wet peel strength of OCM. Further, which -NH₂ group content residue in protein plays more important role in enhancing the wet peel strength was investigated. Effects of aging time and dosage of protein on wet peel strength were also investigated.

68.

SURFACE ACETYLATION OF PAPER BY GASEOUS ACID TREATMENTS. *Huihong Yuan and Shigenori Kuga, Graduate School of Agricultural & Life Science, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan, Fax: +81-3-5684-0299, yuan@sbp.jp.a.u-tokyo.ac.jp*

We developed a gaseous esterification method for paper, intending to make it hydrophobic while keeping the fibrous texture. Although this goal can be achieved by esterification with trifluoroacetic anhydride (TFAA) vapor treatment, the obtained ester was unstable in ambient atmosphere. Stabilization could be achieved by ester exchange of TFA to acetic acid (AcOH). In the first step, TFA esterification of filter paper was carried out in mixed vapor of TFAA/TFA, giving overall degree of substitution (DS) up to 0.2. The second step, ester exchange, was possible by AcOH/TFAA vapor treatment, resulting in final acetyl DS of 0.16. The hydrophobicity of the resulting paper was evaluated by automatic scanning absorptometry (automated Bristow's measurement). In spite of rather low total DS, that on the fiber surface was high enough to give significant hydrophobicity. Also it could be controlled by the vapor treatment conditions.

69.

CARBON-NANOTUBE-TEMPLATED AND PSEUDOROTAXANE-FORMATION-DRIVEN GOLD NANOWIRE SELF-ASSEMBLY. *Toby Sainsbury, Department of Chemistry, University College, Dublin, Belfield, Dublin 4, Ireland, Fax: 353-1-716-2127, toby.sainsbury@ucd.ie, and Donald Fitzmaurice, Department of Chemistry, University College Dublin*

To achieve a greater level of control over the bottom-up assembly of nanoscale structures, the ability to control the behaviour of nanoscale materials in solution is seen as an important goal. In particular the self-assembly and self-organization of nanoscale materials in solution and at substrates is seen as a viable means to this end. The modification of the surfaces of nanoscale materials with specific chemical functionality is therefore necessary in order to control the behaviour of these materials in solution. It is in this context that we report the preparation of MWCNTs which have been covalently modified with a dibenzylammonium cation moiety. The dibenzylammonium cation modified MWCNTs are used to template the non-covalent self-assembly in solution of crown modified gold nanoparticles. The driving force for self-assembly is formation of the surface-confined pseudorotaxane that results from the electron poor cation threading the electron rich crown. TEM is used in order to characterise the self-assembly of the materials in solution. Relevant control experiments are used in order to support the hypothesis that pseudorotaxane formation is the driving force for the self-assembly process.

70.

HIGH ASPECT RATIO GOLD NANORODS GROWN DIRECTLY ON SURFACES: SYNTHESIS, MANIPULATION AND GROWTH MECHANISM EXPLORATION. *Zhongqing Wei, Aneta Mieszawska, and Francis P Zamborini, Department of Chemistry, University of Louisville, 2320 South Brook Street, University of Louisville, Louisville, KY 40292, Fax: 502-852-8149, z.wei@louisville.edu, f.zamborini@louisville.edu*

Here we describe the synthesis of Au nanorods directly on glass surfaces using seed-mediated deposition of Au from AuCl₄⁻ onto surface-attached 3-5 nm diameter Au nanoparticles (AuNPs) in the presence of cetyltrimethylammonium bromide (CTAB). The average length (200 nm to 1.2 μm) and aspect ratio (6-22) of the nanorods increases with increasing AuCl₄⁻ concentration. Short, low aspect ratio Au nanorods are manipulated with an atomic force microscopy (AFM) tip, while longer, high aspect ratio nanorods are bent and broken with the AFM tip. We directly observe the formation of nanorods from a single 3-5 nm Au seed, from which a growth mechanism for the nanorods is proposed.

71.

MULTI-WALLED CARBON NANOTUBE TEMPLATED SELF-ASSEMBLY OF GOLD NANOWIRES. *Fionn Griffin¹, Toby Sainsbury¹, Paul Beecher², Aidan Quinn², Gareth Redmond², and Donald Fitzmaurice³.* (1) Department of Chemistry, University College, Dublin, Belfield, Dublin 4, Ireland, Fax: 353-1-716-2127, fionn.griffin@ucd.ie, (2) National Microelectronic Research Center, University College, Cork, (3) Department of Chemistry, University College Dublin

The demand for nanoscale devices has led to the rapid development of the nanomaterials field. The principle objectives of this field of research are to develop nanomaterial components and processes, which may then be incorporated into the manufacturing of nanoscale devices such as nanoswitches and nanowires. The use of carbon nanotubes to template the self-assembly of nanowires from gold nanoparticles is one such process. It is in this context that we report the assembly of an aqueous dispersion of 4-(dimethylamino)pyridine, DMAP, stabilized gold nanoparticles at the surface of thiol-modified multi-walled carbon nanotubes, MWNTs. Deposition of these gold nanowires onto a silicon substrate patterned with interdigitated gold nano-gap electrodes followed by gold enhancement forms continuous gold nanowires with diameters of 35 nm. The resulting gold nanowires were structurally characterised using electron and scanning probe microscopies. The nanowires are conducting, with a resistivity of $2 \times 10^{-4} \Omega\text{m}$.

72.

VIBRATIONAL SPECTROSCOPY OF OXYGEN CONTAINING FUNCTIONAL GROUPS AND THEIR INFLUENCE ON THE ADSORPTION OF SMALL MOLECULES ON SINGLE WALLED CARBON NANOTUBES. *Xue Feng,*

Department of Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, PA 15260, xuf2@pitt.edu, Radisav Vidic, Civil and Environmental Engineering, University of Pittsburgh, and Eric Borguet, Chemistry Department and Surface Science Center, University of Pittsburgh

Vibrational spectroscopy provides a convenient means to detect and identify the functionality on SWNT surface and follow its evolution in situ. In principle, IR can also enable one to investigate molecular adsorption on SWNT and to differentiate between different adsorption sites. Transmission infrared spectroscopy was applied to probe the fate of these functional during thermal treatment. These groups decompose during thermal treatment under vacuum as revealed by IR. Removal of these groups presumably opens the entry ports for adsorption on the inner surface of SWNTs and leads to increasing adsorption for non-polar molecules (propane and hexane). However, the uptake rate of SWNTs for polar species (pyridine and acetone) decreased after thermal treatment. Removal of those polar functional groups appears to decrease the affinity of the surface for polar molecules. The behavior of polar and non-polar adsorbates reveals distinct molecular interactions with SWNTs exterior, interior and surface functional groups.

73.

HIGH ASPECT RATIO GOLD NANORODS (AUNRS) GROWN DIRECTLY ON SURFACES. *Aneta Mieszawska and Francis P Zamborini, Department of Chemistry, University of Louisville, 2320 South Brook Street, University of Louisville, Louisville, KY 40292, Fax: 502-852-8149, ajmies01@louisville.edu*

We study the growth mechanism of gold nanorods (AuNRs) directly on surfaces. The seed-mediated method incorporates 3 – 5 nm Au nanoparticles (AuNPs) attached to glass or silicon as the active sites for further Au deposition from AuCl₄⁻ in the presence of micelles (cetyltrimethylammonium bromide CTAB). The aspect ratio of AuNRs (6 – 22 nm) is controlled by varying AuCl₄⁻ concentration. UV – vis monitoring and scanning electron microscopy (SEM) were used to determine growth kinetics and average length of gold nanorods with time. The yield of AuNRs was increased by varying parameters of synthetic conditions. Patterning surfaces with and controlling alignment of AuNRs was investigated as well.

74.

NOVEL MEDIATOR-TEMPLATE ASSEMBLY ROUTE TOWARDS SIZE AND SHAPE-TAILORABLE NANOPARTICLE ASSEMBLIES. *Mathew M. Maye¹, Stephanie Lim¹, Jin Luo¹, Navaid Khan¹, Zia Rab¹, Daniel Rabinovich², Tianbo Liu³, and Chuan Jian Zhong¹.* (1) Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6000, cjzhong@binghamton.edu, (2) Department of Chemistry, University of North Carolina, (3) Department of Physics, Brookhaven National Laboratory

The ability to assemble nanoparticles into three-dimensional architectures is important for exploiting the nanostructured properties for practical applications.

This presentation describes a novel “mediator-template” protocol in which multidentate thioether with mono-, bi-, tri-, and tetra- binding sites (e.g., tetra(alkylthio)methyl)silane) were utilized as mediators to assemble gold nanoparticles encapsulated with alkylammonium bromides as template shells. The reaction kinetics were monitored with UV-visible spectrophotometry. The structures were characterized using FTIR. The morphological evolution from isolated particles to their assemblies with controllable diameters between 60–260 nm was characterized by transmission electron microscopy, SAXS, and dynamic light scattering technique. Based on thermodynamic modeling of the assembly reaction and simulation of the optical properties, we have been able to correlate the molecular interactions in the nanoparticle assembly with the interparticle spatial properties, which have important implications to the fine-tuning of the nanostructures.

75.

AFM AND IR STUDY OF ISOCYANIDE MOLECULAR WIRES. *Zeeshan Habeeb¹, Tasneem A Siddiquee¹, Dennis W. Bennett², and W. T. Tysoe³.* (1) Department of Chemistry and Biochemistry, University of Wisconsin-Milwaukee, 3210 N Cramer St, Milwaukee, WI 53211, zhabeeb@uwm.edu, (2) Department of Chemistry, University of Wisconsin Milwaukee, (3) Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee

This work will describe the characterization of potential organometallic molecular-level conductors with subunits, $(\text{CNC}_6\text{H}_4\text{NC})_{m+1}(\text{W}(\text{dppe})_2)_m$, where dppe is $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$. Thus, electron rich tungsten metal centers are linked by conductive molecular bridging ligands, $\text{CNC}_6\text{H}_4\text{NC}$, which maintain π overlap throughout the molecule suggesting that it should act as a molecular-level conductor. In addition, the axial dppe ligands protect the metal center against oxidation and should also inhibit intermolecular electron transfer. Furthermore, ligation of the terminal isocyanide group maintains π overlap with a surface. We present data for simple isocyanides adsorbed on Pd (111) in ultrahigh vacuum, which shows that they are strongly bound to the surface (with a binding energy of ~ 110 kJ/mol). The adsorption from solution of the linker $(\text{CNC}_6\text{H}_4\text{NC})$ is studied in situ on gold and palladium surface using thin metals films evaporated onto a zinc selenide attenuated total internal reflection cell and conductivities measured using atomic force microscopy.

76.

MECHANISM AND GROWTH KINETICS OF COLLOIDAL GOLD NANORODS. *Oscar R Miranda, DEPARTMENT OF CHEMISTRY, VILLANOVA UNIVERSITY, 800 LANCASTER AVENUE MENDEL 321, Villanova, PA 19085, Fax: 610-519-7167, oscar.miranda@villanova.edu, and Temer S Ahmadi, DEPARTMENT OF CHEMISTRY, VILLANOVA UNIVERSITY*

Mechanism and growth kinetics of photochemically synthesized colloidal gold nanorods are studied using UV-VIS spectroscopy and TEM imaging. We are showing how surface plasmon bands, colloidal nanoparticles' lengths, geometry and population can be controlled as the UV irradiation time and the chemical environment of the growing particles are changed. Spectroscopic and electron-microscopic evidence for the evolution of nanoparticle shapes within ‘soft templates’ are presented. Our mechanism indicates that a synergy between photon flux density and local temperature is responsible for the growth of anisotropic colloidal gold nanorods.

77.

SIZE-CONTROLLED SYNTHESIS OF SILVER NANOPARTICLES AND MEASUREMENT OF THEIR EXTINCTION, ABSORPTION, AND SCATTERING CROSS-SECTIONS. *David D. Evanoff Jr. and George Chumanov, Department of Chemistry, Clemson University, Biosystems Research Complex, Clemson, SC 29634, Fax: 864-656-0567, devanof@clemson.edu*

Metal nanoparticles are of great interest due, in part, to their unique optical properties that arise due to the collective oscillation of conduction electrons. Silver nanoparticles interact with light extremely efficiently making them attractive for use as an optical label and the standard choice for surface-enhanced spectroscopy. In this work we present a novel method for the synthesis of ‘spherical,’ single-crystal silver nanoparticles through the reduction of silver (I) oxide with hydrogen gas in ultra-pure water. The reaction produces particles of any diameter from ca.15 to 200nm with narrow size distribution. By spectroscopic methods the scattering and absorption components of the particles extinction spectrum were measured. By development of a “standard subtraction” technique, we also report the extinction, absorption, and scattering

cross-sections for particles of many diameters. The extinction efficiency of these particles range from four to ten, substantiating silver's ability to efficiently interact with light.

78.

INVESTIGATION OF PHARMACEUTICAL BIOCOLLOIDS USING HIGH-RESOLUTION ULTRASONIC SPECTROSCOPY. *Sinead Hickey, Vitaly Buckin, G. R. Ivanitskii, and M. J. Lawrence, Department of Chemistry, University College, Dublin, Belfield, Dublin 4, Ireland, Fax: 353 1 716 2127, Sinead.t.hickey@ucd.ie*

High-Resolution Ultrasonic Spectroscopy (HR-US) is a novel approach for the analysis of materials, in a non-invasive manner and provides information regarding their microstructure. In the present work we use HR-US to examine two colloidal systems. The first system involved construction of a pseudo-ternary phase diagram for a system consisting of pharmaceutically accepted components, water/isopropyl myristate/soybean lecithin and a cosurfactant, propanol. The transition points and pre-transition aggregation (including microemulsion phase) and particle size were measured for various water/oil/surfactant concentrations. The second system involved examination of the effect of dissolved gases in a fluorocarbon-based oxygen delivery emulsion, Pftoran (JSC SPF PERFTORAN). Sedimentation and effects of saturation with various respiratory gases were measured. Changes in ultrasonic velocity and attenuation in the MHz frequency range was monitored for both systems using a High-Resolution Ultrasonic Spectrometer (Ultrasonic Scientific Ltd.). The data obtained provided information on the structure of the micelles present in each case.

79.

STRUCTURE OF DNA-DTAB COMPLEXES. *Caroline Dunne and Vitaly Buckin, Department of Chemistry, Lab G46, University College, Dublin, Belfield, Dublin 4, Ireland, Fax: 353 1 7162436, caroline.dunne@ucd.ie*

Previously we have reported the formation of micelles of dodecyltrimethylammonium bromide (DTAB) surfactant on the surface of DNA in aqueous solutions. In the present work we used Atomic Force Microscopy to analyse the structure of these complexes with plasmid DNA on a hydrophilic mica surface and on a chemically inert gold surface. A thiolated poly amino acid facilitated DNA anchorage and the surfactant DTAB was added. At low DTAB concentrations, between 0 and 5mM, we found the formation of surfactant aggregates covering part of the DNA surface. At higher concentrations, above 5mM, only large globular structures were observed which include 'collapsed' DNA and surfactant. Analysis of the change in DNA conformation, which occurred both on the mica and the gold surface, was performed.

80.

ATOMIC FORCE MICROSCOPY CHARACTERIZATION OF CHOLESTEROL CRYSTAL DISSOLUTION IN THE PRESENCE OF BILE ACID SALTS. *Richard S. Abandan and Jennifer A. Swift, Department of Chemistry, Georgetown University, 37th and O Streets, NW, Washington, DC 20057, Fax: 202-687-6209, rsa@georgetown.edu*

Human gallstones and arterial plaques contain significant quantities of crystalline cholesterol. Atomic Force Microscopy (AFM) techniques have been used to characterize the structure and chemical functionality of the (001) surface of cholesterol monohydrate single crystals in different solution environments. In situ AFM imaging also provides a direct visualization of the dynamics of crystal surfaces undergoing growth and/or dissolution depending on the crystal environment. The real-time dissolution at the crystal surface under environments enriched with bile salts is of particular interest, as such agents are used in the oral dissolution therapy of gallstones. Under our AFM conditions, dissolution in the presence of chenodeoxycholate results in chemically heterogeneous surfaces that are not otherwise observed in aqueous solution environments. The real-time dissolution mechanism(s) and kinetics with bile salt concentrations below and above the critical micelle concentration will be discussed.

81.

FABRICATION AND CHARACTERIZATION OF THE COUPLING LAYERS FOR THE PROTEIN CHIP APPLICATIONS. *Sung wook Choi¹, Jin Ho Park¹, Jae Ho Kim¹, and Kwangnak Koh². (1) Department of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea, Fax: 82-31-214-8918, jhkim@ajou.ac.kr, (2) College of Pharmacy, Pusan National University, Pusan 609-735, South Korea, koh@pusan.ac.kr*

Successful immobilization of biological materials on solid substrates often requires carefully designed self-assembled monolayer of the coupling agents. In order to address problems associated with immobilization of biomaterials including low surface concentration and non-specific binding, we investigate the effect of coupling layers and the surface morphology. Either carboxylic or amine terminated coupling agents including dendrimers with different chain length were used for sequential immobilization of the protein A, anti-human IgG (antibody) and human IgG (antigen). We also investigated the effect of BSA on conformational changes of anti-human IgG. In this study, it was found that the optimal coupling layer was sensitively depended on the size and surface charge of the immobilized protein. We also found that presence of BSA enhances specificity and efficiency of the immuno-specific interaction by acting as an effector protein as well as a blocking agent. Therefore, the optimal coupling layer should be tailored by the characteristics of immobilized protein.

82.

HIGH RESOLUTION IMAGING OF TETANUS TOXIN ON LIPID BILAYERS VIA IN SITU SCANNING PROBE MICROSCOPY. *Andrea Slade¹, Anne E. Hibbard¹, Christopher M. Yip², and Darryl Y. Sasaki¹. (1) Biomolecular Materials and Interfaces Department, Sandia National Laboratories, P.O. Box 5800, MS 1413, Albuquerque, NM 87185, (2) Department of Chemical Engineering and Applied Chemistry / Institute of Biomaterials and Biomedical Engineering, University of Toronto*

Binding characteristics of tetanus toxin on planar lipid bilayers have been characterized via nanoscale imaging with in situ atomic force microscopy. Clostridial neurotoxins, such as botulinum and tetanus, are generally thought to invade neural cells through a process of high affinity binding mediated by gangliosides, internalization via endosome formation, and subsequent membrane penetration of the catalytic domain activated by a pH drop in the endosome. This internalization process is still not understood well with regard to what specific membrane features the toxins target, the intermolecular interactions between bound toxins, and the molecular conformational changes that occur as a result of pH lowering. We will describe our recent efforts towards understanding these related events using membranes containing solid and "raft"-like domains, and through a pH gradient study. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

83.

HEAVY METAL ION DETECTION VIA OPTICAL SENSING WITH LIPID BILAYER COATED BEADS. *Jennifer L. Pincus¹, Anne E. Hibbard¹, S. D. Menake E. Piyasena², Gabriel P. Lopez², and Darryl Y. Sasaki¹. (1) Biomolecular Materials and Interfaces Department, Sandia National Laboratories, P.O. Box 5800, MS 1413, Albuquerque, NM 87185, (2) Chemical Engineering and Chemistry, University of New Mexico*

Lipid bilayers capable of detecting sub-ppb levels of heavy metal ions have been fused onto glass beads for improved stability and facile assembly of optical sensor materials. The lipid membranes contain pyrene-labeled lipids functionalized with receptors that respond to metal ion presence with a change in the fluorophore's excimer to monomer intensity ratio (E/M), resulting in a green to blue optical response. By themselves, however, the bilayers are fragile and difficult to incorporate into an optical sensor platform. Previous efforts to incorporate the bilayers in a silica sol-gel matrix were compromised by transport issues. By applying the bilayers onto glass spheres followed by assemblage of the spheres into lattices it will be possible to circumvent the interaction of the analytes with the silica matrix. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

84. INCOMPATIBILITY OF MIXING OF PROTEINS IN 2-D FILMS AT THE OIL-WATER INTERFACE. *Sandhya Sridhar*, Department of Food Science, University of Wisconsin-Madison, 1605 Linden Dr. Rm118, Madison, WI 53706, *sridhar@wisc.edu*, and *Srinivasan Damodaran*, University of Wisconsin - Madison

Competitive adsorption between several protein pairs at Triolein-water interface was studied by surface radiotracer technique. Most protein pairs did not follow the simple Langmuir model for protein adsorption. Deviation from ideal behavior originates from incompatibility of mixing of proteins at the interface. Binding affinity of proteins was altered by this incompatibility. Extent of incompatibility between proteins was measured by graphical method and incompatibility parameter (X_{12}) was calculated for 15 protein pairs. The X_{12} showed a linear relationship with absolute difference in the Flory-Huggins protein-solvent interaction parameter $|\chi_{1s} - \chi_{2s}|$ of constituent proteins. Based on this observation we hypothesized that incompatibility of mixing of proteins exists at oil-water interface and this might lead to two-dimensional phase separation of proteins in the mixed film, which might be a cause of instability in protein stabilized emulsion system.

85. MONITORING ASSEMBLIES OF POLYMER-ENZYME CONJUGATES AT THE OIL/WATER INTERFACE. *Lifang Wang*, *Bi min Zhang*, *Newby, Guangyu Zhu*, and *Ping Wang*, Department of Chemical Engineering, The University of Akron, Akron, OH 44325-3906

The reduction of interfacial tension in the presence of a mediator, a polymer-enzyme conjugate, at an organic-aqueous interface was followed using the pendant drop method. The variation of interfacial tension as a function of assembly time was monitored for the conjugate to assemble at the interface. In general, the interfacial tension decreases rapidly during the first few minutes and reaches almost a constant in about 60 minutes. First studied was the influence of polymer-enzyme conjugate concentrations in the organic phase on the assembly behaviors. The interfacial tension in terms of bulk concentration of conjugates was fitted to the empirical adsorption isotherm model. Adsorption behaviors of polymer-enzyme conjugates at the organic-aqueous interface affected by the polymeric nature, polarity of the organic solvents, ionic strength and pH level of the aqueous phase were also examined. The polymeric nature was found to be the most significant parameter for the assemblies.

86. PHASE TRANSITION BEHAVIOR OF ALBUMIN ADSORPTION AT AIR-WATER INTERFACE. *Ping Chieh Wu*, *Shan An Liu*, *Mei Yun Chang*, and *Ruey Tsay*, Institute of Biomedical Engineering, National Yang Ming University, 155, Li-Nong St., Sec.2, Peitou, Taipei, Taiwan, R.O.C, Taipei, Taiwan, Fax: 886-2-28210847, *chieh@bme.ym.edu.tw*

In order to delineate the dynamic adsorption behavior and the state of protein adsorbed at interface, long-term dynamic surface pressure and surface film thickness of protein adsorptions were monitored. Most of the dynamic adsorption curves of surface pressure show a two-step increase pattern. The time required to reach the first plateau of surface pressure decreases with increasing bulk concentration and it is in general within twelve hours. For higher bulk concentration or lower temperature, it reveals adsorption curves only one step with increasing in surface pressure. The adsorption isotherms based on the surface pressure and film thickness at pseudo steady state both show phase transition behavior. It is believed that those transitions appeared in the adsorption isotherms correspond to the molecular rearrangement of native protein at the interface.

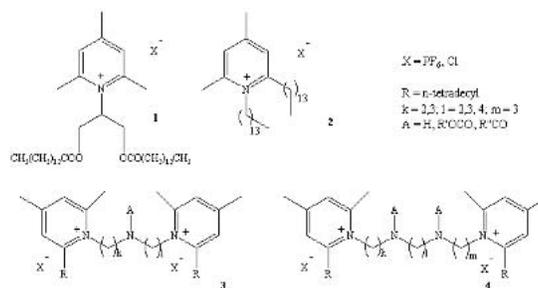
87. PROTEIN-LIPID INTERACTIONS AT THE AIR-WATER INTERFACE. *Rebecca J. Green*, *Mitaben D. Lad*, and *Fabrice Birembaut*, School of Chemistry, University of Reading, PO box 224, Whiteknights, Reading RG66AD, United Kingdom, *rebecca.green@reading.ac.uk*

External reflection FTIR spectroscopy and surface pressure measurements have been used to probe protein-lipid interactions and protein structural change at the air-water interface. Monomolecular layers of stearic acid and dipalmitoyl phosphatidyl choline were prepared at the air-water interface and protein adsorption to these layers was investigated. Contrasting interfacial behaviour of

the proteins, albumin and lysozyme, was observed. The rate of adsorption of lysozyme to the air-water interface increased dramatically in the presence of stearic acid due to strong electrostatic interactions between the negatively charged stearic acid head group and lysozyme, whose net charge at pH 7 is positive. Introduction of albumin to the subphase resulted in solubilisation of the stearic acid via the formation of an albumin-stearic acid complex. Structural changes of both lysozyme and albumin were observed during adsorption but these were dramatically reduced in the presence of a lipid layer compared to that of adsorption to the pure air-water interface.

88. STRUCTURE-ACTIVITY RELATIONSHIPS IN TWO SERIES OF PYRIDINIUM GEMINI SURFACTANTS FOR GENE DELIVERY. *Marc A. Ilies*¹, *Betty H. Johnson*², *William A. Seitz*¹, *Ed L. Ezell*², *Aaron Miller*², *E. Brad Thompson*², and *Alexandru T. Balaban*¹. (1) Marine Sciences Department, Texas A&M University at Galveston, 5007 Avenue U, Galveston, TX 77551, Fax: 409-740-4787, *iliesm@tamug.tamu.edu*, (2) Department of Biological Chemistry and Genetics, University of Texas Medical Branch

During our program for generating new cationic lipids for gene delivery bearing pyridinium polar heads we identified several lead compounds such as 1 and 2 that displayed better transfection profiles than commercial transfection systems. Using the reaction of pyrylium salts with primary amines on which our general strategy was based, we were able to synthesize new Gemini surfactants of type 3 and 4. We present an extensive structure-activity relationship study with these two series of amphiphilic compounds, which revealed lipidic formulations that are superior to several commercial transfection systems.



89. CONCENTRATION DEPENDENT VESICLES MICELLE TRANSITION IN AQUEOUS MIXTURES OF CATIONIC AND ANIONIC SURFACTANTS. *Hisanori Nakanishi*¹, *Koji Tsuchiya*², *Takahiro Ohkubo*¹, *Hideki Sakai*¹, and *Masahiko Abe*¹. (1) Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan, Fax: 81-4-7124-8650, *j7203704@ed.noda.tus.ac.jp*, (2) Faculty of Science and Technology, Science University of Tokyo

Aqueous mixtures of cationic and anionic surfactants have attracted attention because of the spontaneous of molecular assemblies such as vesicles and rod-like micelles. These mixtures also exhibit an interesting phase behavior in which vesicles formed at low concentrations are transformed into mixed micelles at high concentrations. No such phase behavior is observed for ordinary surfactant solutions. This present study deals with phase behavior of aqueous mixed solutions of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, and sodium octyl sulfate (SOS), an anionic surfactant, focusing on the concentration dependent vesicle-micelle transition. 1H-NMR results confirm that the interactions between each surfactants headgroups tightly bound in the vesicles region. On the other hand, in the micelles region electrostatic interaction is weaker suggesting that main component of the micelles is SOS molecules.

90. FORMULATION SCAN OF FATTY ACIDS IN SURFACTANT/OIL/WATER SYSTEMS. *Nelson Márquez*, *Bélgica Bravo*, *Gerson Chávez*, *Ana Beatriz Caceres*, *Roberto Bauza*, and *Fredy Ysambert*, Lab. Petroquímica y Surfactantes, Departamento de Química-Facultad de Ciencias, Universidad del Zulia, Maracaibo 526, Venezuela, Fax: 58-261-7598125, *nmarquez@zul.reacciun.ve*

The phase behaviour of surfactant/oil/water systems depends upon the hydrophilic-lipophilic interaction at interface. In pH variable systems, the surfactant is

produced by a mixture of two different species, one which is undissociated, (acid specie), and the other which is the ionized counterpart (carboxylate specie). The acid specie is a very lipophilic non-ionic surfactant, on the other hand, the carboxylate specie is very hydrophilic. Formulation scan was performed with fatty acids by changing the pH of the system. The pH variation of the acid/oil/water system allows attained the transition of WII-WIII-WI. Optimal formulation for different fatty acid studied was enhanced using lipophilic alcohols. Also, the solubility of the carboxylate species was improved. Selective partition of these carboxylic acids was studied by HPLC. Microemulsion contains both species, undissociated and dissociated species respectively.

91.

SELF-ASSEMBLING SEMICONDUCTING FILMS FROM OLIGOTHIOPHENE

SURFACTANTS. Darryl Y. Sasaki¹, Lu Jiang¹, and Robert C. Hughes². (1) *Biomolecular Materials and Interfaces Dept, Sandia National Laboratories, MS 1413, Albuquerque, NM 87185, Fax: 505-844-5470, dysasak@sandia.gov*, (2) *Microsensor Dept, Sandia National Laboratories*

Surfactant molecules composed of a hydrophobic quaterthiophene segment and hydrophilic headgroups have shown self-organizing properties in aqueous solution to form vesicles and ordered multilamellae in cast films. Sonication produced vesicles that had mean diameters of 78 ± 15 nm with an ellipsoidal shape of flat sides, suggestive of the molecule's tendency to pack in crystalline-like sheets. Cast films, prepared from water or polar organic solvents, were found to be multilamellar by XRD with d-spacing of 33Å, translating into a tilt angle of 58° from normal. The cast films showed complex non-ohmic and time dependent conductivities when excited by a 10 Hz sawtooth voltage of several volts. The undoped, bulk conductivity was of the order of 10^{-7} Ω⁻¹cm⁻¹ with photoconductive behavior observed using visible light. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

92.

SPECTROSCOPIC DELINEATION OF THE SURFACTANT MICROSTRUCTURES IN CATIONIC AND ANIONIC MIXTURES.

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The self-assembly of binary mixtures of surfactants in aqueous solution generates a wide variety of microstructures including spherical and rod-like micellar structures, vesicles, and lamellar liquid crystalline phases. Of special interest are those systems that yield thermodynamically stable spontaneous unilamellar vesicles. We have characterized both cationic (mixtures of oppositely-charged surfactants) and bicationic systems using fluorescence and light scattering techniques. In particular, we demonstrate that the polarity-sensitive fluorophore prodan can be used to demarcate the surfactant microstructures in the aqueous systems of (1) cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium octyl sulfate (SOS), (2) cationic dodecyltrimethylammonium bromide (DTAB) and anionic sodium dodecyl sulfate (SDS), and (3) cationic DDAB (didodecylidimethylammonium bromide) and cationic DTAC (dodecyltrimethylammonium chloride). As the fluorescence signature of this probe is dependent on the nature of the surfactant aggregates present, our method is a promising new approach to effectively map complex surfactant phase diagrams.

93.

TRANSPORT AND RELEASING OF WORM MICELLES. Younghoon Kim¹, Yan Geng², Paul Dalhaimer³, Fariyal Ahmed², and Dennis E. Discher³. (1) *Department of chemical and biomolecular engineering, University of Pennsylvania, 220 South 33rd Street, Room 311A Towne Building, Philadelphia, PA 19104, Fax: 215-573-2093, younghk@seas.upenn.edu*, (2) *Department of Chemical Engineering, University of Pennsylvania*, (3) *Department of Chemical and Biomolecular Engineering, University of Pennsylvania*

Amphiphilic block copolymers have been used to assemble worm-micelles that are flexible, stable and can transport hydrophobic drugs. Possible applications include convective delivery through porous media; and so we have studied transport through gels. Compared to 100 nm size vesicles that are often used to

deliver drugs but are filtered out by such gels, Worm-micelles show excellent permeation through such nano-porous gels. For delivery and degradation purposes, we have also shown that PEG-Polyester-based worm-micelles will degrade over time, breaking down into smaller fragments as monomers are generated by polyester hydrolysis. We observe that the release of hydrophobic compounds from such worm micelles occurs by a mechanism consistent with re-partitioning. In sum, the results show that worm micelles are useful convective for carriers of dyes and drugs.

94.

WETTING CHARACTERISTICS OF SELF-ASSEMBLED POLYELECTROLYTE MULTILAYERS ON PLASMA-MODIFIED POROUS POLYETHYLENE.

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Hydrophilic and chemically reactive porous media was prepared by adsorbing functional polymers at the surface of sintered polyethylene membranes. Modification of the membrane was accomplished by first exposing the membrane to an oxygen glow discharge gas plasma to introduce electrostatic charge at the membrane surfaces. Cationic polyelectrolyte polyethylenimine (PEI) was adsorbed from solution to the anionic charged surface to form an adsorbed monolayer. The adsorption of a second anionic polyelectrolyte onto the PEI layer, allowed further modification of the membrane surface to form a polyelectrolyte bilayer complex. The conformation and stability of adsorbed monolayers and bilayers comprising the modified surface was probed as a function of polymer structure, charge density, and solubility. By using the wicking rate of deionized, distilled water through the porous membrane to gauge the interfacial energy of the modified surface, it was possible to show that the wetting properties of the membrane could be controlled by varying the chemistry of the adsorbing polyelectrolytes and, to a lesser extent, by adjusting the polarity or ionic strength of the polyelectrolyte solution.

95.

AFM STUDIES OF THE HIGH DENSITY POLY (ETHYLENE GLYCOL) GRAFTED LAYERS. Bogdan Zdyrko and Igor Luzinov, *School of Materials Science and Engineering, Clemson University, 161 Serrine Hall, Clemson, SC 29634, bogdanz@clemson.edu*

High density poly (ethylene glycol) (PEG) grafted layers were prepared by melt grafting to the reactive polymer layer. PEGs with different molecular weights were used. Due to the high concentration of the functional groups in reactive polymer layer extremely high-density PEG grafted films were obtained. AFM was used to characterize the films in dry and wet state. Dense grafting resulted in partial crystallization of the PEG chains in the layer. Several distinct types of the dry film morphology were distinguished depending on the grafted layer density and molecular weight. Crystal formation and growth was monitored by AFM.

96.

CONFORMATIONAL REPOSE OF POLYMER CHAINS WITH ATTACHED

MAGNETIC NANOPARTICLES. Roman Sheparovych¹, Yudhisthira Sahoo², Sergiy Minko¹, and P.N. Prasad³. (1) *Department of Chemistry, Clarkson University, Clarkson Ave. 8, Potsdam, NY 13699, sheparrb@clarkson.edu*, (2) *Department of Chemistry, State University of New York at Buffalo*, (3) *Photonics Research Laboratory, State University of New York at Buffalo*

The paper reports on grafting of polymer chains to g-Fe-oxide nanoparticles (15 nm in size). The nanoparticles are coated with a functional surfactant constituting the stabilizing shell. We use the γ -functional groups of the stabilizing shell to bind polyelectrolyte chains. AFM experiments were employed to study the structure of the nano-particle – polyelectrolyte chain assemblies and their response to the applied external magnetic field under aqueous solutions. The polymer chains with the attached nanoparticles were grafted to the solid substrate. The conformational changes of the grafted molecules in the external magnetic field were studied upon changes of ionic strength of the aqueous solutions.

97.

HYBRID MATERIALS COMPOSED OF COLLOIDAL NANOPARTICLES AND POLYMERS: DIRECTED DEPOSITION AND SELF-ASSEMBLY. *Qingling Zhang¹, Ting Xu², Thomas P. Russell², and Todd Emrick³.* (1) *Polymer Science & Engineering Dept, University of Massachusetts Amherst, 120 Governors Drive, Conte Center for Polymer Research, Amherst, MA 01003, Fax: 413-545-0082, qingling@polysci.umass.edu,* (2) *Department of Polymer Science and Engineering, University of Massachusetts,* (3) *Department of Polymer Science and Engineering, University of Massachusetts Amherst*

An efficient method to incorporate CdSe nanocrystals in polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) templates was accomplished using CdSe nanocrystals with negatively charged ligands and a dc electric field. PS-*b*-PMMA templates were prepared with PMMA cylinders standing normal to the surface in a PS matrix. PMMA was degraded by UV irradiation to give polymer templates with 15-20 nm diameter hollow cylinders. CdSe nanocrystals covered with 11-mercaptopundecanoic acid (MUA) were prepared and dispersed in water. An electric field was applied between the template and a clean silicon wafer in a vessel containing the aqueous nanoparticle solution. Transmission electron microscopy revealed an efficient deposition of nanoparticles into the cylindrical regions. The use of E-field enhanced the deposition process relative to control experiments where no field was applied. This protocol may be used to entrap nanoparticles into nanopores of various shapes and sizes, for potential application in storage and high resolution displays.

98.

INFLUENCE OF AGING TIME ON THE POROSITY, MORPHOLOGY AND STRUCTURE OF HEXYLENE-BRIDGED POLYSILSESQUIOXANE GELS. *D. A. Loy, Polymers and Coatings Department, Los Alamos National Laboratory, PO Box 1662, MS E549, Los Alamos, NM 87545, Kimberly A. DeFriend, Materials Science and Technology Division, Los Alamos National Laboratory, J. H. Small, Polymer & Coatings Group, MST-7, Los Alamos National Laboratory, K. J. Shea, Department of Chemistry, University of California Irvine, and McKenzie Minke, Chem & Bio Technologies Department, Sandia National Laboratories*

Bridged polysilsesquioxanes are sol-gel processed gels whose molecular building blocks permit the construction of networks in which siloxane and organic bridging groups are integral components of structure. Through the selection of the bridging group, it is possible to manipulate the ultimate morphology and porosity of the resulting xerogels. Perhaps the most frequently observed effect is that acid-catalyzed sol-gel polymerization of monomers with "flexible" organic groups, such as alkenes comprised of six or more methylenes in length, lead to gels that collapse upon drying to afford non-porous xerogels. The hexylene-bridged system affords gels that are at the boundary between those that collapse and those that do not collapse upon drying. Therefore, subtle changes in the reaction and processing parameters can influence whether or not the final xerogel is porous. In this study, we have varied the aging time of the gels before their drying and examined the resulting changes in porosity by nitrogen sorption porosimetry, morphology by scanning electron microscopy, and chemical structure by solid state NMR.

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

99.

LATERALLY VARYING THICKNESS GRADIENTS OF POLY(ACRYLIC ACID) FORMED BY ELECTROPOLYMERIZATION WITH SPATIOTEMPORAL CONTROL OF THE ELECTROCHEMICAL POTENTIAL. *Paul W. Bohn and Xuejun Wang, Dept. of Chemistry, Univ. of Illinois, 600 S. Mathews Ave., Urbana, IL 61801*

There is currently much interest in generating and utilizing laterally anisotropic (gradient) surface. Laterally varying thickness gradients of Poly(acrylic acid) (PAA) were formed by Zn(II)-catalyzed electropolymerization of acrylic acid (AA) in the presence of an in-plane electrochemical potential gradient applied to Au working electrodes. Because the kinetics of heterogeneous electron transfer vary with the local overpotential, in-plane potential gradients were expected to produce PAA films with laterally varying thickness gradients. Both static in-plane potential gradient (SPG) and time-dependent dynamic in-plane potential gradient (DPG) were exploited to generate PAA gradients. X-ray photoelectron spectroscopy (XPS) and Surface Plasmon Resonance (SPR) imaging were used to characterize these PAA gradients. The in-plane thickness variations of PAA

gradients agreed with predictions of the Butler-Volmer equation at small absolute overpotentials, while at large (negative) overpotentials, mass transport dominates, and the thickness reaches a plateau value independent of local potential. DPG-produced PAA gradients are generally broader than SPG gradients with the same initial potential and comparable effective growth time.

100.

LAYER-BY-LAYER DEPOSITION APPROACH FOR THE FABRICATION OF RESPONSIVE SURFACES. *Maxim Orlov and Sergiy Minko, Department of Chemistry, Clarkson University, 8 Clarkson Ave., Potsdam, NY 13676, orlovmv@clarkson.edu*

One of the newly developed techniques – layer-by-layer polyelectrolyte deposition was used to fabricate polymer films with smart properties. The driving force of the formation of polyelectrolyte multilayers through layer-by-layer deposition of polyelectrolytes originates from the electrostatic attraction between the oppositely charged polymer species. Polyelectrolyte multilayers built up by this process represent a simple pathway to fabricate a film with well-controlled film thickness and composition, balancing hydrophobic and hydrophilic properties of the top layer of the film. The responsive behavior of the film was investigated upon changes of the outside conditions, i.e. pH, salt, and temperature.

101.

POLYDIMETHYLSILOXANE THIN FILMS AS BIOCOMPATIBLE COATINGS IN A MICROANALYTICAL LASING DEVICE. *Sophie L. Peterson¹, Anthony McDonald¹, Paul L. Gourley¹, and Darryl Y. Sasaki².* (1) *Biomolecular Materials and Interfaces Dept, Sandia National Labs, MS 1413, Albuquerque, NM 87185, Fax: 505-844-5470, slpeter@sandia.gov,* (2) *Biomolecular Materials and Interface Science Department, Sandia National Laboratories*

Surface oxidized, thin films of polydimethylsiloxane (PDMS) have been evaluated as biocompatible coatings in a microanalytical lasing device. The PDMS film offers excellent properties as a barrier to biofluids, which can rapidly and irreversibly extinguish the optical emission of vertical cavity semiconductor laser (VCSEL) devices. Self-assembled monolayers and polymethylmethacrylate films were also tested, but could maintain VCSEL lasing for only a couple of minutes or less. A two-micron film of PDMS, on the other hand, resisted biofluid permeation for hours. While the native PDMS surface is poorly supportive of cell growth and promotes clogging of microfluidic structures, oxidation of the film via oxygen plasma yields a biocompatible surface that is supportive of cell adhesion and proliferation under static conditions, yet minimizes channel clogging in a microfluidic device. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

102.

STRUCTURE OF TELECHELIC TRI-BLOCK-COPOLYMER MICELLES IN AQUEOUS ENVIRONMENT VISUALIZED IN AFM EXPERIMENTS. *Robert Lupitsky, Department of Chemistry, Clarkson University, 8 Clarkson Ave, Potsdam, NY 13699, lupitsrm@clarkson.edu, Constantinos Tsitsilianis, Department of Chemical Engineering, University of Patras, and Sergiy Minko, Department of Chemistry, Clarkson University*

We have investigated the association behavior of triblock copolymer of poly(methylmethacrylate)-*b*-poly(dimethylaminoethylmethacrylate)-*b*-poly(methylmethacrylate) in aqueous solutions. The association behavior depends on the concentration of the polymer as well as on the pH of the solution. At low concentrations the copolymer forms core-shell type micelles with hydrophobic core and hydrophilic shell. After the critical concentration the physical network was formed, which was directly observed by Atomic Force Microscopy.

103.

SURFACE GRAFTING OF POLYGLUTAMATE ON SILICA PARTICLES AND PATTERNED SOLID SUBSTRATE. *Jaehyun Park and Daewon Sohn, Department of Chemistry, Hanyang University, Seoul 133-791, South Korea, rokat661@hotmail.com*

Surface-grafted polyglutamate have been prepared by the ring-opening polymerization of benzyl-L-glutamate N-carboxyanhydride (BLG-NCA) monomer from (γ -aminopropyl) triethoxysilane (APS) pretreated silica nanoparticles and patterned silica substrate. FT-IR spectra show a α -helix conformation of the grafted polyglutamate shell without other conformations. The polarized optical micro-

scope images show the PBLG coated nanoparticles have liquid crystal property due to the anisotropic behavior of PBLG. The size of the particle and the shape of the patterned surface were demonstrated by dynamic light scattering and atomic force microscopic images, respectively. The resulting layer of rodlike polyglutamate is of uniform thickness up to 50nm and was found to be very stable.

104.

SURFACE GRAFTING OF POLYSACCHARIDES AND THEIR DERIVATIVES. *Anna Koh, Chemistry Department, Mount Holyoke College, 50 College Street, 1496 Blanchard Student Center, South Hadley, MA 01075, aekoh@mtholyoke.edu, and Wei Chen, Department of Chemistry, Mount Holyoke College*

In this research, polysaccharides (e.g. dextrans) are evaluated as poly(ethylene glycol) (PEG) alternatives for biocompatibility. Amine groups-containing surfaces were prepared by reacting (3-aminopropyl)dimethylethoxysilane with clean silicon wafers in the vapor phase. Oxidation of dextrans (10,000 g/mol) was carried out in sodium periodate aqueous solution at room temperature in the dark for the desired amount of time to control the amount of aldehyde groups formed. Dialysis and lyophilization were performed to purify and dry oxidized dextran samples, respectively. Dextrans of various molecular weights (10,000 to 2,000,000 g/mol) and the oxidized dextrans with varying degree of oxidation were grafted to the amine-activated surfaces at 40C for 4 days; NaCNBH₄ and K₂SO₄ were added the grafting solution to reduce the formed imines to more stable amines and to improve the grafted dextran densities on surfaces, respectively. Protein adsorption studies of surfaces grafted with dextrans and their derivatives were carried out to assess their biocompatibility.

105.

SURFACE GRAFTING OF SYNTHETIC HYDROPHILIC POLYMERS VIA RING OPENING METHATHESIS POLYMERIZATION. *Stephanie Stoddart, Chemistry Department, Mount Holyoke College, 50 College Street, 3170 Blanchard Student Center, South Hadley, MA 01075, sstodda@mtholyoke.edu, and Wei Chen, Department of Chemistry, Mount Holyoke College*

Poly(ethylene glycol) (PEG)'s popularity as a biocompatible material stems from its nonimmunogenicity, nontoxicity, water solubility, and high hydrodynamic volume. Is PEG a unique polymer in this regard? Recently we have turned our attention to other hydrophilic polymers, both natural and synthetic. In this research, head-to-head poly(vinyl alcohol) (hh-PVOH) and hydroxylated polynorbornene (hPNBN) were grafted to silicon wafer surfaces and evaluated as poly(ethylene glycol) alternatives for biocompatibility. Norbornenyl groups were attached to surfaces via silanization followed by covalent attachment of Grubbs catalyst. hh-PVOH and hPNBN are synthesized by hydroxylation of polymers prepared from ring opening metathesis polymerization of cyclooctadiene and norbornene. Polymer chain length and chain density were controlled by silanization time, monomer concentration, and ROMP reaction time. Biocompatibility of these hydrophilic molecules was assessed by protein adsorption. All of the surfaces were characterized by contact angle analysis, ellipsometry, and x-ray photoelectron spectroscopy.

106.

SURFACE MODIFICATION OF POLYSULFONE FILMS BY MEANS OF A FILTERED N₂ AND CO₂ RF PLASMA. *Stephen J. Bransfield¹, D. Howard Fairbrother¹, Sabine Vico², and Francois Reniers². (1) Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, MD 21218, Fax: 410-516-8420, sjb@jhu.edu, (2) Analytical and Interfacial Chemistry, Université Libre de Bruxelles*

The performance of porous polysulfone (PSU) ultrafiltration membranes and PSU-based ion exchange membranes could significantly be improved by an increase of the surface hydrophilicity. Filtered N₂ and CO₂ RF plasmas were used to graft basic and acidic hydrophilic groups on model PSU films respectively. In contrast to most plasma systems, our configuration allows a selection of the reactive particles reaching the polymer surface, filtering out the ions, and allowing only the neutrals and the electrons to interact with the PSU. The films were characterized by XPS and contact angle measurements. The increase in surface energy is correlated to the change in surface composition. XPS analysis of the modified films indicates a progressive reduction of the sulfone groups with both gases. Results will also be presented comparing the effect of nitrogen plasma and nitrogen ion beam treatments on PSU films.

107.

SURFACE MODIFICATION VIA SEQUENTIAL ATRP GRAFTING. *Viktor Klep and Igor Luzinov, School of Materials Science and Engineering, Clemson University, 161 Serrine Hall, Clemson, SC 29634, klep@clemson.edu*

Sequential Atom Transfer Radical Polymerization (ATRP) of different monomers from a surface is reported. Poly (glycidyl methacrylate) (PGMA) was used to bring epoxy functionalities to a substrate. Part of the epoxy groups was converted to ATRP initiator by treatment with bromocarboxylic acids. Oligoethyl-ene glycol methacrylate (OEGMA) was polymerized from the surface in water/ alcohol media using CuBr/CuBr₂/2,2-bipyridine catalytic system. Sequential ATRP of styrene led to poly-OEGMA-block-polystyrene brush. In another approach, OEGMA brush was treated with tributyltin hydride to remove the terminal bromine atoms. Immersion of the deactivated brush into a monomer solution charged with the components for ATRP did not lead to any additional polymer grafting. Then, residual epoxy groups of the PGMA were used for reattachment of the ATRP initiator through the deactivated brush and styrene was successfully polymerized throughout the poly-OEGMA layer. Surface morphology of the grafted layers was studied by AFM and contact angle measurements.

108.

SURFACE MODIFICATION WITH SEGREGATED GRAFTED POLYMER LAYERS. *Yong Liu, Viktor Klep, and Igor Luzinov, School of Materials Science and Engineering, Clemson University, 263Serrine Hall, Clemson, SC 29634-0971, Fax: 864-656-5973, yongl@clemson.edu*

Phase separated ultra-thin polymer film was used as a template to fabricate segregated grafted polymer layers. Both "grafting to" and "grafting from" methods were employed to construct the heterogeneous surfaces. The segregated grafted layers consisted of both hydrophobic and hydrophilic regions. Various ratios of hydrophilic/hydrophobic areas were achieved. AFM was used to characterize the surface structure of these segregated brushes treated with selective solvents to reveal the non-uniform surface response.

109.

STRUCTURE-PROPERTY RELATIONSHIP OF VINYL ESTER RESINS CAUSING REDUCED VOC EMISSION. *Tania Dey¹, John J. LaScala², and Giuseppe R. Palmese¹. (1) Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104, td53@drexel.edu, (2) Army Research Laboratory, Maryland, MD 21005*

The use of polymer composites is expected to increase 100-fold over the next two decades because of their high properties, low weight and low cost. The increasing demand for low-cost composites is accompanied by the need of low-cost processing methods, such as liquid molding, that require low resin viscosity systems (<500 cP). Unfortunately, these systems contain volatile organic compounds (VOC), such as styrene, that are damaging to the environment. VOCs are liberated during all phases of composite fabrication. Federal EPA is highly concerned with hazardous emissions, specifically targeting styrene as a hazardous air pollutant (HAP). One method of reducing styrene emission from vinyl ester (VE) resins is to replace styrene with fatty acid-based monomers. The viscosity and thermo-mechanical properties as well as the cure rate of these binary blends were found to be affected considerably by the nature of the fatty acids like chain length and level of unsaturation.

110.

CONSTRUCTING SURFACE MOUNTED MOLECULAR ROTORS. *Tao Ye¹, Tomohide Takami², James M. Tour³, Ken ichi Sugiura⁴, and Paul S. Weiss¹. (1) Department of Chemistry, The Pennsylvania State University, 152 Davey Lab, State College, PA 16801, tuy1@psu.edu, (2) Visionarts Research, Inc, (3) Department of Chemistry, Rice University, (4) Department of Chemistry, Tokyo Metropolitan University*

We attempt to assemble surface mounted molecular rotors through a shaft-fan design. In a host alkanethiol self-assembled monolayer matrix, a shaft, a pyridine terminated oligo phenylene ethylene thiol is inserted. The fan of the rotor assembly, a metal porphyrin, is attached to the shaft via axial ligation with the pyridine terminal. These supramolecular structures are characterized by scanning tunneling microscopy (STM). We perform a systematic investigation on parameters such as the chain length of the alkanethiol matrix and the meter

center of the porphyrins. We will discuss the STM contrast mechanism of these structures.

111.

CONTROL OF VISCOELASTICITY USING REDOX REACTION. *Koji Tsuchiya, Hideki Sakai, Takahiro Ohkubo, and Masahiko Abe, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan, Fax: +81-4-7122-1422, kojit@attglobal.net*

We report a novel system that enables us to dynamically control the viscoelasticity of fluids by applied electric potential. The system used is a promising candidate for new electro rheological (ER) fluid which will widely be applied to the active controlled release of substances such as dyes and perfumes, ink for inkjet printers, clutch for transmission. Our system is based on a redox-switchable ferrocenyl surfactant [(11-ferrocenylundecyl)trimethylammonium bromide, FTMA] that self-assembles into worm-like micelles in the presence of sodium salicylate (NaSal). An aqueous solution of mixed FTMA (reduced form) and NaSal exhibits a remarkable viscoelasticity due to the three-dimensional network consisting of worm-like micelles. After the oxidation of FTMA, the viscosity of the system dramatically decreases and the elasticity disappears. This remarkable viscoelasticity decrease is caused by a significant change in the aggregation state from worm-like micelles to monomers and/or other smaller aggregates due to the enhanced hydrophilicity of FTMA.

112.

DEPOSITED AND REACTIVELY FORMED EXTREME-PRESSURE LUBRICANT FILMS: A COMPARATIVE STUDY IN UHV. *Feng Gao¹, Octavio J. Furlong¹, and Wilfred T. Tysse². (1) Department of Chemistry and Laboratory for Surface Studies, UW-Milwaukee, 3210 N Cramer St, Milwaukee, WI 53211, Fax: 414-229-5036, fenggao@uwm.edu, ofurlong@uwm.edu, (2) Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee*

Extreme-pressure lubricant additives (e.g., CCl₄) react with iron at the hot interface to form a lubricant film that composes mainly FeCl₂ and sometimes carbonaceous species. FeCl₂ films are both directly deposited onto iron foil and reactively formed (CCl₄ + Fe at 600 K) and their tribological properties investigated with an UHV-compatible tribometer. It is found that friction coefficient reaches a low limiting value following monolayer FeCl₂ film saturation in both cases. The limiting friction coefficient for the reactively formed film is lower than that of the deposited film, presumably because carbon diffuses into iron bulk to increase the substrate hardness. Film mobility and transfer are found in both cases.

113.

INVESTIGATIONS OF OLIGOMERIZATION OF PHENOLIC COMPOUNDS ON ACTIVATED CARBON FIBERS. *Qiuli Lu, Dept. of Civil Engineering, University of Cincinnati, P.O. Box 210071, Cincinnati, OH 45221-0071, Fax: 513-556-2599, luq@email.uc.edu, and George A Sorial, Civil & Environmental Engineering Department, University of Cincinnati*

FT-IR and GC/MS were used to identify the oligomerization of phenolic compounds on the surface of activated carbon fibers (ACFs) in this study. Single solute adsorption of 2-methylphenol, 2-chlorophenol and 2-nitrophenol were conducted on two ACFs, ACC-10 and ACC-15. Binary adsorption of 2-methylphenol / 2-chlorophenol and 2-methylphenol / 2-nitrophenol were also conducted for studying the competitive behavior. Two isotherm conditions were considered, namely, anoxic (absence of molecular oxygen in the test environment) and oxic (presence of molecular oxygen in the test environment). Extractions of ACFs used in the adsorption experiments were conducted. FT-IR measurements were conducted for the ACFs before and after extractions. The extracts were analyzed by GC/MS. Coupling bonds were identified by FT-IR for oxic single and binary solute adsorption on ACC-15. This oligomerization is further confirmed by the dimers and trimers observed in the extracts. For adsorption on ACC-10, only oxic single solute adsorption of 2-methylphenol showed the oligomerization. For other oxic adsorption isotherms conducted on ACC-10, no coupling bonds were observed. None of the anoxic adsorption isotherms showed oligomerization and high extraction efficiency was achieved.

114.

QUANTITATIVE CHEMICAL ENGINEERING OF NANOPARTICLE SURFACE PROPERTIES. *Mark Schadt, Mathew M. Maye, Li Han, Nancy N. Kariuki, Aisley Jacob, and Chuan Jian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, mschadt1@binghamton.edu*

The ability to engineer the surface properties of organic capping materials on metallic nanoparticles is important for manipulating the chemical and physical characteristics of nanoparticle assemblies. Controllable and selective modification (derivatization) of functional groups in the surface organic monolayer on nanoparticles provides the opportunity to develop this ability. Here we describe a novel strategy for the quantitative surface derivatization of gold nanoparticles. Gold nanoparticles capped with a monolayer of alkanethioliates containing mixed functional groups (methyl and carboxylate) combined with surfactants such as tetraoctylammonium bromide were investigated as a model system. We have demonstrated that the derivatization of the mixed shell functionalities can be accomplished quantitatively via a controlled phase-transfer process, and that the resulting dendrite-like molecular capping structure is capable of directing interparticle ordering and assembly. The quantitative nature of the phase transfer process further indicates the viability of sorting nanoparticle sizes during surface derivatization. The chemical and structural properties of the molecularly engineered nanoparticles will be discussed in light of results from UV-Visible, FTIR, TEM and AFM characterizations.

115.

SUBSTRATE-DOMINATED PHASE SEPARATION OF SELF-ASSEMBLED THIOLS ON AU. *Irene Popova, The James Franck Institute, University of Chicago, 5640 S. Ellis Ave, Chicago, IL 60637, irep@uchicago.edu, and S. J. Sibener, Department of Chemistry, University of Chicago*

We have used scanning tunneling microscopy (STM/STS) to study the phase separation of mixed thiol monolayers containing hydrocarbon and semi-fluorinated alkane thiols (10 and 8 carbon chains) on smooth and patterned Au substrates. We find that mixed monolayers prepared by adsorption from an asymmetric disulfide solution yields a 1:1 surface ratio of hydrocarbon and fluorinated components and phase separates upon surface annealing at 373 K. Annealing-induced phase separation, driven by inter-chain repulsive interaction, leads to spontaneous creation of hexagonally ordered hydrocarbon islands surrounded by striped phase-like areas, which contain a mixture of hydrocarbon and fluorocarbon thiol. Islands become more oblong with annealing and align specifically along [112] crystallographic direction. They eventually form 100-200 nm long wire-like structures (width 5-10 nm). Orientation of these nanostructures, dictated by strong anisotropy of S-Au bond, is not altered by the presence of fluorinated thiol and coincides with chain tilt direction observed for hydrocarbon phases.

116.

ANOMALOUS LIGHT SCATTERING FROM COMPLEX FLUIDS. *Thomas A. P. Seery and Maria Cecilia de Mesa, Chemistry Department and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, Fax: 860-486-4745, seery@mail.ims.uconn.edu, mcdemesa@ims.uconn.edu*

The difficulty and complexity of acquisition and interpretation of light scattering data from polymeric and colloidal solutions that absorb light limits the application of scattering techniques to transparent colorless solutions. The dynamic light scattering data of highly absorbing solutions, e.g. polyaniline in NMP, is anomalous showing correlation functions with an oscillatory component. Light absorption heats the sample causing further complications like temperature gradients and thermal lensing resulting in convection within the scattering volume and in changes of the geometry of the experiment. A model for the scattering from a mixture with a bimodal size distribution in a convective flow field was developed. A model system was prepared from low molecular weight polystyrene and coated silica particles in a solvent medium containing a low concentration of dye. Data similar to that seen for the polyaniline was observed. The temperature, laser power, and concentrations of dye, polystyrene and silica particles were studied.

117.

DENSE CO₂ HYDRATE COMPOSITE PARTICLES PRODUCED IN THE DEEP OCEAN. *Costas Tsouris¹, David E. Riestenberg², Monsuru O. Gborigi², Michael J. Lance³, Peter G Brewer⁴, Edward T. Peltzer⁴, and Peter Walz⁴.* (1) Nuclear Science and Technology and Environmental Sciences Divisions, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6181, *tsourisc@ornl.gov*, (2) Environmental Sciences Division, Oak Ridge National Laboratory, (3) Metals and Ceramics Division, Oak Ridge National Laboratory, (4) Monterey Bay Aquarium Research Institute

Direct injection of CO₂ in the ocean is being considered to as a method to manage atmospheric CO₂ levels. A coflow injector, designed to intimately contact liquid CO₂ and water, has been demonstrated in the laboratory to produce a dense solid-like composite consisting of unreacted CO₂, water, and CO₂ hydrate at intermediate ocean depths. Field injection experiments were conducted in the ocean in Monterey Bay, California, at depths of 900-1600 m focussing on laser Raman spectroscopy of the composite, scaling up the injector, and producing a rapidly sinking composite that carries CO₂ to the bottom. In previous ocean injections, neutrally buoyant composite was produced and 25-30% of the CO₂ was converted to hydrate. However, in recent ocean injections, sinking composite was produced by using a larger injector at higher flow rates, and conversion increased to 35-40%. Raman spectra of the composite were also taken and compared well with those obtained in the laboratory.

118.

AB INITIO CALCULATION ON STRUCTURE OF NANO- SIZED SILICA CLUSTER. *Xin Liu¹, Changgong Meng¹, and Changhou Liu².* (1) Department of Chemistry, Dalian University of Technology, PO Box 288, Dalian, 116024, China, *liuxin_dut@hotmail.com*, (2) School of Chemical Engineering, Dalian University of Technology

Sol-gel procedures are widely used in microporous and mesoporous materials synthesis. But there is still little information available on the fundamental mechanisms. We used ab initio methods to study small silica clusters, containing from 1 to 5 Si atoms. The calculation was done with Gaussian 98W software. All the structures were optimised and confirmed to be the minimum point by the frequency analysis. And the structural data showed that condensation was mainly induced by the inter-molecular and intra-molecular hydrogen-bond. In existence of template molecule near the cluster, structure of the silica cluster will be altered by long-range forces due to interaction between the template ion and the cluster. So further condensation reaction can take place at a local minimum on the conformational potential energy surfaces of silica clusters. This accounts for why so many kinds of silicon containing microporous and mesoporous materials can be synthesised with sol-gel method.

119.

ADSORPTION, ORDERING, AND CHEMISTRY OF NITROBENZENE ON Si(100)-2x1. *Semyon Bocharov, Chemistry and Biochemistry, University of Delaware, 170 Brown Lab, Newark, DE 19716, Fax: 302-831-6335, *sammo@udel.edu*, and Andrew V. Teplyakov, Department of Chemistry and Biochemistry, University of Delaware*

The presence of the reaction barrier in a reaction of a nitro-group on Si(100)-2x1 previously established in our laboratory opened an opportunity for surface ordering and manipulation of a bifunctional molecule at cryogenic conditions. An example of a bifunctional molecule with two reactive entities, nitrobenzene, adsorbs molecularly on a clean and well-ordered Si(100)-2x1 surface at 100 K. Upon annealing, nitro group reacts with the surface, while benzene ring stays intact. The saturation coverage of nitrobenzene was found to be ~1 nitrobenzene molecule per surface silicon dimer. The only surface reaction product recorded to desorb into the gas phase is benzene at 670 K and even this product corresponds to only a few percent of the monolayer. Thus, the phenyl groups produced by this approach on a Si(100)-2x1 surface are extremely stable, which should allow for further investigation both in vacuum and at ambient conditions.

120.

AEI: PATTERN STABILITY IN MICROCONTACT PRINTED SELF ASSEMBLED MONOLAYERS. *Jennifer R. Hampton¹, Rachel K. Smith¹, Arrelaine A. Dameron¹, Christina E. Inman², James E. Hutchison², and Paul S. Weiss¹.* (1) Departments of Chemistry and Physics, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802-6300, Fax: 814-863-5516, *jrh@stm1.chem.psu.edu*, (2) Department of Chemistry and Materials Science Institute, University of Oregon

We have used microcontact printing to pattern self assembled monolayers (SAMs) on Au{111} using a variety of molecules with different terminal groups and internal functionalities. The resulting patterned films were monitored over time with scanning tunneling and lateral force microscopies to examine the degree of order of the components and the overall pattern resolution. By varying the molecules used for the printed and backfilled regions of the SAM, we have explored the effect of intermolecular interactions on pattern lifetimes. Pattern stability is enhanced in films that have larger interactions between molecules in one component of the SAM.

121.

AGGREGATIONAL PROPERTIES OF SODIUM DODECYL SULFATE IN IMIDAZOLIUM-BASED QUATERNARY SALTS. *Ayşe Beyaz, Woon Su Oh, and V. Prakash Reddy, Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409, Fax: 573-341-6033, *abeyaz@umr.edu**

Critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS), an anionic surfactant, was investigated in a series of imidazolium-based room temperature ionic liquids (RTILs)/ quaternary salts: 1,3-dimethylimidazolium iodide (1), 1-butyl-3-methylimidazolium chloride (2), 1-hexyl-3-methylimidazolium chloride (3), 1-methyl-3-octylimidazolium chloride (4), 1-methyl-3-octylimidazolium tetrafluoroborate (5), 1-benzyl-3-methylimidazolium chloride (6), and 1-methyl-3-(pentafluorophenyl)imidazolium chloride (7). The CMC studies were done using UV-vis and ¹H NMR spectroscopy. The CMC of SDS was shown to correlate with the hydrophobicity of the RTILs/quaternary salts; the CMC values exponentially decreased with increasing chain-length of the substituents on the imidazole ring. The quaternary salts with fluorinated side chains exhibit dramatically lower CMC values as compared to those of the corresponding nonfluorinated analogues.

122.

AUTONOMOUS MOVEMENT OF COLLOIDAL CATALYTIC MOTORS. *Walter F. Paxton¹, Kevin C. Kistler¹, Christine C. Olmeda¹, Ayusman Sen², Sarah K. St. Angelo¹, Thomas E. Mallouk¹, Paul E. Lammert³, and Vincent H. Crespi³.* (1) Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-8403, *paxton@chem.psu.edu*, (2) Department of Chemistry, Pennsylvania State University, (3) Department of Physics, The Pennsylvania State University

We have recently discovered a catalytic method of moving nano/micro objects in aqueous solutions. Platinum/gold striped rods exhibit asymmetric catalytic activity for the decomposition of hydrogen peroxide (i.e., only platinum decomposes hydrogen peroxide) which results in directed movement towards the platinum end of the rod. Movement of the rods is attributed to a self-generated concentration gradient caused by the continuous production and diffusion of oxygen from the platinum tip. The speed of moving rods is comparable to similar-sized bacteria (10-30 microns/s), and depends on a variety of factors, including rod size, hydrogen peroxide concentration, and activity of the platinum surface. Translational and rotational diffusion coefficients of autonomously moving rods were measured and compared to those moving via Brownian motion.

123.

CHEMICAL BINDING OF CONTAINING-N AROMATIC MOLECULES ON SI SURFACES: MECHANISTIC UNDERSTANDING ON THE SELECTIVITY OF REACTION CHANNELS. *Feng Tao¹, Steven L. Bernasek¹, and Guo Qin Xu².* (1) Department of Chemistry, Princeton University, Washington Road, Princeton, NJ 08544, Fax: 609-258-6746, *ftao@Princeton.EDU*, (2) Department of Chemistry, National University of Singapore

Chemical binding of organic molecules on Si surfaces is an important approach of fabricating molecular architectures to develop Si-based molecular devices and biosensors. Our studies on attachment chemistry of pyrrole, N-methylpyrrole

and pyridine demonstrate the diversity of reaction channels of aromatics on Si surfaces. Pyrrole dissociatively chemisorbs onto Si surfaces through breaking N-H bond, forming a pyrrolyl ring. Due to the absence of N-H bond, N-methylpyrrole covalently binds to Si surfaces via pericyclic reactions. The difference of chemisorption mechanism between pyrrole and N-methylpyrrole shows a strategy of switching reaction channel by introducing substituted group. Besides pericyclic reaction, pyridine can chemically bond to Si surfaces with the formation of SiN dative bond. Compared to pyrrole and N-methylpyrrole, the ability of pyridine to form dative bond results from higher electron density around N atom due to the localization of lone-pair of N-atom for pyridine but participating into aromatic conjugation for pyrrole and N-methylpyrrole.

124. CONFORMATION OF β AMYLOID (1-40) ON ALDEHYDE-SAM MODIFIED GOLD SURFACES. *Jowell G. Bolivar, Department of Chemistry, Louisiana State University, Baton Rouge, 306 Choppin Hall, Louisiana State University, Baton Rouge, LA 70803, Fax: 225-578-3458, Robin L. McCarley, Department of Chemistry, Louisiana State University, and Robert P. Hammer, Department of Chemistry, Louisiana State University*

In this experiment, we investigated the behavior patterns of proteins on chemically modified gold surfaces. Specifically, beta amyloid (1-40) conformations were studied when exposed to a laboratory-synthesized aldehyde-terminated undecane-thiol supported on gold surfaces. The interactions of beta-amyloid (1-40) with the aldehyde surfaces were probed using reflection-absorption infrared spectroscopy. Results from this experiment will be used to study the influence of oxidized neuronal cell surface mimics on the aggregation of beta amyloid (1-40).

125. CONSTRUCTION OF SELF-ASSEMBLED MONOLAYERS USING THE STAUDINGER LIGATION. *Stefan Schweizer¹, David Quincy¹, Claire Dentinger², Peter Kernen³, Peter Wagner², and Aradhana Acharya¹. (1) Department of Organic Chemistry, ZYOMYX, 26101 Research Rd, Hayward, CA 94545, Fax: 510-786-1893, sschweizer@zyomyx.com, (2) Zyomyx, Inc, (3) Zyomyx*

The Staudinger ligation has been successfully used in carbohydrate research and cell surface studies (ref). As presented here, it can also provide versatile orthogonal strategies for the formation of novel self-assembled monolayers as well as the immobilization of biomolecules. In many cases, bioreactive w-functionalities of organic thin films are chemically incompatible with the respective surface-reactive moieties necessary to chemisorb the monolayer onto solid, inorganic substrates. To overcome this problem and to provide new avenues for the construction of mixed monolayer architectures, we present an approach in which the Staudinger ligation is applied to the in situ, tandem synthesis of functionalized self-assembled monolayers. Azide-terminated silane monolayers were created in a first step and transformed into protein-reactive monolayers by Staudinger ligation using a novel oligoethylene glycol crosslinker molecule with an aryl phosphine moiety at one end and a methoxy- or alternatively N-hydroxysuccinimide (NHS) ester group at the opposite end.

126. DEPOSITION AND SORTING OF LYOPHILIC COLLOIDAL PARTICLES BY SIZE ON SURFACES OF PATTERNED WETTABILITY. *Fengqiu Fan, Chemical & Biomolecular Engineering, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218, ffan1@jhu.edu, and Kathleen J. Stebe, Department of Chemical Engineering, Johns Hopkins University*

Surfaces of patterned wettability provide templates to deposit particles by evaporation either from an evaporating drop, or from a dip-coated thin film. As the contact line recedes, the liquid layer becomes discontinuous, pulling back rapidly from the non-wet regions, and filling the wet regions. The discontinuous fluid elements that form can contain small particles if the particle diameter is less than the height of the fluid feature. If the particles are larger than the feature height, they are excluded from the wet patch, and are pulled backwards with the parent drop, or with the fluid from which the thin film is withdrawn. The height of the fluid on the wetted feature varies in proportion to the

dimensions of the wetted patch itself. This provides a means of sorting particles rapidly and in a highly parallelizable fashion by simply patterning a surface with wetted sites of differing dimension, and depositing suspensions which contain particles of differing size. Small particles can be sequestered on the smallest patches, while mixtures of larger and smaller particles will deposit on the larger patches. This can be exploited in the deposition of materials for assays on microarrays, sensors, and the creation of regions of colloidal crystals for exploitation in photonic devices.

127. DESIGN OF CROSS-LINKED LYOTROPIC LIQUID CRYSTAL ASSEMBLIES CONTAINING LIVING/CONTROLLED RADICAL POLYMERIZATION CATALYSTS. *Jizhu Jin and Douglas L. Gin, Department of Chemistry & Biochemistry, and Department of Chemical & Biological Engineering, University of Colorado at Boulder, Boulder, CO 80309, Fax: 303-492-8595, jinj@colorado.edu*

In the past decade, living/controlled free radical polymerization has attracted a great deal of interest in academia and industry. However, very little work has been done in the area of making supported living/controlled radical polymerization catalysts. In this study we have successfully incorporated alkoxyamine, which can initiate living/controlled free radical polymerization of styrene, to the headgroup of a lyotropic liquid crystal (LLC) monomer. The resulting LLC monomer can be templated to form the inverted hexagonal (HII) phase and subsequently photo-cross-linked with retention of the HII phase. In this poster, we will report the detailed phase structure and controlled styrene polymerization within this catalytically active, nanoporous LLC material.

128. DETERMINATION OF THE STRUCTURE OF DISORDERED ORGANIC MOLECULES ON Pd(111) SURFACE FROM THE BRAGG SPOTS OF LOW ENERGY ELECTRON DIFFRACTION. *Tao Zheng¹, Dario Stacchiola¹, H. C. Poon², Dilano K. Saldin², and Wilfred T. Tysoe³. (1) Department of Chemistry, University of Wisconsin-Milwaukee, 3210 N. Cramer Ave., Milwaukee, WI 53201, Fax: 414-229-5530, tzheng@uwm.edu, (2) Department of Physics, University of Wisconsin-Milwaukee, (3) Department of Chemistry and Laboratory for Surface Studies, UW-Milwaukee*

The surface structure of the disordered overlayer formed by ethylene adsorption on Pd(111) at 80K is determined by low energy electron diffraction (LEED) from the effects of chemisorbed molecules on the intensity versus beam energy (I/E) variation of the substrate (1x1) Bragg spots. It is shown that the clean Pd(111) surface is covered by ~85% di-sigma-bonded ethylene and ~15% tilted ethylenic species, proposed to be a vinyl, where the measured geometries are in agreement with the results of previous density functional theory (DFT) calculation. The structure of a disordered overlayer of ethylene on hydrogen-covered Pd(111) at 80K is also measured using LEED and is found to form a pi-bonded species in accord with previous infrared results.

129. EFFECTS OF SURFACE MASS AND PACKING DENSITY ON ENERGY TRANSFER IN GAS COLLISIONS WITH ORGANIC SURFACES. *Brian S Day and John R. Morris, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, bday@vt.edu*

Our research is aimed at developing an atomic-level description of gas-surface energy transfer in collisions between rare gases and organic surfaces. We use molecular beam scattering techniques to record time-of-flight velocity distributions along with model organic surfaces to study gas-surface energy transfer. Molecular beams offer control over energy, angle, and flux of the incident gas atoms while self-assembled monolayers provide a variety of physical and chemical surface environments. Experiments in our lab have revealed the roles that the length of the alkane chain, mass of the terminal group, and chain packing density play in gas-surface collisions. Results from these studies suggest that the most efficient energy transfer occurs when motions involving many atoms along the alkane chains are accessible to absorb the excess translational energy of impinging gas atoms. Dense surfaces or surfaces with heavy atoms seem to impede the ability to transfer energy to these types of motions.

130.

ELECTROCHEMICAL STUDIES OF SOLUTION- AND VAPOR-DEPOSITED ALKANETHIOL SELF-ASSEMBLED MONOLAYERS ON GOLD. *William McNamara¹, Michael J. Tarlov², and Tina H. Huang¹.* (1) Department of Chemistry, Lafayette College, Easton, PA 18042, Fax: 610-330-5714, mcnamarw@lafayette.edu, huangt@lafayette.edu, (2) National Institute of Standards and Technology

Self-assembly of alkanethiols on various substrates has been the subject of extensive studies due to their possible application in the fields of molecular electronics, molecular computing and nano-scale electronics. In this study, cyclic voltammetry and three redox markers with different charges and hydrophobic/hydrophilic properties (ferricyanide, rutheniumhexamine and hydroquinone) are used to study vapor- and solution-deposited alkanethiol self-assembled monolayers (SAMs) on gold surfaces. SAMs grown on two types of gold surfaces (thermal evaporated and template-stripped atomically flat gold) are also investigated. The cyclic voltammograms (CVs) of ferricyanide acquired using the vapor-deposited electrodes showed a decrease in current values when compared to the CVs obtained with solution-deposited and bare-gold electrodes. The lower current observed indicates the vapor-deposited electrode has fewer surface defects than the solution-deposited electrode. The electrochemical data are consistent with results reported in a previous study, which showed that vapor-deposited SAMs exhibited higher packing densities than solution-deposited SAMs based on XPS analysis and resistance measurements. Studies involving assembly rate of the alkanethiols on the gold surface using both depositing methods will also be discussed.

131.

ELECTROCHEMICAL SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF GOLD-COVERED SILICON μ -WELLS. *Mariem R Rosario-Canales¹, Maritè Rivera-Sánchez¹, Ana R Guadalupe¹, and Luis F Fonseca².* (1) Department of Chemistry, University of Puerto Rico, P.O. Box 23346, San Juan, PR 00931, PR, Fax: 787-756-8242, mrosario@rrpac.upr.clu.edu, (2) Department of Physics, University of Puerto Rico

We report on the preparation, the morphological and chemical characterization of porous silicon (PSi) structures grown in sodium fluoride electrolytes. Scanning electron microscopy analyses revealed that the samples consisted of an array of micron-sized wells or macroporous networks depending on anodization conditions. All samples were mechanically robust in aqueous environments for extended time. X-Ray photoelectron spectroscopy showed that the porous framework was covered with a silicon dioxide layer. The PSi substrates were gold-sputtered and characterized to assess any morphological changes and to study their surface composition. Electrochemical characterization of the gold-covered substrates was done with cyclic voltammetry using ferrocene carboxylic acid (Fc-COOH) in phosphate buffer as the electroactive probe. Results indicated that the Fc-COOH redox process was diffusion controlled. Data obtained at various scan rates showed resistance to electron transfer. Formal potential changes as a function of probe concentration points to a chemical interaction between the probe and the surface.

132.

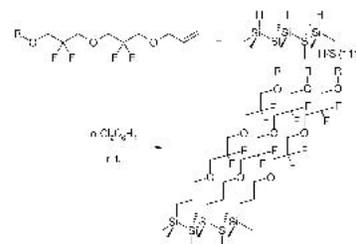
FABRICATE CONTROLLABLE DENSITY GRADIENT NANOPARTICLE ASSEMBLIES UTILIZING WELL-DEFINED STEPWISE GRADIENT SURFACES. *Feng Song and Bi min Zhang Newby,* Department of Chemical Engineering, The University of Akron, P.O. Box 3096, Akron, OH 44325-3096, fs9@uakron.edu

A convenient method is developed to fabricate architectures of nanoparticles on an organosilane modified silicon wafer (Si-wafer). The surface coverage gradient of the organosilane on Si-wafer is produced using a modified contact printing of octadecyltrichlorosilane, followed with a solution deposition of the desired organosilane. The desired organosilane has a particular affinity towards the nanoparticle. The density gradient nanoparticle assemblies are achieved by either the covalent bond formation or the electrostatic interaction between the nanoparticle and the desired organosilane molecule. The number density of nanoparticles within the gradient can be finely tuned by controlling the surface coverage of octadecyltrichlorosilane within the gradient. The fluorescent microscopy and the atomic force microscopy (AFM) were employed to characterize the nanoparticle coverage and its assembly.

133.

FABRICATION OF PIEZOELECTRIC SELF-ASSEMBLED FLUORINATED POLYETHER MONOLAYER ON HYDROGEN-TERMINATED SI(111) SURFACE. *Takashi Okano¹, Hirofumi Inari¹, Nagahiro Saito², and Osamu Takai¹.* (1) EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan, Fax: 81(Jpn)-52-789-5485, okano@cirse.nagoya-u.ac.jp, (2) Department of Molecular Design, Nagoya University

Self-assembled monolayer (SAM) formation of oligofluorinated polyether on metallic silicon surface was carried out by immersing a hydrogen-terminated Si(111) substrate into a solution of terminally allylated or propagylated bis(2,2-difluoro-1,3-propanedioxy) ether in *o*-dichlorobenzene at room temperature. On the silicon substrate, a platinum electrode was sputtered on SAM, and the ferroelectric property was characterized by an impedance analyzer. A ferroelectric polarization-voltage profile was obtained while it was an incomplete hysteresis pattern. AFM scan with bias voltage (8 V) resulted in a protuberant line (ca 0.5 nm height \times ca 100 nm width) on the surface.



134.

FACETING OF METAL SUBSTRATES AND GROWTH OF FACETED CRYSTALLITES. *Hao Wang, Wenhua Chen, Ally S. Y. Chan, and Theodore E. Madey,* Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, Piscataway, NJ 08854, Fax: 732-445-4991, haowang@physics.rutgers.edu

The O/Re(12-31) and Co/W(111) systems have been studied by low energy electron diffraction (LEED), Auger electron spectroscopy (AES), scanning tunneling microscopy (STM) and high resolution soft X-ray photo-emission spectroscopy (HRSXPS). Adsorption of oxygen can induce nanometer-scale faceting of a Re(12-31) substrate upon annealing to $T > 700\text{K}$. At low coverage of oxygen ($\sim 0.5\text{ML}$), the faceted Re features are two-sided ridge-like structures. The facet orientations are identified as (11-21) and (01-10), based on kinematic simulations of the corresponding LEED patterns. At high oxygen coverage ($\sim 1\text{ML}$), a phase transition between 2-sided and 3-sided faceting occurs between 900-1200K. The richness of nano-structures in the O/Re(12-31) system makes it a good candidate substrate to study structural sensitivity in catalytic reactions (e.g., methanol conversion). In a parallel study, the annealed Co/W(111) system exhibits a different behavior: a monolayer of Co does not induce faceting of a W(111) substrate, but multilayers of Co form nano-crystallites with well defined facets. The faceted Co nano-crystallites may have potential applications in magnetic storage.

135.

FIRST OBSERVATION OF CAPPING/UNCAPPING BY A LIGAND OF A ZN PORPHYRIN ADSORBED ON Ag(100). *Owain P. H. Vaughan, Federico J. Williams, Kerry J. Knox, N. Bampos, and Richard M. Lambert,* Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, United Kingdom, Fax: 44-1223-336362, ophv2@cam.ac.uk

STM observations reveal that adsorption of Zn tetra [3,5 di-*t*-butylphenyl] porphyrin (Zn-TBPP) on Ag(100) at 298 K leads to the formation of 3D aggregates which disperse on heating to 520 K to form a 2D layer of individual porphyrin molecules. The molecules are distributed randomly on the terraces with no strongly preferred orientation with respect to the underlying metal lattice, despite the fourfold rotational symmetry of both adsorbate and substrate. This is consistent with the di-*t*-butylphenyl groups at the meso positions lying essentially orthogonal to the plane of the macrocycle, thus inhibiting strong electronic interaction of the molecular p electron system with the Ag surface. At high coverages, porphyrin molecules in the second layer are oriented essentially perpendicularly with respect the flat-lying molecules in the contact layer. At 150 K, treatment of first layer porphyrin molecules with 1,4-diazabicyclo (2,2,2)

octane (DABCO) results in capping of the Zn atoms by the DABCO ligand, which locates centrosymmetrically over the porphyrin. Raising the temperature to 298 K results in reversible desorption of DABCO leaving the underlying porphyrin molecules in their original state. This is the first time that ligand binding/unbinding reactions have been reported for an adsorbed porphyrin, and provides an elegant comparison with the known solution state chemistry. The results represent a significant step on the way to the creation of organo-functionalised surfaces capable of carrying out delicate and selective heterogeneously catalysed reactions of the type normally associated with homogenous systems.

136.

GENERATE WELL-DEFINED GRADIENT SURFACES USING CONTACT PRINTING APPROACH. *Bi min Zhang Newby and Sung-Hwan Choi, Department of Chemical Engineering, The University of Akron, Whitby Hall 101A, Akron, OH 44325-3906, Fax: 330-972-5856, bimin@uakron.edu*

Gradient surfaces are attractive substrates for studying protein adsorption, cell attachment/spreading and for combinatorial experiments to obtain high throughput material properties and behaviors. Recently, we have developed a fast, convenient, and inexpensive method to generate well-defined gradient surfaces. Particularly, we have modified contact printing technique to achieve gradual or stepwise variations of surface properties by controlling the contact rate or contact duration, respectively. The surface coverage of a particular $\text{-(CH}_2\text{)}_n\text{-}$ as a function of contact time was determined, and used as a guide for controlling the contact rate or contact duration to achieve the well-defined gradient. Elastomeric stamps with different geometries and various radii of curvature were used to generate a variety of gradient surfaces at both millimeter and micrometer scales. The quality of the gradient was verified by dewetting or phase separation of polymer thin films and by the movement of nano/picoliter water droplets on the surface.

137.

GOLD-SILICA CORE/SHELL COLLOIDAL NANOPARTICLES AND THEIR THIN FILMS. *SARANG Sangamkar and Temer S Ahmadi, DEPARTMENT OF CHEMISTRY, VILLANOVA UNIVERSITY, 800, LANCASTER AVENUE, # 321 MENDEL, Villanova, PA 19085, sarang.sangamkar@villanova.edu*

Synthesis and optical properties of thin films and colloidal gold nanoparticles coated with silica will be presented. Thin films of silica coated gold nanoparticles are prepared using Langmuir-Blodgett method for the first time. Surface properties of these core/shell particles are studied using FTIR and their effects on the quality of LB-films, their packing geometry studied by TEM, and the resulting optical properties will be reported. In particular, the effects of shell thickness on the optical properties will be elaborated.

138.

GRAFTED POLYETHYLENE GLYCOL SURFACES VIA REACTIVE SAMs FOR THE INHIBITION OF CELL ADHESION IN MICROFLUIDIC DEVICES. *Cheryl R. Gourley, Peter P. Chen, Paul L. Gourley, and Darryl Y. Sasaki, Biomolecular Materials and Interfaces Dept, Sandia National Laboratories, MS 1413, Albuquerque, NM 87185, Fax: 505-844-5470*

A method to surface graft polyethylene glycol (PEG) was evaluated as a coating process to inhibit cell adhesion and growth on semiconductor and glass surfaces in microfluidic devices. The method uses glycidoxysilane self-assembled monolayers (SAMs) as the reactive surface to anchor amine-functionalized PEGs. Good surface density of PEG molecules was achieved, as assessed by ellipsometry and XPS analyses. Adhesion and growth of glial cells in culture studies allowed a comparison of the PEG (MW 5000) surface against other SAM films. Over a period of six days the PEG surfaces remained essentially free of cell growth, whereas bare silicon and an oligoethylene glycol silane SAM supported cell growth. The grafting method will allow efficient and conformal surface coatings of microfluidic devices for use in cell studies. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

139.

HYDROGEN: "MORE THAN JUST A REACTANT". *D. J. Stacchiola, Florencia C. Calaza, and W. T. Tysse, Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, 3210 N. Cramer St., Milwaukee, WI 53211, Fax: 414-229-5030, dstacchi@uwm.edu*

To study the effect of hydrogen on hydrogenation reactions, the adsorption of ethylene on a hydrogen pre-covered Pd(111) surface was studied by reflection absorption spectroscopy (RAIRS). The effect of either surface or subsurface hydrogen on the state of ethylene hybridization was studied by making use of the order-disorder transition of hydrogen on Pd(111) at low temperatures, during which the proportion of surface and subsurface hydrogen varies. The results indicate that subsurface hydrogen is responsible for the formation of pi-bonded ethylene on hydrogen-covered Pd(111). Another reaction that has been extensively studied is the formation of benzene from acetylene. Under reaction conditions, the reaction is poisoned by the formation of a crowded vinylidene layer, but the addition of hydrogen enhances the rate of benzene formation. Under these conditions, hydrogen transforms the surface layer to a more open surface form by ethylidyne.

140.

INDIRECT DETECTION OF GLUCOSE IN AN AQUEOUS SOLUTION USING SURFACE-ENHANCED RAMAN SCATTERING. *Jouliana M. El Khoury¹, Hui Wang¹, Debanjan Sarkar², Serhan Boduroglu¹, Stephanie T. Lopina³, and Jun Hu¹. (1) Department of Chemistry, The University of Akron, 190 E Buchtel Ave., Akron, OH 44325-3601, mje6@uakron.edu, (2) Department of Chemical Engineering, The University of Akron, (3) Department of Chemical Engineering and Biomedical Engineering, The University of Akron*

Raman spectroscopy provides detailed structural information by revealing the characteristic vibration modes of analytes. It is particularly immune to the interferences in biological samples such as water. Therefore this technique is most promising for the development of non-invasive or minimum invasive clinical analytic tools and for real-time monitoring of critical care patients. However, common Raman spectroscopy suffers from low scattering cross-sections of the analytes and chemical noises from laser induced fluorescence background. Herein we report a new approach in fabricating a gold nanoparticle-based surface enhanced Raman (SERS) glucose sensor for blood glucose. We will report the chemical synthesis, structure, and Raman characteristics of the molecular recognition motif and the nanofabrication of polymer shell/metal core nanoparticles.

141.

INFLUENCE OF SURFACE REACTION ON THE MORPHOLOGY OF SURFACE-BOUND NANOSTRUCTURES SYNTHESIZED BY ELECTRODEPOSITION. *Rahul V. Magan and R. Sureshkumar, Department of Chemical Engineering, Washington University in St. Louis, One Brookings Drive, CB 1198, St. Louis, MO 63130, rvm1@cec.wustl.edu*

A generic Brownian Dynamics simulation (BDS) methodology was developed to examine the influence of the surface reaction rate on the morphology of nanostructures synthesized via electrodeposition. The balance between the interfacial reaction rate and bulk diffusion is incorporated into the simulations through a reaction probability, P_s , that approaches unity for diffusion controlled deposition. The BDS methodology was applied to the growth of metallic nanoparticles by irreversible deposition onto randomly distributed nucleation sites. The simulation results, in qualitative agreement with experiments, indicate that the size uniformity of the growing nanoparticles improves with slower surface kinetics. The simulations were extended to study the formation of nanostructured films on circular fibers. It was observed that as the P_s increases, the coating transitions from a dense to a loose, porous morphology. The effect of P_s on the evolution of descriptors of the coating morphology (thickness, roughness, pore size distribution, deposit correlation functions) will be discussed.

142.

INVESTIGATION OF NUCLEOTIDE IMMOBILIZATION ON SOL/GEL SUPPORTS USING SOLID-STATE NMR SPECTROSCOPY. *Roderick A Fry¹, Caner Durucan², Carlo G. Pantano², and Karl T. Mueller¹.* (1) Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-8403, raf191@psu.edu, (2) Department of Materials Science and Engineering, The Pennsylvania State University

This solid-state NMR study explores nucleotide-solid host interactions to understand the functionality, reactivity, and hybridization dynamics of DNA when adsorbed or confined within a solid host. Current DNA microarray technology utilizes amine coated glass slides for the immobilization of DNA. Porous oxides with amine functionalization are potential high surface area substrates for microarray technologies, and therefore extended knowledge of DNA-host interactions may lead to improvements in DNA sensor technologies for lab-on-a-chip applications. Mononucleotides serve as an idealized model for understanding the molecular-level interactions between specific functional groups in DNA and the surface sites on the sol/gel supports. Herzfeld-Berger analysis of the NMR spectra provides the components of the chemical shift anisotropy (CSA) tensors, detailing the local structures of the phosphate groups within these systems. Quantitative studies have shown that aminopropylsilane (APS) coated oxide gel is the most efficient in immobilization of mononucleotides, 31P CSA parameters are very different for pure A,C, and G nucleotides yet similar for A,C,G nucleotides bound to oxide supports, and a standard UV cure process does not affect the local environment of the 31P nuclei. Our current investigation focuses on nucleotide immobilization on pure porous oxide (sol/gel derived silica), aminosilane coated porous oxide, and amine-functionalized porous oxide (hybrid gels).

143.

INVESTIGATION OF TETANUS TOXIN ADSORPTION AND DISRUPTION OF LIPID MEMBRANES VIA LEAKAGE STUDIES. *Anne E. Hibbard, Andrea Slade, and Darryl Y. Sasaki, Biomolecular Materials and Interfaces Department, Sandia National Laboratories, P.O. Box 5800, MS 1413, Albuquerque, NM 87185, aehibba@sandia.gov*

Tetanus toxin binding and pore formation studies on lipid membranes, via pH activation, were conducted through a combination of fluorescence leakage analysis, dynamic light scattering, and AFM imaging. Currently, it is believed that Clostridial neurotoxin act first through recognition of gangliosides on the cell surface followed by internalization via lysosome formation. The lysosome's pH is then lowered via proton pumps that triggers the injection of the toxin's light chain into the cell catalyzing the disruption of neurotransmitter transport. In this presentation we will describe our recent efforts to clarify some issues involved with ganglioside selectivity of the neurotoxin and pore formation driven by pH change. The focus of our research has been on Tetanus toxin and its proposed binding partner the ganglioside GT1b. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

144.

IRON OXIDE AND COMPOSITE NANOPARTICLES FOR CATALYSIS AND SENSORS. *Lingyan Wang, Li Han, Jin Luo, and Chuan-ian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, lwang2@binghamton.edu*

Iron oxide nanoparticles are attracting increasing interests for applications such as information storage, drug delivery, medical imaging, catalysis, and sensors. In this presentation, we will describe recent results of an investigation of the synthesis of iron oxide nanoparticles and their composite nanoparticles, which contains gold and other metals in core-shell type nanostructures. Gama-Fe2O3 and Fe3O4 nanoparticles in 1-20 nm size range have been prepared. By controlling the reaction temperatures and manipulating the capping agent properties and solution compositions, the size, shape, composition, and monodispersity can be tailored. The nanoparticles are characterized by an array of techniques, including TEM, ED, DCP, XPS, XRD, FTIR SQUID and Electrochemistry techniques. Preliminary results of the study of the catalytic activities and sensory properties of the nanoparticle assemblies will also be discussed.

145.

KINETIC ANALYSIS OF SODIUM HYPOCHLORITE DEGRADATION IN ALKALINE SOLUTION. *Yasuo Nomura¹, Noriko Takahashi², Takayasu Kubozono¹, Fumitomo Noritake³, Naoki Mizushima¹, and Nobuyuki Yamamoto¹.* (1) Material Science Research Center, Lion Corp, 13-12, Hirai 7-Chome, Edogawa-ku, Tokyo 132-0035, Japan, Fax: +81-3-3616-5376, nomura-y@lion.co.jp, (2) Aromatic and Perfumery Center, Lion Corp, (3) Research Planning and Administration Dept, Lion Corp

We have explored degradation mechanism of sodium hypochlorite in alkaline solution by measuring self-decomposition rate constants of hypochlorous acid and hypochloric ion. From a detailed comparison of the rate constants for these two reactions with those for catalytic decomposition of hypochlorous acid and hypochloric ion caused by metal contaminants, we showed that hypochlorite degradation is attributed mainly to catalytic decomposition of hypochloric ion at pH 12, and to self-decomposition of hypochlorous acid at pH 10, respectively.

In addition, some methodologies to preserve sodium hypochlorite in alkali solution are discussed.

146.

METHOD OF SURFACE CHARGE DETERMINATION OF CDTE NANOCOLLOID. *Vladimir A. Sinani¹, Alexander A. Yaroslavov², Anna A. Efimova², Anna A. Rakhnyanskaya², Ekaterina G. Yaroslavova², and Nicholas A. Kotov¹.* (1) Department of Chemical Engineering, University of Michigan, 2300 Hayward St, 3426 G.G. Brown, Ann Arbor, MI 48109, Fax: 734-764-7453, vsinani@engin.umich.edu, (2) School of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899, Russia, Fax: 7-095-9390174, yaroslav@genebee.msu.su

Semiconductor nanocolloids have gained special interest because of their strong fluorescence making them promising for optical and biomedical applications. The surface charge of colloidal particles is an important parameter, which determines their electrokinetic behavior and stability in water and polar solvents. We have developed a simple method for quantitative determination of the amount of charge forming groups on the surface of CdTe nanocolloid. The method is based on titration of nanocolloid with solution of oppositely charged polyelectrolyte. Addition of polyelectrolyte, a fluorescence quencher, to nanocolloid is accompanied by decreasing of fluorescence intensity of CdTe nanocolloid. Obtained results are in a good agreement with theoretical estimation of CdTe nanoparticles charge based on X-ray data.

147.

MOLECULAR ENGINEERING TO TEST THE MECHANISM OF CONDUCTANCE SWITCHING FOR A VARIETY OF CONJUGATED MOLECULES. *Amanda M. Moore¹, Brent A. Mantooth¹, Zachary J. Donhauser¹, Arrelaine Dameron¹, Francisco M. Maya², Jacob W. Ciszek², Yuxing Yao², James. M. Tour², and Paul S. Weiss¹.* (1) Departments of Chemistry and Physics, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-5516, amm420@psu.edu, (2) Department of Chemistry and Center for Nanoscale Science and Technology, Rice University

Phenylene ethynylene oligomers have been studied as candidates for molecular electronic devices using scanning tunneling microscopy. These molecules were inserted into host alkanethiolate self-assembled monolayers for isolation and individual addressability. Many different hypotheses and theoretical predictions have been put forth to describe conductance switching. We have tested several of these through variations in the molecular design of our molecular switches and have concluded that the only mechanism consistent with all the switching data are that changes in the molecule-substrate bond hybridization leads to the observed conductance changes.

148.

MOLECULAR GRADIENT SURFACES. *Rose Ndong, Chemistry Department, Mount Holyoke College, 50 College Street, 2053 Blanchard Student Center, South Hadley, MA 01075, rsndong@mtholyoke.edu, and Wei Chen, Department of Chemistry, Mount Holyoke College*

In this research, we are interested in controlling molecular geometries using surface chemistry. Silicon wafers were first treated with a fluorinated silane, tridecafluoro-1,1,2,2-tetrahydrooctyl-dimethylchlorosilane, adsorbed with poly(vinyl alcohol) (PVOH) from aqueous solution, and then reacted with an acyl chloride, heptafluorobutyl chloride (HFBC) in vapor phase to take advantage of

the versatile reactivity of -OH groups. A maximum thickness increase of 46 Å was observed after reaction with HFBC. Surface geometries and perfluoroalkyl group gradients were controlled by the location of HFBC source relative to PVOH-adsorbed samples and relative rates of HFBC diffusion across the samples and reaction with the samples. Variants under investigation are reactor design, source temperature, reaction temperature, and reaction time. Using surface chemistry to control surface topography on the molecular level is a novel approach. This type of materials also provides a wide range of functional group densities across surfaces, which could be useful in combinatorial studies.

149.

NATURE OF ORGANIC/METAL INTERFACIAL INTERACTIONS: APPLICATION OF THE QUANTUM THEORY OF ATOMS IN MOLECULES. *Petar M. Mitrasinovic, Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3, Canada, pmitrasinovic@yahoo.ca*

The acrylonitrile/Cu₉(100) (neutral and charged (-1)) system is investigated as a model within the conceptual framework provided by natural population analysis and the quantum theory of atoms in molecules. The B-VWN/DZVP density functional theory method and the MP2/6-31+G* strategy have been employed. By this approach, the interfacial interactions are given physical definitions free of any assumptions and are visualized by using the topological features of the electron density. A natural link between the total electron density and the shapes (not energies) of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is clarified. Thus, the success of frontier molecular orbital theory to rationalize the organic/metal charge migration process may depend upon whether the spatial extents of the HOMO and LUMO resemble those of the negative (charge locally concentrated) and positive (charge locally depleted) Laplacian of the total electron density, which determines the reactivity.

150.

NOVEL MODIFIED ZEOLITES FOR ENERGY-EFFICIENT HYDROCARBON SEPARATIONS. *Mutlu Ulutagay-Kartin, Chem. and Bio Technologies, Sandia National Laboratories, PO Box 5800, MS 0734, Albuquerque, NM 87185-0734, Fax: 505-844-1480, mkarti@sandia.gov, Tina M. Nenoff, Chemical and Biological Technologies, Sandia National Laboratories, and Gary Gray, Chemical R&D, Goodyear Chemical*

In this talk we present initial synthesis and testing results of our applied research project, which focuses on the effects of surface and skeletal modification of zeolites for significant enhancements in current hydrocarbon separations. Zeolites are commonly used by the chemical and petroleum industries as catalysts and ion-exchangers. They have high potential for separations owing to their unique pore structures and adsorption properties and their thermal, mechanical and chemical properties. Because of zeolites separation properties, low cost, and robustness in industrial process, they are natural choice for use as industrial adsorbents. This is a multidisciplinary effort to research, design, develop, engineer, and test new and improved materials for the separation of branched versus linear organic molecules found in commercially important hydrocarbon streams via adsorption based separations. In this presentation we will discuss the initial results of the synthesis, characterization and separation properties of modified zeolites. For the characterization and the property measurements of the new and improved materials powder X-ray diffraction (PXRD), thermal analysis (TGA/DTA), FT-IR, Electron Microscopy (SEM/EDAX), temperature programmed desorption (TPD) and surface area techniques were utilized. The modified zeolites will advance current separation technology towards greater energy efficient and waste reducing processes. This project is funded by DOE/OIT/Industrial Materials of the Future program.

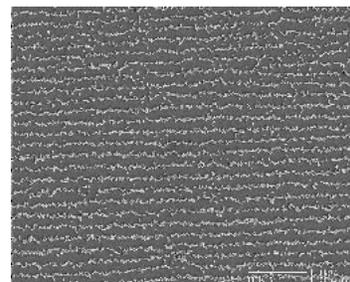
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94-AL85000.

151.

PATTERNING OF FUNCTIONALIZED POLYMER COLLOIDS BY SELF-ASSEMBLY. *Matthew A. Ray and Li Jia, Department of Chemistry, Lehigh University, 6 E. Packer Ave., Bethlehem, PA 18015, Fax: 610-758-6536, mar5@lehigh.edu*

Traditional fabrication of submicron features involves a top-down approach such as photolithography. Self-assembled patterning is an attractive alternative to these traditional methods. We report the formation of a self-assembled regular linear pattern on the submicron scale. The pattern is formed by a stick-slip

mechanism at the three-phase contact line of the colloidal suspension droplet. The ordering mechanism as well as the tunability of the system will be discussed.



152.

POTENTIAL APPLICATION OF IRIIDIUM AS CATALYST IN FUEL CELLS: AMMONIA DECOMPOSITION ON IR SURFACES. *Wenhua Chen, Ivan Ermanoski, and Theodore E. Madey, Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, Piscataway, NJ 08854, Fax: 732-445-4991, wchen@physics.rutgers.edu*

The adsorption and decomposition of ammonia and hydrogen on clean planar Ir(210) and on clean nanoscale-faceted Ir(210) have been studied. Nanoscale facets develop on the initially planar Ir(210) surface when it is covered with oxygen and annealed at $T \geq 600\text{K}$; we have developed a chemical method to remove the surface oxygen and prepare clean, faceted Ir(210) routinely in situ using H₂ at 400K. Our temperature programmed desorption (TPD) data show that Ir(210) is very active for ammonia decomposition and that the recombinative nitrogen desorption peak temperature ($\sim 500\text{K}$) is much lower compared to other transition metals. Striking differences have been found in recombination and desorption of molecular hydrogen, and in thermal decomposition of ammonia over clean faceted Ir(210) versus clean planar Ir(210), which are attributed to the nanoscale structures on the faceted surface. Moreover, ammonia decomposition on Ir(210) exhibits size effects on the nanometer scale. The results presented here indicate that Ir may be a useful catalyst component for CO_x-free hydrogen production for potential fuel cell applications; faceted Ir(210) is an excellent model catalyst for exploring structure sensitivity and size effects in surface chemistry.

153.

PREPARATION OF NITROGEN-DOPED TiO₂ PARTICLES USING A METALLOTHERMIC REDUCTION METHOD AND THEIR PHOTOCATALYTIC PROPERTIES. *Takahito Akita, Hirobumi Shibata, Takahiro Ohkubo, Hideki Sakai, and Masahiko Abe, Faculty of Science and Technology, Tokyo University of Science, 2641, Yamazaki, Noda, Chiba 278-8510, Japan, Fax: +81-4-7122-1442, j7203603@ed.noda.tus.ac.jp*

Nitrogen-doped titanium dioxide (N-doped TiO₂) is known to show photocatalytic activity even under visible light irradiation and various methods doping nitrogen atom into TiO₂ crystalline structure have been reported. We have shown that metal nitrides and borites can be synthesized from their oxides at relatively low temperature using metalothermic reduction methods with magnesium metal as a reductant. In this study, we prepared N-doped TiO₂ particles keeping anatase crystal structure by using the metalothermic reduction method and evaluated the photocatalytic activity under UV and visible light irradiation. Anatase TiO₂ particles were mixed with Mg powders (reductant) and sodium azide (nitrogen source) and calcined at 600°C. The obtained particles had the onset of absorption around 500 nm while kept anatase crystalline structure. These samples had slight photocatalytic activity against oxidation of 2-propanol under visible light irradiation.

154.

PREPARATION OF ULTRAHYDROPHILIC SURFACES BY OXIDATION REACTION OF ALKYL SILANE MONOLAYERS. *Jung Ah Lee and Thomas J. McCarthy, Department of Polymer Science and Engineering, University of Massachusetts, 120 Governors Dr, Conte A533, Amherst, MA 01003, Fax: 413-577-1510, jungah@polysci.umass.edu*

Hydrophobic surfaces prepared by the reaction of alkylmonofunctional silanes with silicon wafers in the vapor phase were hydrophilized by oxidation with

potassium chlorate/sulfuric acid. Oxidation of polyethylene surface is a well known convenient method to prepare a wettable surface. In this study, the oxidation kinetics of alkylsilane monolayers on silicon surfaces was accomplished through characterization by contact angle analysis, X-ray photoelectron spectroscopy, and ellipsometry. Ultrahydrophilic surfaces with contact angle values less than 5° were obtained by increasing the number of acidic functionalities that could be introduced after oxidation reaction.

155.

PROBING CHIRALLY TEMPLATED SURFACES. *Luke A. Burkholder, Dario J. Stacchiola, and Wilfred T. Tysoe, Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, 3210 N. Cramer St., Milwaukee, WI 53211, Fax: 414-229-5036, lb4@uwm.edu*

The enantioselective chemisorption of R- and S-propylene oxide is measured on a Pd(111) surface chirally modified using a series of small chiral template molecules. Propylene oxide adsorbs reversibly on Pd(111) at 80 K without undergoing any thermal decomposition thus providing an ideal probe of surface chirality. Template molecules studied are: R- and S-2-butanol, R- and S-2-methylbutyric acid, L-alanine, L-2-aminobutyric acid, L-norvaline, L-proline, L-valine, L-leucine, L-isoleucine, and S-1-(1-naphthyl)ethylamine. Characterization by reflection-absorption infrared spectroscopy (RAIRS) is presented for propylene oxide, 2-butanol, and 2-methylbutyric acid. Propylene oxide coverage is measured via TPD on 2-butanol and 2-methylbutyric acid, and by the King and Wells method on all other template molecules. Template coverages were measured by TPD. RAIRS data suggest that adsorbed 2-butanol forms 2-butoxide species when heated to ~150 K. The coverage of R-propylene oxide adsorbing on an R-2-butoxide-covered surface, ratioed to that on one covered by S-2-butoxide, reaches a maximum value of ~2 at a relative 2-butoxide coverage of ~25% of saturation, and decreases to unity at a coverage of ~50% of saturation. Similar results are seen for L-alanine, and the maximum enantioselective ratio decreases as the aliphatic side-chains of the amino acids become larger. No enantioselectivity is observed for R- or S-2-methylbutyric acid, L-valine, L-leucine, or S-1-(1-naphthyl)ethylamine, which suggests that the interaction between the template and probe molecules is very specific.

156.

REACTION OF ORGANOSILICON HYDRIDES WITH SOLID SURFACES: AN EXAMPLE OF SURFACE CATALYZED SELF-ASSEMBLY. *Roy Helmy and Alexander Fadeev, Department of Chemistry and Biochemistry, Seton Hall University, 400 South Orange Avenue, South Orange, NJ 07079, Roy_Helmy@Merck.com*

Organosilicon hydrides (RSiH₃) reacted with a range of inorganic solids and produced supported self-assembled monolayers (SAMs) with a high grafting density ~4.5-5 of R groups per 1 nm². According to the FTIR and ²⁹Si NMR, molecules in the SAMs demonstrated "horizontal" cross-linking (Si-O-Si and Si-OH . . . HO-Si bonds) and little or no "vertical" bonds with the metal oxide forming an amorphous, yet ordered film. Based on the activity of different metal oxides, we concluded that the hydrolysis of C₁₈H₃₇SiH₃, the key step in the reaction mechanism, is catalyzed by water adsorbed on acidic and basic centers (Lewis and Brønsted) of the solid surfaces. Metal oxides and solids with weak acidic and basic properties, like silica, carbon, and organic polymers, do not react with RSiH₃ even in the presence of excess of surface water. Increasing the temperature of the reaction or doping neutral surfaces with acids or bases greatly increases their activity in the reaction with RSiH₃.

157.

REACTIONS OF DISPLACEMENT OF ORGANOSILICON MONOLAYERS SUPPORTED ON SI. *Joseph W. Krumpfer and Alexander Fadeev, Department of Chemistry and Biochemistry, Seton Hall University, 400 South Orange Ave, South Orange, NJ 07079, krumpfjo@shu.edu*

This work investigates the reactions of the displacement of organosilicon monolayers supported on silicon by solutions of organosilanes. Reactions of covalently-attached monolayers of octadecyldimethyl-, trimethyl-, and perfluoro-alkyldimethylsilanes by low molecular weight alkylsilanes were investigated. The kinetics of the displacement reactions were studied using optical ellipsometry.

Wettability of these prepared surfaces was studied using contact angles with water and hexadecane.

158.

REACTIONS OF OXIDIZING GASES WITH OLEFIN-CONTAINING ORGANIC SURFACES. *Larry R. Fiegland and John R. Morris, Department of Chemistry (0212), Virginia Tech, Blacksburg, VA 24061, Fax: 540-231-3255, lfiegland@vt.edu*

The reactions of strongly-oxidizing pollutants on organic surfaces, especially olefin-containing surfaces, play a role in atmospheric chemistry as well as the reactions that occur at the surface of the human lungs. Olefins also exist in many man-made materials: automotive tires, textiles, etc. These double bonds are potential reaction sites for ozone. Our research is aimed at constructing a mechanistic understanding of reactions between ozone and olefin-functionalized materials. Our approach involves using functionalized self-assembled monolayers (SAMs) for the creation of model surfaces containing olefins. Reflection absorption infrared spectroscopy (RAIRS) and x-ray photoelectron spectroscopy (XPS) are used to monitor the key functional groups during monolayer exposure to ozone under ultrahigh vacuum conditions. Preliminary results indicate that aldehydes form on the monolayer surface after exposure to ozone. A mass spectrometer is used to monitor the products that desorb away from the surface upon exposure to ozone.

159.

REACTIVITY STUDIES OF CHEMICAL-WARFARE-AGENT SIMULANTS ON HIGHLY POROUS MgO. *Jeffrey A. Carter, Department of Chemistry, Virginia Tech, Blacksburg, VA 24060, jecarte1@vt.edu, and John R. Morris, Department of Chemistry (0212), Virginia Tech*

Our research continues to probe the catalytic nature of MgO pertaining to the dissociative adsorption of chemical warfare agents (CWA). Employing new reactive-beam-deposition techniques to grow highly porous MgO films, we have explored the catalytic reactivity of these new surfaces exposed to dimethyl methylphosphonate (DMMP). Reflective absorption infrared spectroscopy and mass spectrometry probe any adsorbed species in situ while the simulant is dosed via a molecular beam in ultra-high-vacuum conditions. The reaction products are further determined ex situ with temperature-programmed desorption and x-ray photoelectron spectroscopy. Initial results indicate a very high uptake probability that appears to be nearly independent of exposure. Subsequent temperature programmed desorption measurements indicate that molecular DMMP desorption is accompanied by the desorption of formic acid, the major decomposition product. This poster will present further work aimed at understanding the structural affects of MgO on reactivity, the uptake probability for different classes of CWA simulants on MgO, the reaction pathways of CWA simulants, and the role of surface bound hydroxyl groups in the decomposition process.

160.

REAL-TIME MEASUREMENT OF NITRIC OXIDE GENERATION FROM DIAZENIUMDIOLATE CONTAINING SOL-GELS USING SCANNING ELECTROCHEMICAL MICROSCOPY. *Bong K. Oh, Mary E. Robbins, and Mark H Schoenfisch, Department of Chemistry, University of North Carolina at Chapel Hill, Venable Laboratories, CB#3290, Chapel Hill, NC 27599-3290, bkoh@email.unc.edu*

Nitric oxide (NO) plays a pivotal role in a variety of biological functions including the regulation of platelet adhesion, vasodilation, and reducing microbial biofilm formation. Recently, polymeric sol-gel coatings synthesized to release NO have proven useful for improving the biocompatibility of glucose sensors. Both the NO release rate and localized surface concentration of NO are important parameters governing the utility of such polymers. Herein, scanning electrochemical microscopy (SECM) is used to measure NO concentration profiles as a function of the distance from the NO releasing sol-gel interface. The SECM probe is modified with a silicone rubber (SR) gas permeable membrane to improve the probe's selectivity for NO in the presence of nitrite and other interferents. Ultimately such data will be used to correlate the local NO flux to observed cell adhesion characteristics.

161.

REVERSIBLE SURFACE MODIFICATION FOR CONTROLLED WETTABILITY.

Susan C. D'Andrea and **Alexander Fadeev**, *Department of Chemistry and Biochemistry, Seton Hall University, 400 South Orange Ave, South Orange, NJ 07079, Fax: 973-761-9772, dandresu@shu.edu*

Surfaces with controlled, reversible wetting are of fundamental interest for the direct conversion of excess interfacial energy into mechanical work. In this work, temporary surface modification with biopolymers is investigated as a means to reversibly change the wettability from hydrophilic to hydrophobic. Silicon wafers and glass capillaries with covalently grafted alkyl and fluoroalkyl-silane monolayers were modified through cycles of adsorption of proteins and phospholipids followed by enzymatic cleavage or specific desorption of adsorbed layers. Adsorption of proteins such as, bovine serum albumin, lysozyme, and thrombin, from solution onto hydrophobic surfaces, increase wettability, i.e. produce hydrophilic surfaces. Adsorbed proteins can be completely removed using proteolytic enzymes, detergents and chaotropic salts, restoring the surface's hydrophobic properties. Adsorption of lipids onto alkylsilane modified surfaces, which act as an anchored layer of a lipid bilayer, produce a more wettable, hydrophilic surface. Phosphodiesterases and phospholipases are then used to fully restore the hydrophobic surface through removal of the adsorbed lipid layer. The thickness of the adsorbed layers was determined by ellipsometry, while the capillary rise method and contact angles were used to determine the dynamics of wetting.

162.

SELF-ASSEMBLED MOLECULAR AGGREGATES IN SOLUTION AND ON FUNCTIONALIZED SUBSTRATES: OPTICAL AND MORPHOLOGICAL STUDIES.

Fleumingue Jean-Mary, *Department of Chemistry and The Center for Analysis of Structures and Interfaces, The City College and the Graduate School of the City University of New York, Convent Avenue at 138th Street, New York, NY 10031, jfean-mary@gc.cuny.edu, and Daniel L. Akins, Department of Chemistry and The Center for Analysis of Structures and Interfaces, The City College of the City University of New York*

Small self-assembled groupings of molecules (in particular, the so-called J-type molecular aggregates) can possess remarkable linear and nonlinear optical responses to radiation. Such inherent responses coupled with the enhanced efficiencies of optical processes when noble metal nanostructures are present may engender composite systems with useful functionalities. In this report, covalent attachment of nanometer-scale colloidal Ag and Au particles to organosilane-coated substrates is shown to be a flexible and facile approach to the formation of well-defined nanostructural Ag and Au substrates. Variations in subsurface material (e.g., glass, quartz, ITO), functional group (e.g., -SH, -NH, -CN), and nanoparticle dimension (2.5-120 nm) are possible, and are discussed. Information about particle coverage and interparticle spacing has been obtained using atomic force microscopy, while surface macroscopic properties have been probed with optical spectroscopy. Additionally, we have formed J-aggregated cyanine adsorbates on the nanoparticles that exist on the functionalized substrate surface. Resulting systems have been characterized by AFM, NSOM, absorption and photoluminescence spectroscopies. Crucial system preparation parameters, such as purity of chemicals, roughness of surfaces, and deposition time are also discussed.

163.

SELF-ASSEMBLED MULTILAYERS CREATING TAILORED RESISTS FOR NANOSTRUCTURE FABRICATION.

Mary E. Anderson¹, **Erin M. Carter¹**, **Adam R. Kurland¹**, **Charan Srinivasan²**, **Mark W. Horn²**, and **Paul S. Weiss³**. (1) *Department of Chemistry, Pennsylvania State University, 152 Davey Lab, Box 3, University Park, PA 16802, Fax: 814-863-9556, mea151@psu.edu*, (2) *Department of Engineering Science and Mechanics, Pennsylvania State University*, (3) *Department of Chemistry and Physics, Pennsylvania State University*

Self-assembly in combination with lithographic processing can be used to create nanostructures with precise spacing and edge resolution reaching the nanometer-scale. A molecular ruler resist of self-assembled multilayers is selectively deposited on initial lithographically defined gold structures. This resist can be tuned to a desired thickness based on the number of layers deposited. Then, metal is deposited on the sample and the resist is removed, yielding spacings between metal structures dependent on the tailored resist's dimensions. Work is

underway to build molecular ruler resists independently either by capping selected regions of growth or by orthogonal growth of two different multilayer systems. A scheme in development is electroless metal deposition of the secondary metal to improve resist lift-off. Molecular ruler resists can withstand the rigors of lithographic processing and are being developed to advance this method toward device fabrication.

164.

SPECTROPHOTOMETRIC CHARACTERIZATION OF NANOPARTICLE ASSEMBLIES IN SOLUTIONS.

Stephanie Lim, **Mathew M. Maye**, **Jin Luo**, and **Chuan Jian Zhong**, *Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, cjzhong@binghamton.edu*

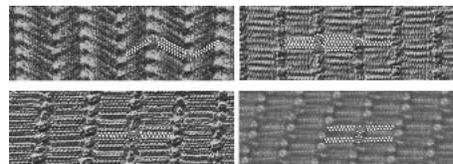
Nanoparticles in 1-20 nm diameters are interesting because it is this range over which many types of nanoparticles undergo a transition from atomic to metallic properties, leading to unique or new electronic, optical and chemical/biological properties. A challenge for the exploration of such properties is the development of abilities to precisely construct the nanoparticles into ensembles of controllable sizes, shapes and interparticle spatial properties. In this presentation, we describe latest findings of an UV-Visible spectrophotometric investigation aimed at determining both kinetic and thermodynamic parameters for the assembly of gold nanoparticles via a mediator-template strategy. Monolayer-capped gold nanoparticles, tetraoctylammonium template, and multidentate thioether (e.g., (MeSi(CH₂SMe)₃) mediator were studied as a model system. The spectrophotometric changes associated with surface plasmon resonance band of the nanoparticles and the assemblies were analyzed based on selected models for the reaction kinetics, thermodynamics, and optical resonance. Implications of the results to the manipulation of the nanostructures will also be discussed.

165.

SPONTANEOUS ASSEMBLY OF COMPLEX 2-D CRYSTALS.

Katherine E. Plass, *Department of Chemistry, University of Michigan, 930 N University, Ann Arbor, MI 48109-1055*, **Kibum Kim**, *Department of Macromolecular Science and Engineering, University of Michigan*, and **Adam J. Matzger**, *Department of Chemistry and Macromolecular Science and Engineering, University of Michigan*

The response of two-dimensional crystal structure to changes in molecular structure was scrutinized through scanning tunneling microscopy studies of a homologous series of 1,3-disubstituted benzenes physisorbed at the liquid-graphite interface. Remarkably, slight changes in molecular functionality and geometry in the 1,3-disubstituted benzene system induced drastic changes in the two-dimensional space group, the number of inequivalent molecules in the asymmetric unit, and the conformation of those molecules. This constitutes the most complex packing behavior observed to date in this type of monolayer and illuminates several issues of importance in three-dimensional crystal packing. The intermolecular interactions responsible for the occurrence of inequivalent sites on the surface and those stabilizing various packing motifs were determined. The monolayer density, as well as the geometry and electrostatic properties of the isolated molecules, were found to be structure determining.



166.

STM STUDIES ON THE SELF-ASSEMBLY OF ESTERS AND ANHYDRIDE ON GRAPHITE: THE DISTORTION OF MOLECULAR CHAIN AND THE FORMATION OF MULTI-ADSORPTION STRUCTURES FOR ESTER AND THE FORMATION OF ENANTIOMORPHOUS DOMAINS FOR ANHYDRIDE.

Feng Tao and **Steven L. Bernasek**, *Department of Chemistry, Princeton University, Washington Road, Princeton, NJ 08544, Fax: 609-258-6746, ftao@Princeton.EDU*

Self-assembled carboxylic ester monolayer and anhydride monolayer were investigated with STM. Esters with a bent angle at their carboxylic group are distorted into a long-chain alkane-like linear shape to maximize its interaction with substrate when self-assemble on graphite. In the formed lamellae, long alkyl chain of ester molecule always aligns with long chain of its adjacent molecules. Ester molecules self-assemble into four classes of domains (A, B, C

and D) with molecular chain-trough angles of 90°, 73°, 61° and 49° by shifting 0, 1/2, 1 and 3/2 units from their adjacent molecule, respectively. In domains B and D, enantiomeric pairs are observed. For arachidic anhydride, the achiral molecules spontaneously forms two classes of homogenous domains (m and m \bar{c}) with mirror symmetry upon adsorption. Domains m and m \bar{c} are 2-D enantiomers with opposite chirality. This finding demonstrates the spontaneous formation of highly ordered homogeneous enantiomorphous domains on graphite through weak van der Waals forces, from the achiral anhydride molecules.

167.

STUDIES OF HYDROGEN ON Pd{111} AT 4 K UTILIZING SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY. *Luis C. Fernández-Torres, E. Charles H. Sykes, Patrick Han, Sanjini U. Nanayakkara, and Paul S. Weiss, Departments of Chemistry and Physics, The Pennsylvania State University, 152 Davey Lab, University Park, PA 16802-6300, Fax: 814-863-5516*

The interaction of hydrogen with Pd{111} has been investigated with low temperature scanning tunneling microscopy and spectroscopy. Palladium is unique in its ability to both *adsorb* and *absorb* hydrogen. Adsorption of low exposures of hydrogen has allowed for the observation of tip-induced hydrogen atom diffusion at 4 K. The diffusion of atomic hydrogen at 4 K has been ascribed to inelastic tunneling of electrons; inelastic electron tunneling spectroscopy (IETS) corroborates this assignment, and the hydrogen atom diffusion barrier has been determined. Adsorption of high exposures of hydrogen results in formation of two ordered overlayer structures: (1x1)-H and (3x3)-2H. Absorption of hydrogen into subsurface sites in Pd, concurrent with H diffusion from the bulk, have been attributed as the predominant reasons for two observed phenomena: tip-induced vacancy ordering, and Pd{111} lattice distortion.

168.

AEI: STUDIES OF NANO-SCALE SYSTEMS WITH ELECTRONICS APPLICATIONS. *Marcus Lay, Department of Chemistry, Columbia University, Havemeyer Hall, 3000 Broadway, New York, NY 10027*

The formation of large-scale ordered arrays of carbon nanotubes (CNTs) is presented. These ordered arrays were formed from aqueous CNT dispersions, using fluidics to obtain orientation control. Field-effect transistors (FETs) formed from these electrically continuous arrays were anisotropic, with on/off ratios dependent on CNT orientation. Additionally, the results of electrochemical scanning tunneling microscopy (EC-STM) studies of single atomic layers of cadmium, tellurium and sulfur on Au were used to determine the ideal growth conditions for II-VI compound semi-conducting thin films using electrochemical atomic layer epitaxy (EC-ALE), the electrochemical analogue of atomic layer epitaxy (ALE). In each EC-ALE cycle, an element is alternately deposited from its solvated precursor. In this manner, a film of a practical thickness can be grown. The Au (111) reconstruction was used as a nano-scale template for the formation of Au-Cd alloy nanostructures. An EC-STM flow cell was constructed for further studies.

169.

STUDIES ON ACID-NEUTRALIZING REACTION BY OVERBASED DETERGENTS IN MODEL W/O LUBRICANTS. *Jianzhong Fu¹, Yunfeng Lu¹, Curt B. Campbell², and Kyriakos D. Papadopoulos¹. (1) Chemical and Biomolecular Engineering, Tulane University, 300 Boggs Center, New Orleans, LA 70118, (2) Detergents and Chemicals, Chevron Oronite Company, LLC*

A transparent heating capillary reactor, which has inside diameter of about 200 μ m and can generate temperature up to 287 °C or more, has been fabricated to simulate the reaction between acid droplets and overbased detergent reverse micelles in lubricating films. It simultaneously satisfies three key requirements to simulate real engine conditions: (1) thin lubricant film, (2) high temperature, and (3) acid droplets. The acid-neutralizing reaction was recorded through a video-microscopy system and then quantitatively analyzed with ImagePro. It was found that at high temperature, carbon dioxide and needle-like crystal products formed inside acid droplets, and the acid droplets first got bigger, then shrinked, and finally broke down by the needle-like residues. A new interfacial reaction mechanism has been suggested based on such observation and compared with previous studies.

170.

SUPRAMOLECULAR ORDERING OF TRIPOD DYES AT THE AIR/WATER INTERFACE. *Sung Jin Park¹, Young Wook Choi¹, Young Soo Seo², Sushil K. Satija², Soo Young Park³, and Daewon Sohn¹. (1) Chemistry, Hanyang University, 17 Hangdang Dong, SungDong Gu, Seoul 133-791, South Korea, Fax: +82-2-2299-0762, sss_psj@hanmail.net, dsohn@email.hanyang.ac.kr, (2) Center for Neutron Research, NIST, (3) School of Materials Science and Engineering, Seoul National University*

Monolayer of 2-(3,4,5-tris-dodecyloxy-phenyl)-[1,3,4] oxadiazole based "tripod" dye, P2G, has been studied at the air-water interface with X-ray reflectivity. Compression induces a transition in the monolayer to an ordered phase, which represents supramolecular assemblies with a unique spatial distribution and orientation of the molecules. The monolayer of tripod dye molecules, having hydrophilic chromophore on the center and hydrophobic alkyl chains on the ends, shows reversible hysteresis process at low surface pressure but irreversible at the high surface pressure in the π -A isotherm. The presence of water-insoluble alkyl chains is responsible for the conformational changes upon compression. The molecular conformations are analyzed with X-ray reflectivity as a function of the surface pressure. At low pressure, the molecules having face-on orientation are interdigitated by the three arms. After first transition in the π -A isotherm, the molecular conformation is turned into edge-on orientation, where the molecules are self-assembled into supramolecular structures. We provide the electron density profile of the monolayer and suggest that the molecular conformation changes from horizontal to perpendicular with respect to the water surface confirmed by the molecular dynamic simulation and X-ray reflectivity.

171.

SYNTHESIS AND CHARACTERIZATION OF NEW MAGNETIC NANOPARTICLES. *Sébastien N. Gallet¹, Thierry Verbiest², and André Persoons². (1) Chemistry/Laboratory of chemical and biological dynamics, Laboratory of chemical and biological dynamics, University of Leuven, Celestijnenlaan 200 D, Leuven B-3001 Belgium, Leuven B-3001, Belgium, sebastien.gallet@fys.kuleuven.ac.be, (2) Laboratory of chemical and biological dynamics, University of Leuven*

We present experimental results on a new type of magnetic nanoparticles composed of iron oxide and cobalt. The synthetic procedure is based on the thermal decomposition of iron and cobalt complexes which yields superparamagnetic particles of 10 nm diameter with very low dispersity. By using a combination of suitable surfactants, the particles can be readily solubilized in water. Furthermore, additional functionality can be introduced by coating with chromophoric surfactants. The resulting particles are unique in the sense that they combine magnetic properties of the core with the optical properties of the coating. The colloids were characterized by electron microscopy, UV/Vis absorption, light scattering and nonlinear optics.

172.

SYNTHESIS OF NOVEL SURFACTANTS HAVING INCLUSION FUNCTIONALITY. *Hidetoshi Ichige¹, Yukishige Kondo², Norio Yoshino², Ken ichi Oyaizu¹, Makoto Yuasa¹, Takahiro Ohkubo¹, Hideki Sakai¹, and Masahiko Abe¹. (1) Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan, Fax: 81-4-7122-1442, (2) Faculty of Engineering, Science University of Tokyo*

Cyclodextrin is a cyclic oligosaccharide consisting of from six to eight glucopyranose units and has an ability to form inclusion complexes with many hydrophobic substances. Introduction of various functional moieties to cyclodextrin has been studied extensively in order to expand its applicability. Recently, cycloamylose, a cyclic glucan consisting of from seventeen to several hundreds glucopyranose units, has been found and these molecules were also shown to have capability forming inclusion complexes with hydrophobic substances. However, amphiphilic molecules bearing cycroamylose units as a hydrophilic moiety have not been synthesized. In this study, chemical modification methods introducing alkyl chains to cycroamylose unit have been developed and their solution properties were investigated. Cycroamylose was reacted with p-toluenesulfonyl chloride in sodium hydroxide solution and tosyl moieties-moeified cycloamylose was synthesized. In addition, fluoroalkyl chain could be also introduced to the cycroamylose unit by reacting with sodium perfluorocarboxylic acid.

173.

SYNTHESIS, CHARACTERIZATION, AND OPTICAL PROPERTIES OF COLLOIDAL LEAD IODIDE SEMICONDUCTOR NANOPARTICLES AND THEIR THIN FILMS.

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The optical properties of layered semiconductor nanoparticles changes as their environment is altered. H₂O/sodium bis (2-octyl)-sulfosuccinate (AOT)/n-Heptane water-in-oil microemulsion medium has been employed as a means to prepare a nanocolloidal dispersion of lead Iodide (PbI₂). Elemental X-ray analysis, transmission electron microscopy and scanning electron microscopy have been employed to examine the shape and size distribution of these colloidal dispersions. Surfaces of PbI₂ nanoparticles were modified in order to prepare their monolayers using the Langmuir-Blodgett method. The role of surface and surface-adsorbed species on the optical properties of colloidal particles and their assembly within Langmuir-Blodgett films will be presented.

174.

ADSORPTION AND REACTION OF CIS-STILBENE ON AG/GE SINGLE CRYSTAL SURFACE.

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The adsorption and reaction of cis-stilbene (CSB) on Ag/Ge(111)-(√3×√3)R30°X (Ag/Ge-√3) have been studied using the combination techniques of Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature programmed desorption (TPD). The Ag/Ge-√3 surface was prepared by thermal deposition of Ag onto Ge(111) substrate of 100 K, followed by postannealing to 500 K for 2 min. The Ag coverage, estimated from AES measurement, was about 1 ML. The surface structure was confirmed by LEED. TPD studies showed that for CSB molecular desorption, only one single peak was observed at T_p(peak temperature)=265 K at coverages below 0.5 L. As CSB exposure increased to 1 L, a new peak, attributed to a more weakly bonded adsorption state appeared at T_p=222K. The coverage dependent TPD spectra for CSB molecular desorption from Ag/Ge-√3 showed the zeroth-order desorption kinetics, suggesting the pre-aggregation of CSB molecules on Ag/Ge-√3 before desorption. These results are compared to the previous STM study in which the structure of CSB cluster formed on Ag/Ge-√3 upon annealing was reported.

175.

PHOTOPHYSICAL PROPERTIES OF AGGREGATED ORGANIC DYES/NANOPARTICLE COMPOSITES.

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The use of dye sensitized nanoparticles have long found use as the active component in solar energy conversion systems, photographic mediums, and numerous electrooptical devices. The same properties that make these nanoparticle composites well suited for the above applications, also make them attractive candidates for the use as the active component in nonlinear optical switching devices. In order to show the feasibility of using these composites for in devices, various nanoparticles have been coated with organic dyes, that are known to form aggregates. These coated nanoparticles are then dispersed in either solution or intercalated within solid matrices. The photophysical properties of these nanoparticle composites have been studied using both steady state, and time resolved methods.

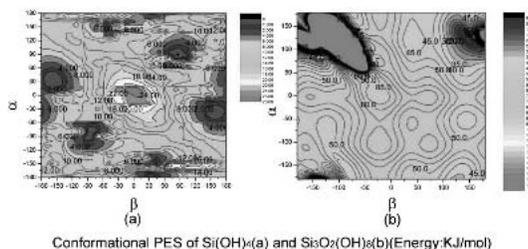
176.

THEORETICAL STUDY TOWARDS LIQUID PHASE CRYSTAL TRANSFORMATION OF ZEOLITE.

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In recent years, liquid phase transformation of zeolites is attracting more attention, but there is still little knowledge available on the fundamental

mechanisms. In this work, we used ab initio methods to study silica chains. All the structures were optimised, and confirmed to be the minimum point by the frequency analysis first. And then scan on relaxed potential energy surfaces were carried out. All the calculation was done with Gaussian 98W. And the results showed that conformational potential energy surfaces are smooth. In this case, small changes in its surrounding condition will result in its conformational change, moving from one local minimum to another, especially in existence of template molecule. Also further condensation reaction will take place at a local minimum on it. This accounts for why liquid phase crystal transformation of zeolite can take place at a certain condition and result in a certain type of zeolite.



177.

THERMAL DESORPTION OF ORGANIC MONOLAYERS SUPPORTED ON SOLIDS.

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Organic monolayers and thin films supported on mineral surfaces are being widely used as polymer fillers, pigments, fire-retardant materials, adsorbents, stationary phases and catalysts. This work investigates the thermal degradation processes of organic surfaces supported on inorganic solids using Thermogravimetric Analysis (TGA). The minerals studied were monolayers of organophosphonic acids (RP(O)(OH)₂), chloroorganosilanes (R(CH₃)₂SiCl) and organosilicon hydrides (RSiH₃), supported on calcium hydroxyapatite, talc, silica gels, titanium and zirconium dioxides. These minerals were studied using a TA Hi-Res 2950 Thermogravimetric Analyzer. The kinetics of thermal degradation of the supported surfaces were studied at ~300-550°C (nitrogen atmosphere), and followed a first-order process. The activation energies of the degradation process (E_a) were determined using the Arrhenius equation. The monolayers from RP(O)(OH)₂, yielded an E_a of ~45 kJ/mol. The monolayers from R(CH₃)₂SiCl and RSiH₃, ranged from ~100 to 130 kJ/mol depending on the chemical nature of the molecules grafted to the surface.

178.

3-D ORDERING OF COLLOIDAL PARTICLES USING HYPERBOLIC QUADRUPOLE ELECTRODE.

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Techniques for arranging colloidal particles have been used for a development of new functional materials. For instance, it can be applied for creation of photonic or colloidal crystals. In this study, three-dimensional structures of colloidal particles in the center of hyperbolic quadrupole electrodes were made by use of dielectrophoresis (DEP) with hyperbolic quadrupole electrodes under the electric fields. The particles of polystyrene latex (from 2 to 10 μm in diameter) particles dispersed in aqueous solution were used for our experiment. We also investigated the condition making particles arrange with higher density and larger thickness. The arrangement changed depending on the voltage of alternating current, the thickness of electrodes and surfactant concentration in the medium. The colloidal particles arranged with higher density with an increase in each parameter. These results can be explained by an increase in DEP force.

179.

ULLMANN COUPLING REACTION: STRUCTURE AND INTERACTIONS OF THE REACTIVE INTERMEDIATES AND PRODUCTS OF A SURFACE-CATALYZED REACTION.

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We present an atomic-scale study of the Ullmann coupling reaction between aromatic halides, which form biaryls on a Cu(111) surface, utilizing low temperature scanning tunneling microscopy and spectroscopy. Chemical identification of the surface-bound intermediates has been achieved using their spectroscopic signatures. We demonstrate that when the bromobenzene molecules dissociatively chemisorb at 293 K, they form phenyl intermediates, which travel distances of up to a few 1000 Å over bare Cu(111) terraces to bind preferentially at step edges. We attribute this effect to the anisotropic electron density distribution at the steps. We illustrate that C-C bond formation only takes place at the steps, and once phenyl intermediates combine to form biphenyl molecules and the adsorption sites at the steps are saturated, these molecules diffuse onto the terraces. Our observations of intermolecular interactions on the molecular scale are explained in terms of the local electronic perturbations by surface defects and adsorbates.

180.

UPTAKE AND REACTIVITY OF NERVE AGENT SIMULANTS ON NANOSTRUCTURED SILICON OXIDE SURFACES.

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The catalytic ability of oxides to decompose organophosphonates, the core of many chemical warfare agents (CWAs), has been of significant interest in the development of sensors, filters, and sorbent materials. Novel polyhedral oligomeric silsesquioxane (POSS) molecules are used to create thin films containing reactive functional groups for the decomposition of CWA simulants. Reflection absorption infrared spectroscopy (RAIRS) data show that hydroxyl groups of trisilanophenyl-POSS molecules provide a necessary site for chemical interactions to take place. Dimethyl methylphosphonate (DMMP) and methyl dichlorophosphate (MDCP) adsorb under mild conditions. Temperature programmed desorption measurements indicate that DMMP molecules desorb molecularly with a single energy of desorption at about 93 kJ/mol. In contrast, RAIRS and mass spectrometry data indicate a reaction between MDCP and the hydroxyl groups of the POSS molecules. Sticking probability measurements yield further insight into the interaction between POSS films and CWA simulants by revealing decomposition pathways and reaction probabilities.

181.

SULFUR IMPREGNATION ON ACTIVATED CARBON FIBERS THROUGH H₂S OXIDATION FOR VAPOR PHASE MERCURY REMOVAL.

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Activated carbon sorbents impregnated with sulfur have shown to be effective for vapor phase elemental mercury removal from gas streams. Previous studies showed that not only the sulfur content, but the form and distribution of sulfur on the adsorbent surface also play an important role in mercury uptake. Sulfur was impregnated onto activated carbon fibers (ACFs) through H₂S oxidation catalyzed by the sorbent surface in a fixed-bed reactor. By changing the temperature and duration of sulfur impregnation process, ACFs with different sulfur contents were developed. Characterization of ACFs before and after sulfur impregnation was done by BET analysis, SEM-EDAX, TGA, and temperature programmed oxidation, with special attention to pore size, sulfur distribution, and sulfur forms. Vapor phase mercury adsorption experiments were carried out in a fixed-bed reactor using nitrogen as a carrier gas. Under the experimental conditions used in this study, sulfur was impregnated mainly in the form of elemental sulfur and the amount of sulfur deposited on the ACF increased with an increase in impregnation temperature. Higher temperature leads to more uniform sulfur distribution inside the sorbent pores. More sulfur was found in the internal pores than in the external surface layer. The impregnation process

can be explained by a combination of pore filling and monolayer adsorption with the former mechanism predominating at low temperature. In the absence of sulfur, mercury adsorption capacity can be correlated with surface area and pore volume with medium (0.72nm < d < 0.90nm) and big micropores (d > 0.90nm) being more important for mercury uptake. Medium micropores are the most important for mercury uptake by sulfur impregnated sorbents.

182.

SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT SILICA NANOPARTICLES AND GOLD-SILICA NANOCOMPOSITES FOR FUEL CELL APPLICATIONS.

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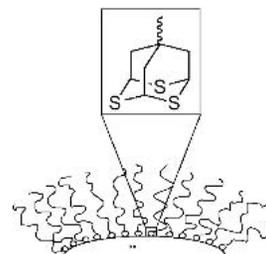
We hope to improve the efficiency and reliability of fuel cells by monitoring the changes in pH, temperature and water content that occur in a fuel cell over time using fluorescent probes. We have embedded our probes into coated silica nanoparticles and have created a wide range of particle sizes, and fluorophore concentrations. The surface coatings are designed to direct the nanoparticles to specific chemical phases and to mediate the fluorescent probe sensitivity. Another area of our research is to use gold-silica nanocomposites to determine the location of the fluorophore within the silica nanoparticle. Because silica nanoparticles are porous, it is difficult to determine the exact location of the fluorophore. By attaching the fluorophore to a gold surface and then growing the silica around the gold seed, we hope to better understand the mode of incorporation of the fluorescent probes.

183.

SELF-ASSEMBLING OF A RIGID, TRIPODAL SURFACE ANCHOR, 7-METHYL-2,4,9-TRITHIA-TRICYCLO[3.3.1.1^{3,7}]DECANE, ON NOBLE METAL SURFACES.

Chalermchai Khemtung and Jun Hu, Department of Chemistry, The University of Akron, 190 E Buchtel Comm, Akron, OH 44325-3601, Fax: 330-972-7370, ck6@uakron.edu

A new synthesis of 7-methyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane will be reported. The title compound is useful as a structurally well-defined tridentate transition metal ligand or surface anchor for the formation of supramolecular assemblies on surfaces. Its coordination chemistry and surface binding characteristics will be presented. Its applications in molecular electronics will be discussed.



184.

PUSHING THE SENSITIVITY OF NUCLEAR MAGNETIC RESONANCE IMAGING WITH FORCE-GRADIENT DETECTION.

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Magnetic resonance force microscopy (MRFM) is an emerging imaging technology which combines magnetic resonance and scanned-probe techniques, with the ultimate goal of subsurface, three-dimensional, atomic scale imaging. We have demonstrated a new type of MRFM in which we invert sample spins to create a local force gradient which shifts the mechanical resonance frequency of a magnet-tipped microcantilever. Employing a very low spring constant cantilever at cryogenic temperatures we have demonstrated our approach in GaAs, detecting ⁷¹Ga nuclear magnetic resonance at very high sensitivity. In contrast to previous MRFM methods, with our method there is no need to spin-lock sample magnetization during detection, allowing signal to be collected

for a time approaching the full spin-lattice relaxation time — an innovation which will make MRFM applicable to a much wider array of samples.

185.

EFFECT OF SILVER PARTICLE SIZE ON METAL ENHANCED FLUORESCENCE OF A LABELED PROTEIN. *Jian Zhang, Biochemistry, University of Maryland School of Medicine, 725 West Lombard Street, Baltimore, MD 21201, Fax: 410-706-4808, jian@cfs.umbi.umd.edu, and Joseph R Lakowicz, Center for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland at Baltimore*

We studied the effect of particle size on metal-enhanced fluorescence. Silver films of varying thickness and /or particle size were prepared by vapor deposition and characterized by atomic force microscopy (AFM). Morphology of surface was dependent on the deposition thickness as well as rate. The plasmon absorption shifted from 490 to 670 nm and eventually became undetectable for the thickness over 10 nm. We found a correlation between particle size and metal-enhanced fluorescence of AlexaFluor 555-labeled Rabbit Immunoglobulin. Fluorophore was quenched when the particles were small (thickness of 2 – 3 nm) and enhanced when the particles were larger (thickness near 10 nm), reaching saturation near 20 nm. The fluorescence lifetime was lowest for a metal thickness near 20 nm, and then increased for thicker layer. The 10 nm thick silver was coated with silica, and a maximum enhancement was found for the 10 – 15 nm silica. These results suggested the properties of silver surfaces needed for maximum increases of fluorescence intensity. Additionally, these results are consistent with our theory that metal-enhanced fluorescence can be predicted for the scattering component of metal particle extinct.

186.

ELECTRONIC CONDUCTIVITY OF NANOPARTICLE MONOLAYERS AT THE AIR/WATER INTERFACE. *Shaowei Chen, Yiyun Yang, and Sulolit Pradhan, Department of Chemistry, Southern Illinois University, Carbondale, IL 62901, schen@chem.siu.edu*

The lateral electrical/electronic conductivity of alkanethiolate-protected nanoparticles was evaluated by using the Langmuir method with an interdigitated arrays (IDA) electrode perpendicularly aligned at the air|water interface where a particle ensemble was trapped between the IDA fingers. For gold particles with short protecting monolayers (C4Au and C5Au), the current-voltage profiles exhibited ohmic behaviors with conductivity several orders of magnitude smaller than that of bulk gold. The conductivity is found to decrease exponentially with increasing interparticle spacing. This is interpreted on the basis of electron tunneling/hopping between neighboring particles where the tunneling coefficient is found around 0.5 ± 3^{-1} . With longer alkyl protecting layers (C6 and above), the nanoparticle monolayers demonstrated rectifying charge-transfer characters. This transition from ohmic to diode-like responses can be attributable to the nanocomposite structure of the particle molecules, where the chemical nature of the core and the protecting monolayers, along with the interparticle environment and ordering, are found to play an important role in regulating the electrical/electronic properties of the nanoassemblies.

More importantly, using sensitive pulse voltammetric techniques, we also observed quantized charge transfer across a gold nanoparticle monolayer at the air|water interface. Differential pulse voltammetry revealed a series of well-defined voltammetric peaks, which are ascribed to the single electron transfer of the particle ensemble. This observation was interpreted on the basis of relatively weak electronic coupling between neighboring particles where the particles behave more individually.

The experimental protocol was also used to examine the conductivity properties of semiconductor nanoparticles. PbS and CdTe nanoparticles were used as the illustrating examples. The ensemble conductivity properties were very sensitive to photoexcitation, which provides an additional degree of manipulation of charge transfer at nanoscale interfaces.

187.

ELLIPSOMETRIC APPROACH FOR SECOND HARMONIC POLARIZATION CHARACTERIZATION AND LABEL-FREE PROTEIN ADSORPTION. *Ryan Plocinik, Department of Chemistry, Purdue University, 425 Central Drive, West Lafayette, IN 47906, rplocini@purdue.edu, and Garth J Simpson, Department of Chemistry, Purdue University*

Nonlinear optical null ellipsometry (NONE) was developed to interpret polarization information of the second harmonic generated (SHG) light at thin surface

films. The experimentally simple instrument design allows for a mathematically straightforward evaluation of the data and yields greater information content than comparable intensity based techniques. The polarization-dependence of the SHG light yields the fully complex valued $\chi^{(2)}$ nonlinear susceptibility tensor elements. The $\chi^{(2)}$ tensor elements can then be related back to the structure of molecules at the silica/aqueous solution interface. In one specific application, NONE has allowed detection of the adsorption of bovine serum albumin (BSA) at the silica/aqueous solution interface in real time and without requiring the use of labeled protein.

188.

ATTENUATING NEGATIVE DIFFERENTIAL RESISTANCE IN AN ELECTROACTIVE SELF-ASSEMBLED MONOLAYER-BASED JUNCTION. *Ronald A. Wassel¹, Grace M. Credo², Ryan Fuierer¹, Dan Feldheim¹, and Christopher B. Gorman¹. (1) Department of Chemistry, North Carolina State University, Raleigh, NC 27695, (2) Waters Corp*

The negative differential resistance (NDR) peak current observed in redox active self-assembled monolayer-based molecular junctions has been attenuated by controlling the composition of the molecular junction. Two approaches studied here include capping the electroactive ferrocenyl groups with β -cyclodextrin and functionalizing the scanning tunneling microscope tip used to probe the SAM with n-alkanethiols of different lengths. These are the first examples of systematic modification of the magnitude of the NDR response in a molecule-based system.

189.

NANOSTRUCTURED ULTRAFAST ELECTROCHROMIC DISPLAYS. *Seungil Cho¹, Sang Bok Lee¹, and Sang Ho Kim². (1) Department of Chemistry and Biochemistry, University of Maryland, Chemistry building, University of Maryland, College Park, MD 20742, sicho@wam.umd.edu, (2) LG Chem, Korea*

Electrochromic display is one of the most attractive candidates for paper-like displays, so called electronic paper, which will bring revolutionary advances in the display technology, owing to attributes such as thin and flexible materials, fast switching time, low-power consumption. However, current electrochromic technologies cannot play moving images due to their slow color-switching rates. Poly(3,4-ethylenedioxythiophene), PEDOT, and its derivatives are an ideal electrochromic materials for the electronic paper due to their good color and mechanical stabilities and facile fabrication. The color-switching rate of the PEDOT is limited by the diffusion rate of counter-ions into the film during the redox process. Here, we show that an extremely fast electrochromic display (switching time less than 10 ms) can be fabricated based on well-defined nanotube arrays of PEDOT. Thin nature of the nanotube walls offers a short ion-diffusion distance and results in ultrafast switching rate. The arrayed long-nanotube structure gives a strong coloration for displays. A new mechanism for nanotube synthesis is proposed and this synthetic method is applicable in various types of electrochemical devices and power sources.

190.

DEXTRAN IMMOBILIZATION ON SILICON OXIDE SUBSTRATES: GRAFTING DENSITY AND SURFACE PROPERTIES. *Davide Miksa¹, Elizabeth R. Irish², Russell J. Composto², and David M. Eckmann¹. (1) Department of Anesthesia, University of Pennsylvania, 331 John Morgan Building, Philadelphia, PA 19104-6112, miksad@uphs.upenn.edu, (2) Materials Science and Engineering, University of Pennsylvania*

Biomimetic surfaces were prepared by chemisorption of oxidized dextran (Mw = 110 kDa) onto SiO₂ substrates that were previously modified with aminopropyltriethoxy silane (APTES). The kinetics of dextran oxidation by sodium metaperiodate (NaIO₄) were quantified by ¹H NMR and pH measurements. The extent of oxidation was then used to control the morphology of the biomimetic surface. Oxidation times of 0.5, 1, 2, 4, and 24 hours resulted in <20, ~30, ~40, ~50 and 100% oxidation, respectively. The surfaces were characterized by contact angle analysis and atomic force microscopy (AFM). Surfaces prepared with low oxidation times revealed a more densely packed "brushy" layer when imaged by AFM than those prepared at low oxidation times. Finally, the contact angle data revealed, quite unexpectedly, that the surface with the greatest entropic freedom (0.5 h) wetted the fastest and to the greatest extent ($\theta_{\text{APTES}} > \theta_{\text{1h}} > \theta_{\text{2,4h}} > \theta_{\text{0.5h}}$).

191.

CAPILLARITY-DRIVEN ASSEMBLY OF CELLULAR CARBON NANOTUBE FOAMS.

Nirupama Chakrapani¹, Bingqing Wei², Alvaro Carrillo³, Pulickel M. Ajayan⁴, and Ravi S. Kane¹. (1) Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180, *chakrn@rpi.edu*, (2) Department of Electrical & Computer Engineering, Louisiana State University, (3) Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, (4) Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute

Carbon nanotubes have numerous potential applications as a result of their outstanding mechanical and electronic properties. The pursuit of these applications is hindered by the difficulty of manipulating these nanomaterials and organizing them into macroscopic structures. We use capillary forces to direct the assembly of carbon nanotubes into cellular foams. We will describe the mechanisms by which these structures are formed. We will also discuss methods for controlling the length scale, orientation, and shape of the cellular structures. Applications of these nanostructured materials will also be discussed.

192.

RELATIONSHIPS BETWEEN REDOX PROPERTIES OF POLYOXOMETALATES AND THEIR EFFECTIVENESS AS OXIDATION CATALYSTS.

Mark A. Barteau¹, Katherine P. Barteau¹, In Kyu Song¹, Vincent A. Durante², Paul E. Ellis³, Shahid N. Shaikh³, and James E. Lyons¹. (1) Department of Chemical Engineering, University of Delaware, Newark, DE 19716, Fax: 302-831-8201, *barteau@che.udel.edu*, *lyonscat@aol.com*, (2) Catalyst Technology Development, W. L. Gore & Associates, Inc, (3) SABIC Technology Center, SABIC Americas, Inc

Regular metal oxide clusters such as the well-known Keggin ions are used as catalysts for a number of industrial processes including the oxidation of methacrolein to methacrylic acid. Recent investigations demonstrate the roles of redox properties, acidity, molecular structure and catalyst supports on the effectiveness of polyoxometalates as oxidation catalysts. Scanning tunneling spectroscopy is shown to be particularly useful in determining surface redox properties that correlate well with catalytic effectiveness in the oxidation of a wide array of substrates. Several additional techniques for measuring redox properties of POMs, both supported and in solution, are under development and will be discussed. These studies have important implications for the synthesis of potentially superior oxidation catalysts and may have predictive value in extending the application of POMs as catalysts for a large number of useful oxidation reactions.

193.

IN-SITU QUANTIFICATION OF THE ACTIVE ACID SITES OF H6P2W18O62.NH2O HETEROPOLY-ACID THROUGH CHEMISORPTION AND TEMPERATURE PROGRAMMED SURFACE REACTION OF ISOPROPANOL.

Luis A. Gambaro, Centro de Investigación y Desarrollo en Ciencias Aplicadas –Dr. Jorge J. Ronco, Universidad Nacional de La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Calle 47 No 257, C.C. No 59, (B1900AJK), La Plata (Buenos Aires), Argentina, Fax: 00, *briand@quimica.unlp.edu.ar*, and *Laura Briand,* Centro de Investigación y Desarrollo en Ciencias Aplicadas, UNLP, 47 No 257, La Plata B1900AJK, Argentina, *briand@quimica.unlp.edu.ar*

Isopropanol chemisorption and temperature programmed surface reaction analyses were used to determine the nature, amount and acid strength of the active sites of bulk WO₃, monolayer supported tungsten oxide over titania and phospho-tungstic Wells-Dawson and Keggin type heteropoly-acids. Additionally, the influence of the degree of hydration on the amount and acid strength of the active sites of the Wells-Dawson acid was investigated. The temperature conditions were adjusted in order to cover the surface of the catalysts with a stable monolayer of intermediate chemisorbed isopropoxy species avoiding physisorption or surface reaction during the chemisorption process. Chemisorbed species dehydrate towards propylene over the investigated catalysts. The amount of active sites (Ns) was determined as the amount of propylene desorbed during the TPRS analysis. Heteropoly-anions possess the highest amount of active sites and acid strength among the investigated solid catalysts. Isopropanol chemisorbs both at the surface and the bulk of the heteropoly-

anions due to the pseudo-liquid phase property of these materials. Moreover, the high acidity of the Brønsted and Lewis acid sites of the heteropoly-acids catalyze the reaction of the adsorbed isopropoxy species at a lower temperature (~100 °C) than WO₃ and monolayer supported tungsten oxide species WO_x/TiO₂.

194.

THE FUNCTION OF VXOY SPECIES IN SELECTIVE OXIDATION: AN IN-SITU

HIGH PRESSURE XPS STUDIES. *Robert Schlogl, Detre Teschner, Axel Knop-Gericke, Michael Haevecker, Efgueni Kleimenov, and Dangsheng Su, Dep. of Inorganic Chemistry, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany, *acsek@fhi-berlin.mpg.de**

Pure and supported forms of high-oxidation state vanadium oxides were studied by in-situ XPS in the selective oxidation of butane with oxygen. Pressures up to 2 mBar and temperatures up to 673 K were applied. Non-destructive depth profiling revealed a complex pattern of oxygen transport as pre-requisite for catalytic function.

Reference samples showed a dynamical response of their surface termination to the gas environment and were always reduced under standard XPS conditions. HT-TEM observations revealed that such transformations are also associated with bulk transformations when the particles are nanostructured. The determination of an "oxidation state" becomes quite arbitrary and the results explain the debate about numbers of oxidation state found in the literature.

The results point to the formation of a metastable sub-oxide as catalytically active form that requires to have defects in its termination for catalytic action. The results are discussed in terms of the "bulk and surface MvK mechanism" paradigm. Relations to VPP and MoVTe systems will be indicated.

195.

RAMAN MICROSCOPY, A POWERFUL TOOL TO STUDY THE PREPARATION OF

SUPPORTED METAL-OXIDE CATALYST BODIES. *Jaap A. Bergwerff¹, Tom Visser¹, Bob R. G. Leliveld², Brenda D. Rossenaar³, Krijn P. de Jong¹, and Bert M. Weckhuysen¹.* (1) Department Inorganic Chemistry and Catalysis, Universiteit Utrecht, Debye Instituut, Sorbonnelaan 16, 3508 TC Utrecht, Netherlands, *J.A.Bergwerff@chem.uu.nl*, (2) Akzo-Nobel Catalysts BV, (3) Akzo Nobel Chemicals Research

Pore volume impregnation of extrudates is usually the method of choice in the industrial preparation of supported catalysts. In this study, Raman microscopy is used for the first time to study the physico-chemical processes that take place during the different steps in the preparation of catalyst bodies. The nature and concentration of metal-oxide complexes inside the pores of the support can be monitored as a function of time and space. As an example, the speciation of different Mo⁶⁺ complexes is monitored during the synthesis of Mo-Al₂O₃ extrudates. The influence of the support (point of zero charge and pore size distribution) and the addition of complexing agents, such as citrate and phosphate, have been studied as well.

196.

STUDY ON HIGH TEMPERATURE (1000 C) PROPANE OXIDATION AND AUTOTHERMAL REFORMING (ATR) OVER SUPPORTED PD/ALUMINA WITH IN SITU UV-RAMAN SPECTROSCOPY.

*Xiang Wang and Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, 7 Asa Drive, Bethlehem, PA 18015, Fax: 610-758-6555, *xiw3@lehigh.edu**

In situ UV-Raman spectroscopy was employed to characterize a supported 1 wt. % Pd/Al₂O₃ catalyst during propane oxidation and autothermal reforming (ATR) at 1000 °C. Under oxidizing conditions (25% O₂/He), crystalline PdO (with characteristic Raman bands at 628 cm⁻¹) was observed from room temperature to 1000 °C. However, the PdO structure is dynamic and responds to the reaction atmosphere and temperature. The surface structural changes of the catalyst are correlated to its reaction performance for propane oxidation and ATR. In contrast to the successful in situ UV-Raman spectra at 1000 °C, corresponding visible Raman spectra were not obtainable at 800 °C and higher temperatures due to black body radiation. The details of this study will be presented and discussed at the meeting.

197.

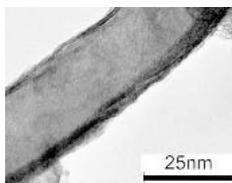
NANOTUBES SYNTHESIZED BY TRANSPORT REACTION. *Maja Remskar, Solid State Physics, Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia, Fax: 386-1-4263269, maja.remskar@ijs.si, and Ales Mrzel, Complex Matter, Jozef Stefan Institute*

The MoS₂ and WS₂ nanotubes synthesized by chemical transport reaction represent the longest known inorganic nanotubes grown up to several millimetre lengths. Their diameter ranges from several micrometers to less than ten nanometers. The nanotubes grown at nearly equilibrium conditions contain extremely low density of structural defects. They have been successfully alloyed with metals suppressing by such a manner the tube chirality and changing electrical properties. While microtubes usually grow as single tubes, the nanotubes combine some ropes formed by side-by-side growth of primary nanotubes. The self-assembly tendency is the most obvious in the sub-nanometer MoS₂-xly nanotubes, which have been synthesised using C60 as a growth promoter. Due to the metallic behaviour these smallest known inorganic nanotubes belong to the family of promising molecular wires. The conditions of synthesis will be explained and foreseen applications will be discussed. Results of transmission electron microscopy and scanning tunneling microscopy will be presented.

198.

TEMPLATE SYNTHESIS OF MoS₂ NANOTUBE. *Hiroiyuki Enomoto, Academic Frontier Promotion Center, Osaka Electro-Communication University, Hatsu-cho 18-8, Neyagawa, Osaka 572-8530, Japan, Fax: +81-72-824-0014, h-enomot@isc.osakac.ac.jp, Takahide Fujiwara, Department of Materials Science, Osaka Electro-Communication University, and Hiroshi Shioyama, National Institute of Advanced Industrial Science and Technology*

MoS₂ nanotubes were synthesized by the template method. (NH₄)₂MoS₄ precursor was thermally decomposed in an atmosphere of 10 % H₂/N₂ to form MoS₂ nanotube within a porous aluminum oxide template. MoS₂ nanotube was characterized by X-ray diffraction and scanning/transmission electron microscope (SEM/TEM). Proper control of the reaction time and the reaction temperature was critical to success. Mixture of MoS₂, MoO₂, and MoO₃ was formed at higher reaction temperature or for longer reaction time. It was found that MoS₂ nanotube can be obtained in pure form at 350 °C for 1 h. Figure shows TEM image of MoS₂ nanotube after removal of aluminum oxide template.



199.

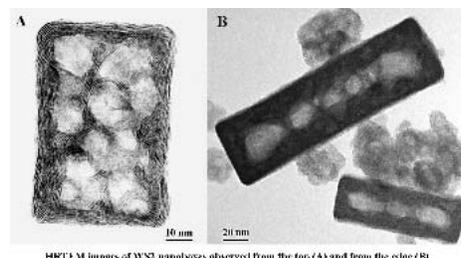
MECHANICAL PROPERTIES OF INDIVIDUAL TUNGSTEN DISULFIDE NANOTUBES. *Ifat Kaplan-Ashiri¹, Sidney R. Cohen², Konstantin Gartsman², Rita Rosentsveig³, H. Daniel Wagner³, and Reshef Tenne¹. (1) Materials and Interfaces, Weizmann Institute of Science, P.O.Box 26, Rehovot 76100, Israel, Fax: 972*8-9344137, ifat.ashiri@weizmann.ac.il, (2) Chemical Research Support, Weizmann Institute of Science, (3) Materials and Interfaces, Weizmann Institute of Science*

The Young's modulus of tungsten disulfide nanotubes is an important property for various applications. Measurements of the mechanical properties of individual nanotubes are challenged by their small size. Lately, measurements of the Young's modulus by buckling of an individual nanotube within atomic force microscope resulted in an average value of 171 GPa. Further study of the buckling behavior, is performed within the scanning electron microscope and some preliminary results are shown. Moreover, tensile tests of individual nanotubes are performed within a scanning electron microscope. Preliminary results of these experiments show the following results: Young's modulus value of 137 GPa, tensile strength value of 11.8 GPa and maximal elongation of 12.3%. These results are a manifestation of the tungsten disulfide nanotubes perfect crystalline shape.

200.

SYNTHESIS OF INORGANIC FULLERENES AND NANOBXES OF MoS₂ AND WS₂ BY SPRAY PYROLYSIS. *Stéphane Bastide¹, Jean pascal Borra², Dominique Duphil¹, and Claude Lévy-Clément¹. (1) Laboratoire de Chimie Métallurgique des Terres Rares, CNRS - UPR 209, 2-8, rue Henri Dunant, Thiais 94320, France, Fax: 33 149 78 12 03, bastide@glvt-cnrs.fr, (2) Laboratoire de Physique des Gaz et des Plasmas, CNRS - UMR 8578*

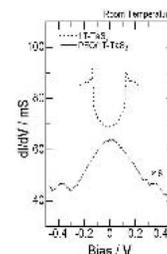
We present a new route to synthesize inorganic fullerenes (IF) of MoS₂ and WS₂, based on the spray pyrolysis at high temperature of aqueous or ethanolic solutions of tetrathiomallate salts. Preliminary results show that it also can lead to new IF morphologies. For instance, WS₂ particles can adopt an original type of nested structure, exhibiting the shape of a parallelepiped, with multilayer walls and an empty core, thus describing a "closed nanobox" (figure). The influence of parameters such as the droplet size, the nature of the solvent, or the temperature, on the IFs' morphology will be presented and discussed. The spray pyrolysis method may also provide an "easy way" to test the ability of other inorganic lamellar compounds to form IF and has the potential to lead to an industrial process, an important point in view of their use as catalysts or solid lubricants.



201.

TUNNELING STUDY ON POLYMER/TaS₂ NANOCOMPOSITES. *Hiroiyuki Enomoto, Academic Frontier Promotion Center, Osaka Electro-Communication University, Hatsu-cho 18-8, Neyagawa, Osaka 572-8530, Japan, Fax: +81-72-824-0014, h-enomot@isc.osakac.ac.jp, Hiroiyuki Takai, Department of Materials Science, Osaka Electro-Communication University, Hajime Ozaki, Department of Electrical Engineering and Bioscience, Waseda University, and Michael M. Lerner, Department of Chemistry, Oregon State University*

Electronic structures near the Fermi level of polymer/TaS₂ layered nanocomposites have been studied by tunneling spectroscopy. Polymer/TaS₂ nanocomposites were synthesized by using the exfoliation-adsorption technique. Single crystals of layered transition-metal dichalcogenides of 1T-, 2H-, and 4H-TaS₂ were used as host materials. PEO and PEI were adopted as guest intercalants. Powder X-ray diffraction patterns showed that all samples of polymer/TaS₂ layered nanocomposites contain organic polymer between all individual TaS₂ sheets. Figure shows the tunneling spectra of 1T-TaS₂ single crystal and PEO/1T-TaS₂ nanocomposite measured at room temperature. Although the tunneling spectrum of 1T-TaS₂ single crystal shows a clear CDW structure with CDW gap of 0.26 eV, that of PEO/1T-TaS₂ nanocomposite has no CDW gap and shows a metallic behavior.



202.

CONTROL OF MoS_x NANOPARTICLES PROPERTIES BY USING SURFACTANTS IN CHIMIE DOUCE CONDITIONS. *Karin E. Marchand, Maud Tarret, Tivadar A. Cseri, and Slavik Kasztelan, Catalysis and separation / Heterogeneous catalysis, IFP, BP n°3, Vernaison 69390, France, Fax: 33478022066, karin.marchand@ifp.fr*

The morphological control of the sulfide phase of hydrotreating catalysts remains a topical issue. Classical preparations (sulfidation of an oxidic precursor

or thermal decomposition of thioesters at high temperature under H₂S/H₂ flow) produce MoS₂ nanoparticles with low stacking and a large range of slab lengths. *Chimie douce* conditions, combined with the use of surfactants, have thus been used to tailor the size and properties of MoS_x nanoparticles. We wish to report here two routes, leading to MoS_x nanoparticles further characterized by HRTEM, XRD, XPS. The first one is a one pot synthesis using AHM, a reductor, a sulfiding agent, and a surfactant as a structuring agent to control the crystallinity of the nanoparticles obtained. In the second one, surfactants involved in the formation of a reverse microemulsion phase (of AOT/n-heptane/water) which has been thoroughly characterized (cryofracture/TEM), enabled us to control the size of the nanoparticles obtained.

203.

BIMETALLIC SULFIDES PREPARED VIA THERMAL DECOMPOSITION OF HETEROPOLY COMPOUNDS MICROEMULSIONS. *C. E. Scott¹, Emir Escalona¹, Pedro R. Pereira², J. Castillo³, Jeannette Hung⁴, and C. Bolívar¹.* (1) *Centro de Catálisis Petroléa y Petroquímica, Universidad Central de Venezuela, Apartado 47102, Los Chaguaramos, Caracas 1041-A, Venezuela, Fax: 58-2-605 1220, cscott@strix.ciens.ucv.ve,* (2) *Chemical and Petroleum Engineering Department, University of Calgary,* (3) *Labs of Espectroscopía Laser, Facultad de Ciencias,* (4) *Centro de Física, Instituto Venezolano de Investigaciones Científicas*

Microemulsions were prepared by adding a surfactant to deahydronaphthalene (1:10 by weight) and the resulting solution was stirred using a Rushton turbine. To this solution an aqueous solution of (NH₄)₃(NiMo₆O₂₄)₇H₂O (ammonium heptamolybdate or Ni nitrate for monometallic solids) was added and then further stirred. To the microemulsions thus obtained CS₂ was added, followed by thermal decomposition in a 300 cm³ Parr autoclave at 573 K and 70 bars of hydrogen. Finally the solids were recovered by centrifugation and washed with toluene. Solids were characterized by X ray diffraction, confocal microscopy, BET surface area and TPO. Thiophene hydrodesulfurization was performed in a continuous flow microreactor at 553 K and 1 bar of hydrogen. XRD results show that all solids present poorly crystallized structures. For Ni and Mo the XRD patterns can be assigned to Ni₉S₈ and MoS₂ respectively. The diffractogram for NiMo did not show any peak at all. All the solids present similar particle diameters, i.e. 0.483±0.173, 0.371±0.103 and 0.558±0.224, for NiMo, Mo and Ni respectively. However, HDS activity for conversion of thiophene is 2.22 10⁻⁵ mol g⁻¹ s⁻¹ for NiMo, 1.49 10⁻⁵ for Mo and 0.53 10⁻⁵ Ni, indicating that we succeeded in preparing small particles of a mixed NiMo sulfide. Acknowledgement: Authors are grateful to FONACIT (G-97000658) for the financial support.

204.

SURFACE METAL OXIDE MONOLAYERS: MOLECULAR STRUCTURES AND SURFACE CHEMISTRY. *Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, 7 Asa Drive, Bethlehem, PA 18015, Fax: 610-758-6555, iew0@lehigh.edu*

The surface metal oxide monolayer represents the ultimate thin film for metal oxide materials and thereby serves an ideal model system for the study of molecular structure-reactivity/selectivity relationships for metal oxide catalysts. The surface nature of the metal oxide monolayer readily allows for its molecular structural determination, even under reactive environments, with various spectroscopic characterization methods. Furthermore, the two-dimensional amorphous surface phases also assure that they contain the catalytically active surface sites. Thus, surface metal oxide monolayer systems are ideal for establishing the influence of different functionalities (e.g., M=O, M-O-M, M-OH), oxidation states, number of participating surface metal oxide sites, local molecular structure, electronic effects, promoters and poisons upon the catalytic behavior for a specific reaction. This fundamental information is allowing the establishment of molecular structure-reactivity/selectivity relationships and is enabling the molecular design and theoretical modeling of metal oxide catalytic materials.

205.

SELF-ORGANIZATION OF COLLOIDAL SUSPENSIONS. *Darsh T. Wasan, Department of Chemical and Environmental Engineering, Illinois Institute of Technology, 10 West 33rd Street, Room 228, Chicago, IL 60616, Fax: 312-567-3003, wasan@iit.edu*

Suspensions of nanometer-sized particles are used in a variety of technological contexts. For example, their spreading and adhesion behavior on solid surfaces

can yield materials with desirable structural and optical properties. The structure and stability of colloidal dispersions depend highly on the interaction forces between colloidal particles and the confining geometry. Such is especially the case in a concentrated colloidal dispersion when particles are more likely to come in close contact with one another and become more ordered in the restricted environment. The study of the structure of colloidal suspensions has a long history dating back to Langmuir. The last decade has seen an intensified interest in the understanding of the role of depletion and structural forces in structure formation and stability of colloidal suspensions. The structural forces interact over large distances, up to several diameters of colloidal particles. This presentation will highlight the particle self-organization phenomenon in both the three- and two-dimensional systems. A particular emphasis is placed on the evolution of the in-layer nanoparticle structuring which offers a new mechanism for stabilizing colloidal dispersions, as well as a new tool to engineer self-assembling nanomaterials. Results of computer simulations and statistical mechanical theories are compared with the experiments.

206.

AN EASY METHOD FOR CONSTRUCTION OF PORTABLE BIOFUEL CELLS USING CHEMICALLY MODIFIED ENZYMES. *Hongfei Jia, Department of Chemical Engineering, University of Akron, Whitby Hall, Akron, OH 44325-3906, Fax: 330-972-5856, hj2@uakron.edu, and Ping Wang, Department of Chemical Engineering, The University of Akron*

We report an effective approach to the construction of enzyme-based electrodes for biofuel cell applications. Enzymes including glucose oxidase (GOD) were first modified with hydrophobic groups such as decanoyl chloride. The electrodes were then prepared by absorbing the modified enzyme on the surface of conductive carbon papers. Cyclic voltammetry (CV) studies showed desired redox activity of the absorbed enzymes. A biofuel cell was built using modified GOD on the anode along with a gas diffusion oxygen cathode and a Nafion-117 membrane (25 cm²). Electric power generation was observed upon the addition of glucose to the anode chamber. An open circuit voltage of 300 mV and a power density of 2.4 μW/cm² were achieved with the biofuel cell. We expect both micro- and macro-scale biofuel cells can be easily constructed through the same approach.

207.

GLUCOSE-AIR ENZYMATIC BIO-FUEL CELL. *Plamen Atanassov, Frisia Colon, and Vijaykumar Rajendran, Chemical & Nuclear Engineering, University of New Mexico, 209 Farris Engineering Center, Albuquerque, NM 87131, Fax: 505-277-5433, plamen@unm.edu*

Research in our laboratory has been focused on gas-diffusion laccase- and bilirubin oxidase-catalyzed cathodes, operating under "air-breathing" conditions. In this paper, we report on the integration of such gas-diffusion enzyme-catalyzed cathode with a glucose electrooxidizing, nickelocene-mediated glucose oxidase anode. Biofuel cell characteristics, such as, power density, cell voltage, cell design parameters will be discussed. Development of the designs allowing for direct utilization of various fuels harvested from biological sources will be addressed. This will include employment of coupled enzymatic reactions between glucose oxidase and invertase, for example, to provide for the possible use of sucrose as a fuel. One of such basic anode design concepts relies on mediated enzymatic oxidation of glucose. Among the numerous mediators and redox polymers that have been used for the electrical communication between the Gox enzyme and the electrode, we have exploited nickelocene, which has a more favorable quasi-redox potential of around -100mV vs. Ag/AgCl, compared to ferrocene derivatives, and other commonly used redox mediators. The composite electrode was prepared using a mixture of teflonized carbon and carbon black, with the mediator and Gox immobilized by physical adsorption following a previously reported procedure and was designed to serve as anode of the biofuel cell. This electrode demonstrates high activity in glucose conversion and can provide current output exceeding 3 mA/cm² at 0.0 V vs. Ag/AgCl electrode. The polarization studies of the cell will be presented demonstrating cell potential of 0.6 V at a load current of 100 mA/cm². The cell sustains loads up to 250 mA/cm² with a voltage of 0.5 V. The power output of the biofuel cell is in the range of 50-250 mW/cm².

208. INCREASING THE LIFETIME AND CURRENT DENSITY OF AN ETHANOL BIOANODE USING PQQ-DEPENDENT DEHYDROGENASE ENZYMES. *Shelley D. Minteer and Becky L. Treu, Department of Chemistry, Saint Louis University, 3501 Laclede Ave., St. Louis, MO 63103, Fax: 314-977-2521, minteers@slu.edu*

A biofuel cell uses biocatalysts for the conversion of chemical energy to electrical energy. Previous research in our group has focused on ethanol based biofuel cells that employ the use of enzymes immobilized at the surface of electrodes as fuel cell catalysts. In order to increase the lifetime and activity of the bioanode, modified Nafion/enzyme composite electrodes are employed. When Nafion is modified with tetrabutylammonium salts, it forms a more optimal environment for enzymes. The current enzymatic system employing NAD-dependent alcohol dehydrogenase (ADH) has shown as problematic for several reasons. NADH oxidation has a high overpotential on carbon, so an electrocatalyst layer is necessary to decrease the overpotential. The electrocatalyst layers decrease conductivity and add complexity to the bioanode. NAD⁺ is also labile and has a short lifetime in the bioanode. Pyrroloquinoline quinone (PQQ)-dependent alcohol dehydrogenase (ADH) has been chosen to replace NAD-dependent ADH as a fuel cell catalyst due to its unique electrochemistry in order to correct the problems associated with the current enzymatic system.

209. MEDIATED GAS DIFFUSION BIOCATHODES. *Scott Calabrese Barton and Nicholas Hudak, Department of Chemical Engineering, Columbia University, 500 W. 120th St., Room 801, New York, NY 10027, Fax: 212-854-3054, scb2001@columbia.edu*

Oxygen-reducing biocatalysts such as laccase and bilirubin oxidase have several advantages over precious metal catalysts, including low-temperature activity, selectivity against common fuels, and manufacturability at relatively low cost. Biocatalytic electrodes achieve their maximum power density in structures that minimize mass transport limitations. One such structure is the conventional membrane-electrode assembly (MEA), ultimately combined with gas diffusion electrodes. In this presentation, we describe our implementation of a mediated laccase cathode in a MEA, in combination with hydrogen and methanol anodes. Fuel cell cathodes were fabricated by depositing a mixture of laccase, redox polymer, and crosslinking agent onto carbon-fiber paper, previously hot-pressed to a Nafion[®] membrane. The MEA was characterized in a single cell fixture with both interdigitated and serpentine flow fields. The anode was supplied with either hydrogen gas or methanol solution, and the cathode was supplied with oxygen- or air-saturated citrate buffer. Characterization included pseudo-steady-state polarization, impedance, and long-term stability.

210. CHARACTERIZATION OF EXTRACELLULAR MATRIX PROTEIN COATED SURFACES FOR TISSUE ENGINEERING. *John T. Woodward, John T. Elliott, Alex Tona, Kurt J. Langenbach, and Anne L. Plant, Biotechnology Div, National Institute of Standards and Technology, 100 Bureau Dr, STOP 8313, Gaithersburg, MD 20899, john.woodward@nist.gov*

We have developed a suite of atomic force microscope (AFM) based techniques for the purpose of characterizing surfaces used in tissue engineering and an automated fluorescence microscopy system for quantitating the cellular response to these surfaces. Surfaces composed of thin films of native collagen fibers have been characterized topographically by AFM to measure the fiber density. The morphology of smooth muscle cells (SMCs) is correlated with fiber density. Compliance of collagen fibers as measured by pulsed-force AFM shows that collagen thin films that are dried and rehydrated have significantly stiffer fibers than those that are not dried, and SMCs respond differently to the two surfaces. Pulsed-force mode AFM with an antibody-coated tip is also used to measure the density and distribution of biochemically functional sites on relevant surfaces. Together these techniques provide the ability to quantitate the surface derived inputs to cellular behavior.

211. PROBING INTERFACIAL INTERACTIONS OF BACTERIA ON SURFACES USING ATOMIC FORCE MICROSCOPY. *Jin Luo¹, Wei Ben Chan¹, Karin Sauer², David G. Davies², and Chuan-ian Zhong¹. (1) Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, jluo@binghamton.edu, (2) Department of Biological Sciences, State University of New York at Binghamton*

The ability to probe the adsorption of bacteria on surfaces is important for understanding the bacteria-surface interactions. This presentation reports findings on the use of atomic force microscopy (AFM) to probe the adsorption of *Pseudomonas aeruginosa* (*P. aeruginosa*) on atomically-smooth substrates of two different surface properties (hydrophilic and hydrophobic surfaces). Our aim is to demonstrate the viability of AFM in probing the bacteria-substrate interaction, which may have important implications to the understanding of biofilm formation. The AFM data were also compared with data from confocal optical microscopy. It is revealed that the interaction of the hydrophilic surface with *P. aeruginosa* keeps the cell outer membrane relatively "rigid". In contrast, the interaction of the hydrophobic HOPG surface with *P. aeruginosa* renders cell outer membrane relatively "soft". These two distinctive types of surface adhesion and interaction are discussed in terms of the structures and properties of lipopolysaccharide at the bacteria out membrane.

212. CHARACTERIZATION OF SINGLE ENZYME NANOPARTICLES BY USING TAPPING-MODE ATOMIC FORCE MICROSCOPY. *Jungbae Kim, A. S. Lea, and Jay W Grate, Pacific Northwest National Laboratory, 902 Battelle Blvd., PO Box 999, Mailstop K8-93, Richland, WA 99352, Fax: 509-376-5106, Jungbae.Kim@pnl.gov*

We have developed single-enzyme nanoparticles (SENs) by surrounding individual alpha-chymotrypsin molecule with a porous organic/inorganic composite network less than a few nanometers thick. The synthetic procedure, entailing enzyme modification and two orthogonal polymerization steps, yields nanoparticles containing a single enzyme. In stability experiments, the incorporation of alpha-chymotrypsin into the nanostructure dramatically increased its enzymatic stability. Furthermore, the nanoscale structure around the enzyme is sufficiently thin and porous that it does not impose a significant mass transfer limitation on the substrate.

We have used Tapping-Mode AFM (TM-AFM) to characterize single enzyme nanoparticles containing alpha-chymotrypsin (SEN-CT). When compared to transmission electron microscopy (TEM) characterization, which requires sample-drying and many hours of optimization, TM-AFM resulted in much quicker characterization of SEN-CT. Since the SENs are still in a solution state, we obtain size information that is accurate of the actual particle size in a hydrated state. The measured size-distribution from TM-AFM was valuable in assessing the success of the SEN synthesis. We will discuss the comparison of AFM with TEM in characterizing SENs in detail.

213. CHEMISTRY ON A SINGLE PROTEIN, VCAM-1, DURING FORCED UNFOLDING. *Nishant Bhasin, Department of Chemical Engineering, University of Pennsylvania, 112 Towne Building, Philadelphia, PA 19104, nishantb@seas.upenn.edu, and Dennis E. Discher, Department of Chemical and Biomolecular Engineering, University of Pennsylvania*

Cell adhesion to biomaterials generally occurs through receptor proteins that are invariably folded. But folded proteins of many types experience tensile forces in their normal function, and VCAM-1 (Vascular Cell Adhesion Molecule-1) is typical in this. VCAM has seven immunoglobulin (Ig) domains, and each has a disulfide bond (-S-S-) buried in its core that covalently stabilizes about half of each domain against unfolding. VCAM is extended here by single molecule atomic force microscopy (AFM) in the presence or absence of reducing agents. In the absence of reducing agent, a sawtooth pattern of forced unfolding reveals an average period and total length consistent with disulfide locations in VCAM's primary sequence. With increasing reducing agent, accessible disulfides are specifically reduced (to SH) because the average period for unfolding increases up to saturation together with additional metrics of unfolding. Steered molecular dynamics simulations of unfolding indeed show that the core disulfide bond is solvent-exposed long before full length unfolding.

214.

EPITAXIAL GROWTH OF CHOLESTEROL CRYSTALS FROM MODEL BILE SOLUTIONS: A DUAL AFM AND MOLECULAR MODELING STUDY. *M. Crina Frincu*¹, *Andrew L. Rohl*², *Sean D. Fleming*², and *Jennifer A. Swift*¹. (1) Department of Chemistry, Georgetown University, 37th and O Streets NW, Washington, DC 20057, Fax: 202-687-6209, mcf@georgetown.edu, (2) Curtin University of Technology

Epitaxial relationships between the surfaces of inorganic and bioorganic crystals can be an important factor in crystal nucleation and growth processes in a variety of biological environments. Crystalline cholesterol monohydrate (ChM), a constituent of both gallstones and atherosclerotic plaques, is often found in association with assorted mineral phases. Using in situ AFM and well-characterized model bile solutions, the nucleation and epitaxial growth of ChM on calcite (10-14) surfaces in real-time is demonstrated at physiological temperatures. The energetics of various (10-14) calcite / (001) ChM interfaces were calculated in order to determine the most stable interfacial structure. This combination of experimental and theoretical work provides a clearer picture of how preexisting mineral seeds might provide a viable growth template that can reduce the energetic barrier to cholesterol nucleation under some physiological conditions.

215.

MECHANICS OF STIMULUS-RESPONSIVE ELASTIN-LIKE POLYPEPTIDES STUDIED BY FORCE SPECTROSCOPY. *Alexei Valiaev*¹, *Dong Woo Lim*², *Robert Clark*¹, *Ashutosh Chilkoti*², and *Stefan Zauscher*³. (1) Mechanical Engineering and Materials Science, Duke University, 144 Hudson Hall, Box 90300, Durham, NC 27708, av12@duke.edu, (2) Department of Biomedical Engineering, Duke University, (3) Department of Mechanical Engineering and Materials Science, Duke University

Stimulus-responsive biomacromolecules have attracted significant research interest due to their potential applications in drug delivery, molecular motors, and nanoscale actuation devices. Here, we present results from our single-molecule force spectroscopic experiments on elastin-like polypeptides (ELPs) that shed light on their physico-chemical and mechanical properties. ELPs are stimuli-responsive macromolecules that undergo an inverse phase transition triggered by changes in solvent temperature, pH, or ionic strength. Associated with this transition is a significant conformational collapse and change in surface energy. To date, most research on ELPs has focused on the investigation of bulk properties and their aggregation behavior in solution. Our research is the first, we believe, to provide detailed insight into the mechanisms of elasticity and conformational mechanics of ELPs on the single molecule level. The observed force-extension behavior at intermediate and large extensions supports a phenomenological model describing ELPs as kinetically mobile, disordered macromolecules whose elasticity upon extension arises largely from a reduction in the thermal fluctuations of the polypeptide backbone (i.e., a decrease in the number of conformational degrees of freedom) in conjunction with bond angle stretching and torsion. This behavior appears to be mostly unaffected by the phase state of the molecule. We also used hysteresis experiments, whereby one ELP is repeatedly stretched and relaxed, to study the existence of time-dependent structural changes. Our observations suggest that a well-defined supramolecular structure (e.g., a beta-spiral) is not formed when ELP undergoes its inverse temperature transition.

216.

DESIGN RULES FOR BIOMATERIALS FROM FORCE MEASUREMENTS. *Deborah Leckband*¹, *Xi Zhu*¹, and *Francoise M Winnik*². (1) Chemical Engineering, University of Illinois, 600 S. Mathews Ave., Urbana, IL 61801, Fax: 217-333-5052, leckband@scs.uiuc.edu, (2) Faculty of Pharmacy and Department of Chemistry, Université de Montréal

Environmentally responsive "smart" polymers are used in a variety of medical applications. A key objective in the design of these materials is to alter the interfacial polymer properties either by external stimuli or by exploiting environmental changes in vivo. This work describes direct force measurements of the interfacial properties of end-grafted thermally responsive and pH-responsive N-isopropyl acrylamide polymers. The force measurements directly quantify the molecular-level changes in the interfacial properties of these materials in response to changes in pH and temperature. We further show how these measured interfacial changes alter the polymer interactions with biomolecules such as mucin and proteins. These results account for pH-triggered drug release

from polymer-coated liposomes, for example, and provide design rules for targeting materials to specific tissues such as the mucosal lining of the epithelium.

217.

CHARGE EFFECTS IN NEUROFILAMENT NETWORKS. *Paul A Janmey*¹, *Oliver I Wagner*¹, *Chris Mullin*¹, and *Jean Francois Leterrier*². (1) Institute for Medicine and Engineering, University of Pennsylvania, 3340 Smith Walk, Philadelphia, PA 19104, Fax: 214-573-6815, janmey@mail.med.upenn.edu, (2) UMR CNRS 6558, University of Poitiers

Neurofilaments are protein polymers localized to the cytoskeleton of neuronal cells and have physical characteristics that differentiate them from other biopolymers. Neurofilaments are approximately 15 nm in diameter and many microns long, with persistence length less than 1 micron. Extending away from the core of the filament are large unstructured polypeptides that have hydrodynamic diameters ranging from 50 to 110 nm, depending on their extent of phosphorylation. These unstructured sidearms have net charges ranging from near neutrality to -110 per Mr = 50,000. Changes in electrostatic charge alter the effective volume of these brush-like polymers, and interactions of the anionic polymers with polyvalent cations lead to aggregation and re-solubilization that appears to coincide with charge reversal of the polyelectrolyte filaments.

218.

DYNAMIC EVOLUTION OF F-ACTIN MORPHOLOGY IN THE PRESENCE OF LINKERS. *Kun Chun Lee*, *Jennifer Schwarz*, *Ajay Gopinathan*, and *Andrea J. Liu*, Dept. of Chemistry and Biochemistry, UCLA, 405 Hilgard Ave., Los Angeles, CA 90095-1569, Fax: 310-267-0319, klee@chem.ucla.edu

F-actin is a semi-flexible living polymer important to the cellular cytoskeleton. The actin cytoskeleton exhibits structural polymorphism with structures ranging from dilute networks to dense bundles. These structures are formed dynamically by polymerization, depolymerization, and branching. Cells also use proteins that can bind two actin filaments together (linkers) to control morphology. Using computer simulation, we examine systematically how linker properties like actin-binding affinity affect actin self assembly focusing on the interplay between linkers and branching in the living polymer system.

219.

FORMATION OF FIBROUS ASSEMBLIES IN MIXTURES OF LYSINE WITH ALKYL SULFATES. *Yamaira I. González* and *Eric W. Kaler*, Department of Chemical Engineering, University of Delaware, Colburn Laboratory, 150 Academy St, Newark, DE 19716, Fax: 302-831-1048, gonzalez@che.udel.edu

Fibrous structures and gels are observed in aqueous mixtures of lysine with sodium alkyl sulfates with chain lengths from 12 to 16. The formation of these assemblies depends on the molar ratio of surfactant and lysine, pH, temperature, and the chirality of the amino acid. Self-assembly of the fibers occurs only when lysine enantiomers are in solution and for pH conditions in which the majority of the amine groups are protonated (near equimolar amounts of HCl and lysine). Gels form from the entanglement of these fibers, which can be hundreds of micrometers long. With increasing temperature, the gels melt and a single micellar region is observed. Within this region, micelles elongate when pH or temperature are lowered. In addition, viscous micellar solutions are obtained when the acid concentration is higher than the equimolar amount with respect to lysine, regardless of the molar ratios of lysine and alkyl sulfate considered in this work.

220.

INSIGHTS CONCERNING THE ROLE OF APO A-I IN PREVENTING VESICLE AGGREGATION. *Steven P. Wrenn*¹, *Manasa Gudheti*¹, and *Sum P. Lee*². (1) Chemical Engineering Dept, Drexel University, 481 CAT Bldg, 3141 Chestnut Street, Philadelphia, PA 19104, Fax: 215-895-5837, wrenn@coe.drexel.edu, (2) Division of Gastroenterology, University of Washington

This presentation will describe the anti-nucleating mechanism of apolipoprotein A-I on model biliary vesicles in the presence of PLC (phospholipase C), based on results of dynamic light scattering (DLS), steady-state fluorescence spectroscopy, cryo-TEM and UV/Vis spectroscopy. In a cholesterol-free system, PLC induces aggregation of vesicles from an initial, average size of 100 nm to a maximal size of 600 nm, but the presence of apo A-I largely mitigates the effect.

In a cholesterol-enriched system, a similar phenomenon is observed; whereas PLC alone produces aggregates of 300 nm, no aggregation is observed when apo A-I is present along with PLC. However, the ability of apo A-I to inhibit aggregation is seemingly temporary, as 800 nm particles are observed after 8 hours. We show that the larger sizes are not a result of enhanced vesicle aggregation but rather droplets of DAG that arise when apo A-I induces the formation of apo A-I: lecithin: cholesterol complexes. The complexes are similar to the discoidal pre-HDL complexes found in blood. Thus, apo A-I acts as an anti-nucleating agent by two mechanisms, depending on the DAG/apo A-I molar ratio. Inhibition is achieved via shielding of DAG moieties for DAG:apo A-I mole ratios of ~ 100 and less. Above this value, inhibition is achieved via a micro-structural transition.

221.

MOLECULAR THEORY OF BILIARY LIPID AGGREGATES. *R. Nagarajan, Department of Chemical Engineering, The Pennsylvania State University, Fenske Laboratory, University Park, PA 16802, Fax: 814-865-7846, rxn@psu.edu, and Martin C. Carey, Brigham and Women's Hospital, Harvard Medical School*

The aqueous secretion known as bile is produced in the canaliculus of the hepatocytes of the liver. The principal constituents of bile are bile salts, phospholipids and cholesterol. Specific membrane proteins facilitate the unidirectional transport of the biliary lipids from the cytoplasmic side across the canalicular membrane. Since cholesterol is virtually water-insoluble, aggregates formed of bile salts and phospholipids serve as cholesterol recipients in the canaliculus. When bile is stored in gallbladder, water is absorbed, which can lead to changes in aggregate morphologies and possibly result in the crystallization of cholesterol, precursor to gallstone formation. These phenomena call for a molecular level understanding of the aggregation properties of the cholesterol-bile salt-phospholipid systems. Although these systems have been studied widely via many experimental techniques, no attempt has been made to construct a molecular theory of the aggregation process, based explicitly on the molecular properties of the constituent species. In this study, we consider ternary lipid mixtures of bile salt, phospholipid and cholesterol in water as the solvent and formulate a molecular theory of their aggregation patterns. We consider various possible aggregate structures such as spherical or globular micelles, wormlike cylindrical micelles, disk-like micelles and spherical vesicles. We explicitly identify various possible inter-molecular interactions associated with each type of aggregate including the hydrophobic interactions, repulsions between hydrophilic parts of lipids, and hydrophobic domain-water interfacial energy. We also consider occurrence of possible cholesterol-lipid condensation complexes (a concept that has been proposed in explaining raft formation in membranes), within the aggregate structures. Using the universal principles of Gibbs reaction equilibrium and specific free energy models that describe each of the aggregate shapes, we probe theoretically the equilibrium aggregate shapes and sizes as a function of the composition of the lipid mixture as well as of the lipid concentration.

222.

DESIGNING SUPPORTED METAL OXIDE CATALYSTS BY UNDERSTANDING THE EFFECT OF THE KINETIC-PARAMETERS: PROPANE ODH OVER UNMODIFIED AND MODIFIED V2O5/TiO2 CATALYSTS. *Goutam Deo, Department of Chemical Engineering, Indian Institute of Technology Kanpur, 208016, Kanpur, India, Fax: +91-512-2590104, goutam@iitk.ac.in*

The importance of characterization techniques for the fundamental understanding of catalysts is well known. Supplementary to these techniques steady-state reaction analysis provides valuable information through the determination of kinetic-parameters. The kinetic-parameters assist in the improved understanding of the reaction, operating the reactor under optimum conditions and for catalyst design. To illustrate the importance of steady-state kinetic parameter determination the propane ODH reaction over unmodified and modified V2O5/TiO2 catalysts is considered. The unmodified and unmodified catalysts are synthesized by the incipient-wetness impregnation technique and characterized using various techniques to understand the nature of the surface active site. Using information from the characterization techniques an appropriate reaction mechanism is chosen for which the kinetic-parameters are estimated. The kinetic-parameters estimated are then used for the improved understanding of the reaction, optimum operating-condition determination, and catalyst design.

223.

CHARACTERIZATION OF THE INTERACTION OF LOWER ALKANES AND ALKENES WITH SUPPORTED MOLYBDENUM CATALYSTS: PROMOTIONAL EFFECT OF CHLORINE. *Chang Liu, Rick B. Watson, and Umit S. Ozkan, Department of Chemical Engineering, The Ohio State University, 140 W 19th Avenue, Columbus, OH 43210, Fax: 614-292-3769, liuc@che.eng.ohio-state.edu, ozkan.1@osu.edu*

In this study, a series of chlorine-modified molybdenum catalysts supported on silica and titania (Si:Ti) mixed oxides were prepared by a modified sol-gel technique. The catalytic performance of these catalysts was tested for the oxidative dehydrogenation (ODH) of ethane and propane. Catalysts were characterized by DRIFTS, LSR, ESR, XPS, TPD, and DSC techniques to elucidate the nature of the surface molybdena species and their physical-chemical interaction with the Si:Ti support, adsorption/desorption behavior, and the surface alterations present during the ODH reaction. In addition, in-situ measurements have been performed to elucidate the adsorption and transformation of alkanes/alkenes and the reduction of surface molybdena species over the Si:Ti support. Isotopic labeling studies have been performed to investigate the mobility and exchange of oxygen species and reaction pathways involving ethane and ethylene. These characterization results were correlated with the catalytic reaction performance to achieve a better understanding of the catalytic behavior of chlorine-modified catalysts.

224.

SELECTIVE OXIDATION OF PROPYLENE TO OXYGENATES OVER SUPPORTED VANADIUM OXIDE CATALYSTS. *Chunli Zhao and Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, 7 Asa Drive, Bethlehem, PA 18015, chz5@lehigh.edu*

Propylene selective oxidation to oxygenates was investigated over supported vanadia catalysts under differential steady-state reaction conditions and Raman spectroscopy. The specific oxide support was found to have a significant effect on the TOF $V2O5/ZrO2 \sim V2O5/TiO2 > V2O5/Nb2O5 > V2O5/Al2O3 > V2O5/SiO2$. This trend corresponds to the electronegativity of the support cation, and suggests that the active functionality is the bridging V-O-support bond. The supported V2O5/Nb2O5 catalyst exhibited both high TOF and acrolein selectivity over a wide temperature range. For supported V2O5/ZrO2 and V2O5/TiO2 catalysts, the TOF values increased with the surface VOx loading, and the optimum performance was obtained at monolayer surface vanadia coverage. This trend reveals that two surface VOx sites are involved in propylene oxidation to acrolein. The supported V2O5/SiO2 catalyst exhibited different trend and was selective to acetone. The TOF values don't change with the surface VOx loading, which suggests that one surface VOx site is involved in propylene oxidation.

225.

DETERMINATION OF THE NATURE OF ACTIVE SURFACE SITES PRESENT ON BULK MIXED MO-V-TE-NB-O METAL OXIDE CATALYSTS. *J. M. Jehng, Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan, China, Fax: 00, jmjehng@dragon.nchu.edu.tw, Israel E. Wachs, Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, and Wataru Ueda, Catalysis Research Center, Hokkaido University*

CH3OH-Temperature Programmed Surface Reaction (TPSR) spectroscopy was employed to determine the nature of the active surface sites for bulk mixed Mo-V-Te-Nb-O metal oxide catalysts. The CH3OH-TPSR spectra peak temperature, T_p , was found to be sensitive to the specific surface metal oxide as well as its oxidation state. The surface V+5 sites were found to be more active than the surface Mo+6 sites, which in turn were significantly more active than the surface Nb+5 and Te+4 sites. The surface V+5, Mo+6 and Te+4 behave as redox sites and the surface Nb+5 sites behave as acidic sites. However, surface Mo+6 could also exhibit some surface acidic characteristics. Bulk mixed Mo1V0.3Te0.16Nb0.12-Ox metal oxide was found to possess both surface redox sites and surface acidic sites. The surface redox sites reflect the characteristics of surface V+5 and the surface acidic sites reflect the properties normally associated with supported Mo+6 sites.

226.

SELECTIVE OXIDATION OF PROPANE OVER V-MO-NB-W-ALUMINA

CATALYSTS. Giacomo Grasso, Julian R.H. Ross, and Serguei Belochapkin, Centre for Environmental Research, College of Science, University of Limerick, Limerick, Ireland, Fax: +353-61-202602, julian.ross@ul.ie

The selective oxidation of propane has been studied over a range of catalysts prepared by the impregnation of an alumina support using both conventional methods and a robotic preparation system. The samples have been tested in both a conventional microreactor and in a multichannel high throughput screening system and the results using both systems have been compared for the most effective catalyst formulations. The samples have been characterised by a range of techniques including TPR and Raman spectroscopy. It will be shown that the most effective catalysts require both Mo and V oxide phases in close proximity. A comparison with a library of similar catalysts based on a zirconia support will also be made.

227.

SUPPORTED MIXED V-MO OXIDE CATALYSTS FOR PROPANE OXIDATION

REACTIONS. Miguel A. Banares¹, S. J. Khatib², and Rut Guil¹. (1) CSIC-Institute of Catalysis, Marie Curie, 2, E-28049-Madrid, Spain, Fax: +34 915854760, mbanares@icp.csic.es, (2) Institute of Catalysis and Petrochemistry, CSIC

Alumina-supported mixed Mo-V oxide catalysts are prepared by impregnation at different atomic Mo/V ratios and with different total (Mo+V) coverage on alumina support, ranging from 0.2 to 5 times their dispersion limit (monolayers coverage). The characteristics of the calcination, total Mo+V loading and Mo/V atomic ratio is studied during propane oxidative conventional dehydrogenation (ODH and DH) reaction. The nature of surface sites is evaluated by methanol temperature-programmed reaction profiles with online mass spectrometry. The nature of the Mo, V, and mixed Mo-V oxide phases during reaction is evaluated by Raman spectroscopy during propane ODH and DH reactions with simultaneous activity measurement (operando Raman methodology).

228.

MICRO-CANTILEVER DEFLECTION: A TOOL FOR CHARACTERIZING POLYMER BRUSH PROPERTIES AND BIOMOLECULAR RECOGNITION EVENTS.

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The deflection of micro-cantilevers is surprisingly sensitive in detecting molecular recognition mediated binding of proteins and conformational changes in polymer brushes. Here we present two applications where we have made use of cantilever deflection measurements. In the first application we show that the deflection of cantilevers decorated with stimulus-responsive polymer brushes offers a simple way to sense changes in temperature, pH and salt concentration of a solvent, promising great potential for sensing applications in microfluidic devices. Furthermore, we show that these measurements, combined with measurements of cantilever resonance frequency shifts that result from added mass, provides simple means to determine brush properties, such as grafting density and molecular weight. In the second application, we show that deflection measurements sensitively detect the specific binding between human immunodeficiency virus -1 envelope protein gp120 and its binding receptor A32. Our results show that cantilever deflection is quite sensitive to binding events between the two proteins and suggest that the use of the deflection measurements offer an efficient way to detect molecular recognition events.

229.

NOVEL AFM METHOD TO DISTINGUISH HYDROPHOBIC AND HYDROPHILIC PARTS ON A SURFACE WITHOUT TIP FUNCTIONALIZATION.

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Atomic Force Microscopy (AFM) has been widely used to characterize the morphology of various organic samples with high resolution. Unfortunately,

topological information is often not enough to understand the real chemical nature of these samples. We introduce here a new method for imaging self-assembled monolayers based on electrostatic driven phase imaging in tapping mode AFM. It is known that phase images reflect the dissipative component of the mechanic response of the probed sample. By applying an electric field we deactivate, only in the polar parts, some of the dissipative channels that generate the mechanical response, thus producing a localized field-induced phase-shift. Consequently, we distinguish polar from apolar parts in a monolayer without chemically coating the AFM tip. A quantitative analysis of the phase shift as a function of applied bias will be discussed. Also, it will be shown how to locate the conductive channel in a photosynthetic protein (PS I).

230.

AMYLOSE ELASTICITY DEPENDS ON THE SOLVENT DIELECTRIC CONSTANT.

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Amylose is a polysaccharide composed of alpha-D-glucopyranose units connected by 1,4 linkages. AFM stretching experiments on single amylose chains in aqueous media showed that its elasticity is governed by force-induced chair-boat transitions, which produce a characteristic plateau feature in the force-extension relationship. Here we examine the elasticity of amylose in various solvents with the dielectric constant varying from 3 to 80. We report that the plateau feature is greatly reduced and the shape of the force-extension curve changed in the solvents with a low dielectric constant, as compared to water. To clarify the mechanism of this effect we carried out 1-microsecond Steered Molecular Dynamics calculations of the stretching of amylose in implicit solvents with low dielectric constants. We find that these solvents strengthen the inter-residue hydrogen bonding and the networks of these bonds modulate amylose elasticity by shifting the chair-boat transitions to higher forces. Supported by the NSF.

231.

EXAMINATION OF BACILLUS SPORE SURFACES BY THE ATOMIC FORCE MICROSCOPY.

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Spores produced by Bacilli are encased in a proteinaceous multilayered coat and, in some species including *Bacillus anthracis*, further surrounded by an exosporium. We have used atomic force microscopy (AFM) to examine the surfaces of wild type *B. subtilis*, *B. cereus* and the Sterne strain of *B. anthracis*. This analysis revealed that the coat surfaces are encircled by a series of ridges, most of which were oriented along the long axis of the spore. The structures of these ridges differ sufficiently between species to permit species-specific identification. These ridges disappear upon spore germination, suggesting they are formed early in spore formation. AFM analysis of a set of *B. subtilis* coat protein gene mutants revealed three coat proteins, CotA, CotB and CotE, with novel roles in coat ridge pattern formation. These results are consistent with the view that the coat is a dynamic structure that accommodates changes in spore volume.

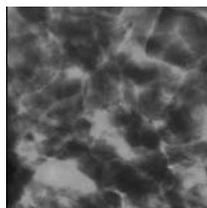
232.

MEASURING MICROELASTIC PROPERTIES OF STRATUM CORNEUM.

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The mechanical properties of stratum corneum (SC) were investigated by probe microscopy. Nano-indentation was used to measure the elastic modulus of SC at varying depths through the use of an atomic force microscope (AFM) as well as a nano-indentor (Hysitron Triboscope). Experiments were conducted with different indentation probes at different force ranges to reveal the effects of indenter geometry and indentation depth on the measured elastic modulus. Furthermore, visco-elastic properties of dry and wet SC were studied by a

nano-dynamic mechanical analyzer (nano-DMA). Results obtained by the three different techniques are compared and discussed.



233.

PROBING THE MEMBRANE PROTEINS ON LIVING CELLS BY THE ATOMIC FORCE MICROSCOPY. *Rong Wang, Chada V. Gopal Reddy, Krystyna Malinowska, and Nick Menhart, Department of Biological, Chemical and Physical Sciences, Illinois Institute of Technology, Life Sciences Building, R 348, 3101 Dearborn St., Chicago, IL 60616, Fax: 312-567-3494, wangr@iit.edu*

Living functions in biological systems are mediated by ligand-receptor interactions. These interactions are in turn governed by protein association and protein distribution. In neural cells, nerve growth factor (NGF) binds to its cell surface receptor TrkA to initiate the survival signal. We have used the NGF-TrkA specific interaction as a probe to identify TrkA on living PC12 cells by the atomic force microscopy (AFM). An NGF modified AFM tip was used to perform force volume (FV) imaging, generating a 2D force map to illustrate the distribution and association of TrkA on cell membrane. It was found that TrkA is highly aggregated at local regions of the cell. This unique protein association may be required to promote its function as a receptor of NGF. The methodology we developed in this study can be adapted by other systems, thus provides a general tool of investigating protein distribution in its natural environment.

234.

NEW NANOCOMPOSITE MATERIALS FROM MICROEMULSIONS. *Liehui Ge, Swapnil Bondre, Danai Mudzudzu, Bill Mata, and John Texter, College of Technology, Eastern Michigan University, Ypsilanti, MI 48197, liehui.ge@emich.edu, jtexter@emich.edu*

Radical chain polymerization in microemulsions has been found useful for producing latexes from oil-in-water microemulsion, hydrogel latexes from reverse microemulsions, and for producing microporous materials from bicontinuous microemulsions. A challenge in all three of these microemulsion systems has been to find reaction conditions and microemulsion formulations and compositions that enable the capture of the nanoscopic length scales present in the respective microemulsions before polymerization. Several reported approaches provide empirical factors that seem to promote the capture of nanoscale structure in microemulsion systems. These are investigated in producing copolymers of methyl methacrylate and 2-ethylhexyl methacrylate nanocomposites that contain 0-15% w/w water. Various comonomers and polymerizable surfactants are found to promote resistance to microphase separation during polymerization. Some of these nanocomposites retain their optical transparency while being polymerized with thermal initiation at 70°C. Markedly improved ignition resistance and fire retardancy are exemplified by many of these systems. Thermal studies indicate much of the incorporated water is non-freezable or is frozen only after significant freezing point depression. Much of this water appears to be captured in droplets only tens of nanometers in diameter. These variations in entrapped water physical state affect transparency and other transport and mechanical properties, including opacity to visible light after polymerization. Heat transport and compositional components such as water and surfactant dramatically affect ignition and combustion resistance.

235.

COMPARISON IN THE COATING OF Mg(OH)₂ ON MICRON-SIZED AND NANOSIZE Nb₂O₅ PARTICLES. *Hongyu Luo, Wan Y. Shih, and Wei Heng Shih, Department of Materials Science and Engineering, Drexel University, 31st and Market St, Philadelphia, PA 19104, Fax: 215-895-6760, hl59@drexel.edu*

Using Mg(OH)₂ coating on Nb₂O₅ particles as a model system, the effect of core particle size and that of aging on coating in an aqueous environment were

investigated. Specifically, two Nb₂O₅ particle sizes were used in this study: micron-sized commercial Nb₂O₅ powder and 17 nm synthesized Nb₂O₅ particles. Coating of Mg(OH)₂ on Nb₂O₅ was carried out by precipitating Mg(OH)₂ from magnesium nitrate in an aqueous Nb₂O₅ suspension. The coating behavior of Mg(OH)₂ on Nb₂O₅ was examined with optical microscopy, zeta-potential measurements, and local chemical analysis by energy dispersion spectroscopy (EDS). The results showed that the size of Nb₂O₅ plays an important role in the coating behavior of Mg(OH)₂. Optical micrographs, zeta potential measurements, as well as local EDS analysis all indicated that coating Mg(OH)₂ on micron-size Nb₂O₅ particles was easier than on nanometer-sized Nb₂O₅ particles. We attribute the difficulty in coating Mg(OH)₂ on nanometer-sized Nb₂O₅ to the enhanced dissolution of Mg(OH)₂ by the nanometer particle size as a result of the Kelvin effect. Aging improved the coating on micron-sized Nb₂O₅ but did not exhibit significant improvement in the Mg(OH)₂ coating on nano-size Nb₂O₅ particles. It is likely that aging modified the coating behavior of Mg(OH)₂ on Nb₂O₅ via a dissolution-reprecipitation mechanism.

236.

COMPLEX GLASSES: EXTENDING THE SCIENCE OF COMPLEX FLUIDS TO THE SOLID STATE. *Carlos C. Co, Chia Chi Ho, and Feng Gao, Department of Chemical and Materials Engineering, University of Cincinnati, 497 Rhodes Hall, Cincinnati, OH 45221-0012, Fax: 513-556-3473, carlos.co@uc.edu*

Usually, microemulsions and complex fluids are liquid mixtures of surfactant, water, and/or oil that self-assemble to form a variety of microstructures. This talk will present a new class of microemulsions and complex glasses that comprise of surfactant, oil, and sugar with practically no water. These mixtures form true glasses at ambient temperatures and are optically transparent and brittle even though they contain up to 50 vol% liquid oil. There are wide ranging applications of these complex glasses including encapsulation, as templates for reactions, and controlled crystallization. The nanostructure of bicontinuous microemulsion glasses, for example, are robust enough to hold up against the thermodynamic forces that result from polymerization. Thus, polymerization does not lead to phase separation.

237.

PHASE DIAGRAM VISUALIZATION AND REAL-TIME WORM-SPHERE DYNAMICS OF A CHARGED DIBLOCK COPOLYMER. *Yan Geng, Fariyal Ahmed, Nishant Bhasin, and Dennis Discher, Department of Chemical Engineering, University of Pennsylvania, 112 Towne Building, Philadelphia, PA 19104, geng@seas.upenn.edu, fariyal@seas.upenn.edu*

Giant vesicle and worm-like micelle phases of a charged diblock copolymer in water are systematically visualized by fluorescence microscopy to reveal aggregate stability and dynamics. At low pH and high salt (NaCl or CaCl₂), the polybutadiene-polyacrylic acid diblock (PBD107-PAA45) has a charged corona that is sufficiently screened to give bilayers in isolated vesicles as well as high order vesicle assemblies. With decreasing salt and at near neutral pH, intracoronary repulsion drives a transition to multi-branched cylinders and highly stable worm-like micelles that are sufficiently thin to thermally flex on supramolecular length scales. In vanishing salt and more basic conditions, the worm micelles shrink in length to spherical micelles seen in AFM. This transition occurs within seconds in Na and within minutes in Ca, consistent with phase diagrams showing that Ca is 5-10-fold more potent than Na in stabilizing all morphologies.

238.

LIGHT SCATTERING FROM AQUEOUS SOLUTIONS OF CETYL-TRIMETHYLAMMONIUM TOSYLATE. *Gary D. Patterson¹, Zhenyu Gu¹, Lynn M. Walker², My Hang Truong², and Simon Tam¹. (1) Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, Fax: 412-268-6897, gp9a@andrew.cmu.edu, (2) Department of Chemical Engineering, Carnegie Mellon University*

Static and dynamic light scattering in both the polarized and depolarized mode have been studied from aqueous solutions of cetyl-trimethylammonium tosylate (CTAT) from below the critical micelle concentration (0.26mM) to above the critical rod concentration (2mM). Aqueous salt solutions of NaCl and sodium tosylate have also been examined to establish the intrinsic ion pair diffusion coefficients for these ion pairs. Micelles are detected at all concentrations. There are even rodlike micelles present at 0.13 mM, as well as spherical micelles and

short rodlike structures, although scattering by CTAT ion pairs dominate the intensity. The distribution of micellar structures changes as the concentration is increased until wormlike micelles dominate the scattered intensity. Depolarized scattering was carried out on 11mM solutions and established that structures with axial ratios in the range from 0.05 to 0.005 were present.

239.

SHEAR AND EXTENSIONAL RHEOLOGY OF AQUEOUS CETYLTRIMETHYLAMMONIUM P-TOLUENE SULFONATE SOLUTIONS.

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Solutions of cetyltrimethylammonium p-toluene sulfonate (CTAT) in water exhibit a pronounced shear thickening phenomenon in a specific concentration range (0.1-0.8%) when they are subjected to simple shear flows, as a consequence of flow-induced self-assembly of wormlike micelles. In this work we explore the behavior of these solutions in purely extensional flows (opposed jets) and complex flows (porous media). Results show that a strong elongational flow field (opposed-jets) does not lead to extension thickening, since the extensional flow prevents and/or destroys micellar association. In flow through a porous medium, a substantial increase in apparent viscosity is observed beyond a critical apparent shear rate, which surpasses increases observed in simple shear flows. This is explained as the result of a synergistic effect of shear and relatively weak elongation on the solution microstructure. Preliminary results using mixtures of CTAT with a high molecular weight poly(ethylene oxide) indicate that surfactant associations promote extension thickening, even in opposed-jets flow.

240.

MEASURING AND MODELING WEAK ADHESION BETWEEN DNA-GRAFTED COLLOIDS. **John C. Crocker¹, Paul Biancaniello², and Anthony J. Kim¹.** (1) *Dept. of Chemical and Biomolecular Engineering, University of Pennsylvania, 220 S. 33rd St., Philadelphia, PA 19104, jcrocker@seas.upenn.edu*, (2) *Dept of Physics and Astronomy, University of Pennsylvania*

We report direct measurements of the specific interactions between two colloidal particles due to the hybridization of grafted single-stranded DNA molecules. The measurements are carried out with a line optical trap and high resolution image centroiding. The observed potentials of mean force are in quantitative agreement with first principles models of entropic repulsion, DNA thermodynamics and mass action reactions of spatially heterogeneous species. The result is a chemically specific, or programmable, weak adhesion which can be engineered a priori and temperature tuned. We will discuss the model in detail, along with its implications for more biological ligand/receptor adhesion systems.

241.

SELECTIVE OXIDATIVE ACTIVATION OF SHORT CHAIN ALKANES: FROM SUPPORTED VANADIA TO MULTICOMPONENT BULK MIXED OXIDES CATALYSTS. **J.M. López Nieto,** *Instituto Tecnología Química, Universidad Politécnica Valencia, Avda. Los Naranjos s/n, 46022-Valencia, Spain, Fax: 0034-96-3877809, jmlopez@itq.upv.es*

V-containing materials have been proposed as active and selective catalysts in the selective oxidative transformation of C2-C4 alkanes to the corresponding olefins, oxygenates and nitriles. Vanadium ions have been proposed as the active sites in the oxidative activation of short chain alkanes, although the coordination, and the environment strongly influence both the catalytic activity and the nature of reaction products. This paper presents a comparative study on the catalytic behaviour of V-containing catalysts, i.e. supported vanadium oxides, V-containing microporous/mesoporous materials, metal vanadates and multi-component bulk Mo-V-Te(Sb)-Nb mixed metal oxides. The influence of both the catalyst structure (including the V-coordination and V-environment) and the physico-chemical properties (especially redox and acid-base characteristics) on

their catalytic behaviour in the selective oxidation of paraffins and alkenes is discussed. In addition, the influence of the incorporation of metal oxide promoters on the selectivity to partial oxidation products is also presented.

242.

SOLUTION CHEMISTRY OF MOVTE SYSTEMS: RELEVANCE OF PRECURSORS. **Robert Schlogl¹, Abd Hamid Sharifah Bee², Dirk Niemeyer¹, Olaf Timpe¹, and Rubia Idris².** (1) *Dep. of Inorganic Chemistry, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany, acsek@fhi-berlin.mpg.de*, (2) *CombiCat Centre, University of Malaya*

The synthesis of MMO systems that are powerful catalysts in selective oxidation of propane to oxygenates is a highly non-reproducible task as has been recently disclosed by several controversial publications in the open and patent literature.

A key issue is the application of intrinsically unstable precursor solutions that prevent the system to be generated from an atomically disperse state. The consequences are microheterogeneities on several length scales.

Chemical and instrumental analytical data will be used to demonstrate the decisive effects of choosing starting conditions such as pH, temperature, concentration and counterions of components. In-situ Raman and UV-VIS data were used to probe the complex formation in solution prior to precipitation. Procedures for more reproducible synthesis strategies will be discussed. The suitability of powder X-ray diffraction as a lead tool in synthesis is questioned in the light of RAMAN and TEM data on highly active systems.

243.

PROPANE AND ISO-BUTANE OXIDATIONS OVER MIXED OXIDE-TYPE AND HETEROPOLY-TYPE MO-V-O CATALYSTS. **Wataru Ueda, Damien Vitry, and Masahiro Sadakane,** *Catalysis Research Center, Hokkaido University, N21-W10, Kita-ku, Sapporo 001-0021, Japan, Fax: 81-11-706-9163, ueda@cat.hokudai.ac.jp*

Catalytic performance of mixed oxide-type Mo-V-Te-Nb-O and heteropoly-type Cs-P-Mo-V-O was compared in gas-phase selective oxidations of propane and iso-butane. It was found that the mixed oxide catalyst was highly active and selective for the propane oxidation to acrylic acid but less active for the iso-butane oxidation, while the heteropoly-type catalyst showed better performance for the iso-butane oxidation to methacrylic acid than for the propane oxidation. The difference depending on the structural type of the Mo-V-O based catalysts is discussed in terms of acid-base property, role of added water, activation mechanism of alkanes, and adsorption state of possible intermediates.

244.

NOVEL MESOSTRUCTURED MIXED NB-M (M= V, MO, AND SB) OXIDES FOR OXIDATIVE DEHYDROGENATION AND AMMOXIDATION OF PROPANE. **Li Yuan,** *Department of Chemical & Materials Engineering, University of Cincinnati, 678 ERC, Cincinnati, OH 45221, yuanli@email.uc.edu*, and **Vadim V. Gulians,** *Department of Chemical Engineering, University of Cincinnati*

Mesoporous mixed metal oxides are highly promising for applications in selective oxidation catalysis because of their tunable "bulk" and surface compositions, variable metal oxidation states, high surface areas, as well as large and uniform pore sizes. In particular, vanadium, molybdenum, antimony and niobium-based mixed oxide phases are very attractive for selective oxidation and ammoxidation of lower alkanes, such as propane. However, preparation of thermally stable mesoporous mixed metal oxides still remains a challenging task. We have recently reported novel mesoporous mixed vanadium-niobium oxides, which displayed good thermal stability up to -500°C and interesting catalytic properties in propane oxidative dehydrogenation (ODH). In this paper we describe synthesis and physicochemical characterization (pore analysis, XRD, SAXS, Raman, ICP, XPS, etc.) of novel mesoporous Nb-M (M=V, Mo and Sb) oxides obtained in the presence of nonionic block copolymers. We further report catalytic performance of these novel metal oxide phases that bridge the gap between bulk dense and supported metal oxides for two model reactions, namely propane ODH and propane ammoxidation. We then compare structural, compositional and catalytic characteristics of these novel oxides with those reported in the catalysis literature for the bulk and supported metal oxides with similar chemical compositions.

245.

ROLE OF SITE ISOLATION AND PHASE COOPERATION IN SELECTIVE LIGHT PARAFFIN (AMM)OXIDATION CATALYSIS. *Robert K. Grasselli, Center for Catalytic Science and Technology, University of Delaware, Newark, DE DE 19716, grasselli@cup.uni-muenchen.de, Arne Andersson, Department of Chemical Engineering, University of Lund, Douglas J. Buttrey, Department of Chemical Engineering, University of Delaware, James D. Burrington, The Lubrizol Corporation, Claus G. Lugmair, Symyx Technologies Inc, and Anthony F. Volpe Jr., Heterogeneous Catalysis, Symyx Technologies*

The concepts of site isolation and phase cooperation will be discussed for the MoVNbTeO system, which is an effective catalyst in the selective oxidation of propane to acrylic acid and ammoxidation to acrylonitrile. This system is comprised of at least two crystalline phases, orthorhombic Mo₇.8V₁.2NbTe_{0.94}O_{28.9} (M1) and pseudo-hexagonal (Mo₄.67V₁.33Te_{1.82}O_{19.82}) (M2). We have recently succeeded to prepare essentially pure M1 and M2 phases. The M1 phase is the key paraffin activating and ammoxidation catalyst, and is by itself fully capable of transforming propane to acrylonitrile. The M2 phase is incapable of propane activation, lacking V⁵⁺ sites, but is a better, propylene to acrylonitrile catalyst than the M1 phase since it possesses a higher concentration of Te⁴⁺ sites. The so attained phase cooperation or symbiosis between the two phases occurs only if the two phases are finally divided, thoroughly mixed and in micro-/nano-scale contact with each other.

246.

DESIGN OF FUNCTIONAL MATERIALS: FROM NANOSTRUCTURED HYBRID MATERIALS TO HIERARCHICAL STRUCTURES. *Clément Sanchez, Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, . 4, Place Jussieu, Tour 54, 5e, Paris, Cedex 05, France 75252, France, Fax: 33 1 44 27 4769, clems@ccr.jussieu.fr*

Sol-gel derived hybrid nano-composites materials can be obtained either through hydrolysis and condensation reactions of functional metal alkoxides or through the assembly of well defined nanobuilding blocks. The properties that can be expected for such materials of course depend on the chemical nature of their components but also on the extend and the nature of their interface. This interface can also be tuned with or without templates to built nano-structured hybrids or even nanostructured metallic oxides. The control of the surface properties of the inorganic nano-building bricks by using nucleophilic groups carried by texturing agents triggers the obtention of a given nano-phase. Considerable effort is being currently directed to the obtention of nanostructured oxides. The use of ordered lyotropic phases as templating agents (surfactants, organogels, bio-polymers), leading to a mesoscopically ordered hybrid precursor. allow the obtention of long-range nanostructured hybrid or oxide phases shaped as bulks or films. Some examples concerning the design of hybrid materials made by using, metal alkoxides precursors or nano-building bricks, to create mesoscopically ordered phases will be presented together with some of our first results concerning materials having hierarchical structures.

247.

MESOPOROUS MOLECULAR SIEVE BASED NANOCOMPOSITES. *James Vartuli, Corporate Research, ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, NJ 08801, Fax: 908-730-3031, Jim.C.Vartuli@ExxonMobil.com*

The discovery of mesoporous molecular sieves offered a well-defined porous material for the formation of organic/inorganic composites. This talk will be a review of the many and varied methods of synthesizing nanocomposites from these molecular sieves. The initial examples were provided by using either the as-synthesized samples that retained the organic template or by post-functionalization utilizing the silanol groups within the pore channels. Each class of materials exhibited unique sorption properties compared to the inorganic counterpart. More recently researchers have been able to synthesize directly organic/inorganic composite materials. Applications of these novel materials will also be discussed.

248.

PREPARATION OF MESOPOROUS METAL OXIDE PARTICLES USING MOLECULAR ASSEMBLIES FORMED AT MIXED SURFACTANT SYSTEM AS TEMPLATES. *Taku Ogura, Takahiro Ohkubo, Hideki Sakai, and Masahiko Abe, Faculty of Science and Technology, Tokyo University of Science, 2641, Yamazaki, Noda, Chiba 278-8510, Japan, Fax: +81-4-7122-1442, j7203621@ed.noda.tus.ac.jp*

Mesoporous materials have found great utility as catalysts and adsorbents because of highly ordered pore structure with high specific surface area. There have been a lot of studies about control of pore size by controlling alkyl chain length of the surfactants. Aqueous mixtures of surfactants have been reported to form various molecular assemblies including rod-like micelles and vesicles. Use of these molecular assemblies as reaction templates would allow us more dynamic control of the pore size and structure. In this study, mesoporous metal oxide particles are prepared with the assemblies formed at surfactant mixtures as the templates. Silicon dioxide and titanium dioxide particles could be prepared by hydrolysis and condensation reactions of each alkoxide in aqueous mixtures of cationic and anionic surfactants with various compositions. Aggregation state of the surfactant assemblies strongly affects the pore size and structure and their precise control is possible by tuning the composition.

249.

SYNTHESIS AND CHARACTERIZATION OF BIFUNCTIONAL HYBRID ORGANIC-INORGANIC CATALYSTS. *John D. Bass, Department of Chemical Engineering, University of California at Berkeley, MC 1462, Fax: 510-642-4778, johnbass@uclink.berkeley.edu, and Alexander Katz, Department of Chemical Engineering, University of California, Berkeley, 201 Gilman Hall, MC-1462, Fax: 510-642-4778, katz@cchem.berkeley.edu*

The synthesis and characterization of bifunctional acid-base catalysts consisting of aminosilane active sites grafted onto the surface of hydrophilic silica are presented. We demonstrate the vital role of surface acidity played by silanol groups in cooperating with base catalytic sites, using the Knoevenagel condensation of aldehydes and activated methylene compounds as model reaction systems. These systems are compared and contrasted with several control catalysts, which, due to their methods of preparation, can involve only monofunctional catalysis at the active site. A mechanism for the significant increase in catalytic activity that is observed in the bifunctional catalyst systems is presented. This information is used for the design and synthesis of second generation optimized base catalysts, relying on a paradigm of incorporating grafted molecular receptors that can act as adsorption centers and decrease the activation barrier for the transition state on the catalyst surface.

250.

EFFECT OF POLYMER MATRIX PROPERTIES ON THE IN SITU SYNTHESIS OF IRON OXIDE NANO-PARTICLE/POLYMER COMPOSITES. *Nily Dan, Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104, Fax: 215-895-5837, dan@cbis.ece.drexel.edu, and Rina Tannenbaum, School of Materials Science*

In situ-synthesis of iron-oxide nanoparticles is used to produce uniformly dispersed polymer/metal nanocomposites. The metal nanoparticles are uniform in size, and their rate of formation, morphology and dimension can be controlled through selection of the polymeric matrix.

251.

UNDERSTANDING CHEMICAL CONTROL OF FILM MORPHOLOGY IN HIGHLY ORDERED SURFACTANT TEMPLATED MESOPOROUS SILICA COMPOSITES. *Erik K. Richman and Sarah H. Tolbert, Department of Chemistry and Biochemistry, UCLA, 607 Charles E Young Dr East, Campus Box 951569, Los Angeles, CA 90095-1569, Fax: 310-206-4038, erichman@chem.ucla.edu*

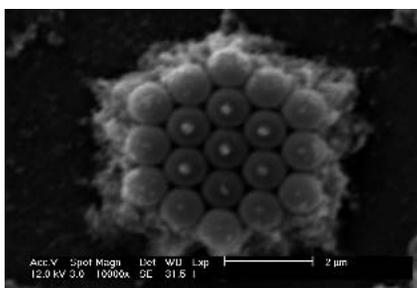
Self-organization of surfactants and silica can be used to produce highly periodic mesoporous thin films. Experiments have shown that such assembly is robust, with the same nanoscale architecture produced despite wide variations in acid content, dip-casting speed, or reagent concentrations. By contrast, the effect of synthetic variables on the large-scale film morphology is unknown. In this work, we use scanning probe microscopy to show how synthetic conditions can be used to systematically change film morphology from large isotropic ribbon meshes to small domain particles aligned with the drying wave of the dip-cast. Specifically, we find that film morphology depends on the acid content

of the solution, with higher acid solutions showing more effects from the anisotropic drying wave. We also find that films cast from higher-concentration solutions and higher dip-cast speeds are more isotropic. Our results indicate that film morphology can be chemically controlled and used for anisotropic material design.

252.

MAGNETICALLY PROGRAMMABLE ASSEMBLY OF MICRO- AND NANO-PARTICLES. Benjamin B. Yellen and Gary Friedman, *Electrical and Computer Engineering Department, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, Fax: 215-895-0280, bby22@drexel.edu*

We investigate the possibility of using magnetization recorded or otherwise patterned on a surface to control assembly of particles in colloidal suspension. Two types of colloidal solutions are considered. One involves dispersion of superparamagnetic beads in otherwise non-magnetic fluid (water). The other involves non-magnetic micro- and nano-beads dispersed together with superparamagnetic nano-particles (ferrofluid). Using patterns of magnetization on surfaces together with external uniform magnetic fields, we will demonstrate that it is possible to programmably assemble various patterns of magnetic and non-magnetic particles on surfaces. An example is shown in the figure.



253.

MAGNETIC FRACTIONATION AND ALIGNMENT OF SINGLE WALL CARBON NANOTUBES. Mohammad F. Islam, Daniel E. Milkie, Omar N. Torrens, Arjun G. Yodh, and Jay M. Kikkawa, *Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, islam@physics.upenn.edu*

We study mechanisms of single wall carbon nanotube (SWNT) alignment in a magnetic field. Through magnetic fractionation, we create SWNT suspensions with varying quantities of magnetic catalyst particles. The degree of tube alignment in magnetic fields up to 9 Tesla is quantified using polarized optical absorbance anisotropy. Continuous measurements of the nematic order parameter of these suspensions in variable magnetic fields provides a way to identify the origin of magnetic torques giving rise to tube alignment. Initial data suggests a transition from catalyst-driven to tube-anisotropy driven orientation as the catalyst fraction is reduced. We relate these results to observations of tube aggregation. This work supported by NSF through DMR-0203378, DMR-079909 and DGE-0221664, NASA through NAG8-2172, DARPA through N00015-01-1-0831, and SENS.

254.

ELASTIC INTERACTIONS AND THE MANIPULATION OF COLLOIDAL WIRES IN A NEMATIC SOLVENT. Clayton Lapointe¹, Anne Hultgren¹, Daniel M. Silevitch², E. Jim Felton¹, Daniel H. Reich¹, and Robert L. Leheny¹. (1) *Department of Physics and Astronomy, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218, clapoint@pha.jhu.edu, leheny@pha.jhu.edu*, (2) *James Franck Institute, University of Chicago*

Nematic liquid crystals, fluids comprised of rod-like molecules, are characterized by an alignment of the long axes of the molecules along a particular direction. Colloidal particles suspended in a nematic can introduce distortions in this alignment due to anchoring of the nematic orientation at the particles' curved surfaces. The tendency to minimize the elastic energy associated with these distortions leads to forces on the particles. For aspherical particles in a nematic, these forces include orientation-dependent torques. In this talk, I describe experiments using magnetic nanowires suspended in the room temperature nematic 5CB in which we quantify these forces. Such elastic forces can also be used to manipulate submicron-scale particles. As an example, I describe

measurements in which a controlled spatial variation in nematic orientation, specifically a twisted nematic, converts the torque on a wire to a translational force that levitates the wire to a specified height.

255.

SELF-DEGRADABLE POLY(ETHYLENE OXIDE)-POLYCAPROLACTONE COPOLYMER WORM MICELLES. Yan Geng, Young Hoon Kim, Fariyal Ahmed, and Dennis Discher, *Department of Chemical Engineering, University of Pennsylvania, 112 Towne Building, Philadelphia, PA 19104, geng@seas.upenn.edu, fariyal@seas.upenn.edu*

Giant and flexible worm micelles were made from Poly(ethylene oxide)-Polycaprolactone diblock copolymers: PE044- α -PCL24 (OCL1) and PE0110-PCL58 (OCL3), by using a cosolvent hydration method. The OCL worm micelles shrink in length with time, until completely break down to spherical micelles. HPLC (GPC, RI detector) analysis on the OCL worm micelle shortening with time demonstrates that the OCL worm micelle shortening is caused by hydrolysis of the hydrophobic polycaprolactone block. The degradation mechanism is chain-end scission dominated, producing 6-hydroxycaproic acid monomer as the overwhelming degradation product accumulated with time. About 40-50% of caprolactone is OCL was hydrolyzed to break down the worms completely to spherical micelles. The degradation rate decreases with lower temperature, higher molecular weight and neutral pH. Based on evaluation of its degradation rate at physiological conditions (PH=7.4, 37.5 $^{\circ}$ C for outside cell and PH=5, 37.5 $^{\circ}$ C for inside cell), higher molecular weight OCL3 shows potential as self-degradable long-circulating drug delivery vehicle.

256.

DIRECT MEASUREMENT OF POLARIZED ABSORPTION CROSS-SECTION OF SINGLE WALL CARBON NANOTUBES. Mohammad F. Islam, Daniel E. Milkie, Charles L. Kane, Arjun G. Yodh, and Jay M. Kikkawa, *Department of Physics & Astronomy, University of Pennsylvania, 209 S. 33rd Street, DRL, Philadelphia, PA 19104, islam@physics.upenn.edu, dmilkie@student.physics.upenn.edu*

We use a combination of polarized Raman scattering and linear optical absorption to infer optical absorption cross-sections of perfectly aligned laser-oven single-wall carbon nanotube ensembles for visible light co- and cross-polarized with respect to the nanotube axes. These data reveal a strong linear absorption anisotropy, and provide a rapid method by which linear absorption spectra can be used to quantitatively measure the orientation of dispersed nanotubes, even in strongly absorbing media for which Raman approaches are complicated by anisotropic re-absorption processes. Comparison with theory shows that local field depolarization plays a crucial role in affecting optical spectra of the nanotubes. This work supported by grants from the NSF, NSF IGERT, SENS, DARPA, and NASA.

257.

MOLECULAR WEIGHT DEPENDENCE OF THE ROTATIONAL DIFFUSIVITY OF RODLIKE POLYMERS IN NEMATIC SOLUTIONS. Aldo Acevedo and Annette D. Shine, *Chemical Engineering Department, University of Delaware, 150 Academy Street, Newark, DE 19716, Fax: 302-831-1048, acevedo@che.udel.edu*

The dynamics of rodlike polymer molecules in the nematic phase are controlled by the rotational diffusivity, D_r , which is highly sensitive to molecular weight. However, few experimental determinations of D_r for nematic polymer solutions have been made, because direct methods such as light scattering are ill-suited for use in these materials with complex supramolecular domain structures. We invoke Doi's theory of liquid crystalline polymer rheology to extract D_r from experimental measurements of the transverse Miesowicz viscosity. Miesowicz viscosities were measured for a series of poly(*n*-hexyl isocyanate) (PHIC) polymers at fixed dimensionless concentration in *p*-xylene, by orienting the director with an electric field. The rotational diffusivity of PHIC was independent of shear rate, and proportional to $M^{-5.21 \pm 0.84}$. This is in reasonable agreement with Doi theory, which predicts that D_r scales as $M^{-5}(\ln M)$ at fixed c/c^* . The experimental values of D_r were compared with theoretical values calculated *a priori* from molecular dimensions.

258.

QUASI-THERMODYNAMIC DESCRIPTION OF FLUIDIZED BINARY POWDERS.

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Equilibrated colloidal suspensions obey the local density approximation and thermodynamics; have osmotic properties, and obey Gibbs phase rule. Here, the properties of dry colloidal powders, not in a host solvent, but which are fluidized under gravity by mechanical vibrations, are investigated. Such fluidized systems are not in any real sense thermodynamic. Experimental observations, however, will demonstrate that fluidised powders can, in certain conditions, be described by quasi-thermodynamic laws. Computer simulations show that the obedience criterion is the amplitude of vibration should be less than the correlation length for interactions between particles. Then the conditions for equipartition of energy are obeyed. There follows a definition of quasi-thermodynamic properties of powders as functions of a granular temperature, and a granular pressure. Thermodynamics can predict whether excited powders prefer to be separate phases, or mixed. A very simple consideration of the mixing criteria of hard spheres that differ only in size, suggests that all powders will mix if vibrated at a sufficiently small amplitude and characteristic frequency. Consider a two-component powder A+B, then the criterion for the mixing process at equilibrium is that the excess Gibbs free energy of mixing should be negative. Pressure enhances mixing if the volume change is negative, and segregation it is positive. Increase in granular temperature, on the other hand, always favors mixing. Even the most difficult binary powders will mix with sufficient kinetic energy. These ideas have resulted in the discovery of an extraordinary phase behavior of binary powders in acoustic vibrations. The granular temperature is close to uniform, whereas the the pressure varies under gravity from zero at the top to the weight of the system at the bottom. The p-gradient can result in pure segregated phases above a homogeneously mixed phase. There are many potential applications.

259.

EVOLUTION OF LOCAL DYNAMICS IN AN AGING COLLOIDAL GLASS FORMED BY CHARGED, NANOMETER-SCALE DISKS.

Ranjini Bandyopadhyay¹, Dennis Liang¹, Matthew A. Borthwick², James L. Harden¹, Simon G. J. Mochrie³, and Robert L. Leheny¹. (1) Department of Physics and Astronomy, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218, Fax: 410-516-7239, ranjini@pha.jhu.edu, harden@jhu.edu, (2) Department of Physics, Massachusetts Institute of Technology, (3) Department of Physics, Yale University

We describe multispeckle x-ray photon correlation spectroscopy studies that determine the dynamic structure factor $f(q,t)$ of a colloidal glass formed by nanometer-sized, highly charged disks at scattering wave vectors q corresponding to interparticle length scales. The slow dynamics of the glass is characterized by a structure factor $f(q,t) \sim \exp[-(t/\tau)^b]$, where $b \sim 1.6$. The characteristic relaxation time τ increases with the sample age t_w as $\tau \sim t_w^\mu$ where μ is approximately equal to 2, and decreases with q as $\tau \sim q^{-x}$, where $x \sim 1$. Such a compressed exponential form of the dynamic structure factor with a characteristic relaxation time that varies inversely with q is consistent with a recent model by Bouchaud and Pitard that describes relaxation in an elastic medium in terms of strain from random, local structural rearrangements. The apparent contrast measured from $f(q,t)$ further implies caged motion of the particles at short times, with an average excursion distance that decreases significantly with sample age.

260.

OXIDATIVE DEHYDROGENATION OF PROPANE OVER METAL OXIDES OF REDOX AND NON-REDOX TYPE.

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The oxidative dehydrogenation of light paraffins to their olefins is still of great practical interest. For this reaction, two types of catalytic materials exist, which

differ in the nature of surface-oxygen species taking part in the hydrocarbon activation: (1) Redox-type metal oxides make lattice oxygen available which is responsible for the formation of selective and non-selective reaction pathways leading to the olefins and carbon oxides. (2) Adsorbed oxygen species are active species over non-redox-type materials including rare-earth and alkali-earth metal oxides. From a fundamental point of view, the present contribution deals with the oxidative dehydrogenation of propane (ODP) over different vanadium-based catalysts (redox-type materials). Particular attention is focussed on the understanding of the nature of the VOx species and their specificity for coordinating active oxygen species by using N2O or O2 as oxidizing agent. Catalytic materials of different VOx loading were characterised by XRD, EPR, UV-VIS, Raman and H2-TPR for identifying structural properties and for deriving insights into the distribution and reducibility of VOx species. For comparison, also non-redox-type catalysts consisting of samarium- and lanthanum-based oxidic materials are dealt with. In contrast to the redox-type catalysts, the latter materials have a better catalytic performance in the ODP reaction with a total yield of ethylene and propene of 31% while the redox-type catalysts are limited to about 18 %. In conclusion it can be stated that for redox-type catalysts weakly interacting MeOx species, in particular VOx are required.

261.

CATALYTIC OXIDATIVE CONVERSION OF ALKANES TO OLEFINS.

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Oxidative conversion of alkanes to olefins is currently of much interest due to the strong demand for olefins. Catalysts based on transition metal oxides with formal red-ox properties have been mostly studied and have not shown promise because re-adsorption of product olefins leads to total oxidation, i.e., olefins yields are usually below 30%. However, our recent studies on catalysts with no formal red-ox properties, for e.g. Li/MgO, reported olefin yields up to 55%. We have shown that Li is essential to yield olefins effectively and that [Li+O-] type active sites are involved. Activation of alkane takes place on the [Li+O-] site by splitting one C-H bond forming [Li+OH-] and an alkyl radical. This radical then undergoes chain propagation reactions in the gas-phase to selectively yield olefins. Thus, enhancement of these defect type concentrations is expected to improve the catalytic activity and olefin yields. High surface area, nano-scale mixed oxide clusters of Li/MgO offer the possibility to increase the [Li+O-] defect concentration. Aim of the current work is to design practical catalysts via stabilisation of the nano-scale oxide clusters and retainment of the high surface area under conditions typical for the oxidative conversion of alkanes. Currently we have been able to prepare high surface area Li/MgO clusters (250 m²/g, 5 nm particle size) by sol gel routes. Details of these studies will be discussed.

262.

FORMATION OF CARBONACEOUS SPECIES ON SUPPORTED CHROMIA CATALYSTS.

Sanna M.K. Airaksinen and A. O. I. Krause, Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FI-02015, Hut, Finland, Fax: 358 9 451 2622, airaksinen@polte.hut.fi, krause@polte.hut.fi

Chromia supported on alumina is widely used as catalyst in the dehydrogenation of light alkanes. However, the use of zirconia as the support has been reported to improve the performance of the catalyst. The disadvantage of both catalytic systems is deactivation during the dehydrogenation, which is presumably caused in part by deposition of carbonaceous species on the catalysts. In this study we have compared alumina- and zirconia-supported chromia catalysts. The formation of various carbon containing species on the catalysts was followed with in situ DRIFT spectroscopy. The measurements were carried out both as a function of temperature and of time. The surface species detected under isobutane at 580 °C included acetates and carbonates in addition to unsaturated and aromatic hydrocarbon species. Formates were stable only at lower temperatures. Based on the observations the differences between the two catalysts will be discussed.

263.

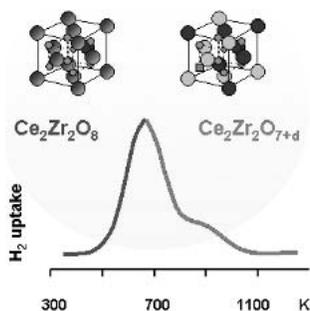
COMPARISON OF GAMMA-ALUMINA SUPPORTED MgO AND BULK MIXED MG-AL OXIDE AS SOLID BASE CATALYSTS. *D. E. Jiang¹, Biying Zhao², Xiaohua Huang², Huizhong Huang², Guangcheng Pan³, Guopeng Ran³, and Enze Min³.* (1) Department of Chemistry and Biochemistry, University of California, Los Angeles, Box 951569, Los Angeles, CA 90095-1569, Fax: 310-267-0319, djiang@chem.ucla.edu, (2) Institute of Physical Chemistry, Peking University, (3) Research Institute of Petroleum Processing, SINOPEC

MgO is a commonly used solid base catalyst, but it is difficult to achieve a high surface area for pure MgO. Using a support or mixing with another oxide are two common ways to increase the surface area. We here compare γ -alumina supported MgO and bulk-mixed Mg-Al oxide for their structure, basicity, and activity as solid base catalysts. We prepare γ -alumina supported MgO, based on the principle of spontaneous monolayer dispersion of oxides on high-surface-area supports, and we obtain bulk mixed Mg-Al oxide by calcining synthesized Mg-Al hydrotalcites. We characterize them with CO₂-TPD, XPS, XRD, BET, and surface extended energy loss fine structure (SEELFS). Finally, we compare their ability as a co-catalyst to convert mercaptans in jet fuel to disulfides. We find that although their base strengths are similar, γ -alumina supported MgO has a higher base site density, better pore size distribution, and a longer lifetime for mercaptan conversion than Mg-Al mixed oxide.

264.

PROMOTION OF REDUCTION IN Ce₂Zr₂O₈: THE PYROCHLORE STRUCTURE AS EFFECT RATHER THAN CAUSE? *Paolo Fornasiero¹, Tiziano Montini¹, Miguel A. Banares², Neil Hickey¹, Roberta Di Monte¹, Jan Kaspar¹, and Mauro Graziani¹.* (1) Chemistry Department, University of Trieste, L. Giorgieri, Trieste 34127, Italy, Fax: 39-040-5583903, pforneasiero@units.it, (2) CSIC-Institute of Catalysis

Ceria-zirconia mixed oxides have attracted widespread scientific interest in the fields of ceramics, catalysis (mainly three-way catalysts) and as potential electrolyte materials for solid oxide fuel cells (SOFCs). Promotion of efficient oxygen release under reducing conditions represents a key objective of research into these materials and, recently, formation of the pyrochlore phase has been implicated as a cause of improved redox properties. Based on in situ Raman spectroscopy, we report the formation of a pyrochlore Ce₂Zr₂O_{7+d} during low temperature reduction of the sample, thereby indicating that it is not necessary to first form this structure in the bulk before low temperature reduction of the material can be induced (Figure 1). Indeed, no direct correlation between the structure of our material and its redox properties was found. Instead, surface modification appears to be responsible for improved performances. In addition, we show that the redox properties can be tuned by altering the treatment conditions. More specifically, in addition to the well-established effect of treatment temperature, we show that reduction can be selectively influenced by changing the concentration of the hydrogen mixture used in prior treatments.

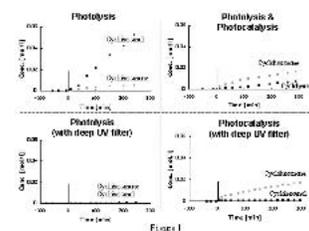


265.

SELECTIVE PHOTO-OXIDATION OF CYCLOHEXANE ON TiO₂: KINETICS AND ENGINEERING ASPECTS OF PHOTOCATALYTIC REACTION ROUTES. *Peng Du¹, Guido Mul², and Jacob A. Moulijn².* (1) DelftChemTech/Reactor and Catalysis Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, Netherlands, p.du@tnw.tudelft.nl, (2) Reactor and Catalysis Engineering, Delft University of Technology

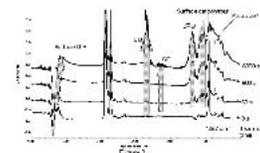
Heterogeneous photocatalysis with TiO₂ has been extensively investigated as a method to oxidize organic pollutants in water and air. However, relatively fewer studies were conducted regarding its utilities in organic synthesis. In this study

we investigate the photocatalytic cyclohexane oxidation on various catalysts. Cyclohexanol and cyclohexanone are the key products under experimental conditions. Comparing with photolysis, the presence of the photocatalyst enhances the selectivity of ketone over alcohol by a factor of 10 (fig.1) due to the strong adsorption of cyclohexanol on TiO₂.



The engineering aspects of photocatalytic oxidation of cyclohexane have been studied in a well-designed photocatalytic slurry reactor. Organic products, cyclohexylhydroperoxide and CO₂ were detected using different methods. Following parameters were varied: temperature, oxygen partial pressure, catalyst concentration and light intensity. Results will be presented and used to provide general recommendations for the design of photocatalytic reactors. In our opinion, the most prospective design should result in an integrated reactor with high catalyst loadings and high illuminated area. An internally monolithic reactor will fulfil these requirements.

A home-made FTIR vacuum reactor were applied to investigate the reaction kinetics spectroscopically (fig.2). Both CO₂ and CO are formed, indicating two kinds of surface carboxyl intermediates. The red-shift of the OH stretching at above 3500 cm⁻¹ reveals the surface modification during the photocatalytic oxidation of cyclohexane. Also an infrared band, centered at 1367 cm⁻¹, was observed for the catalytically active material. All these facts prove that this *in-situ* technique is very suitable for time-resolved analysis of short living species and reaction intermediates.



This general study of cyclohexane oxidation is used as a basis for our ongoing research on photocatalytic reactor design and applications. The authors would like to thank the Dutch Technology Foundation STW for financially supporting this research.

266.

ROUTE TO HIGH SURFACE AREA AND POROSITY IN CRYSTALS. *Omar M Yaghi, Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, MI 48109, Fax: 734-615-9751, oyaghi@umich.edu*

One of the outstanding challenges in the field of porous materials is the design and synthesis of chemical structures with exceptionally high surface areas. Until recently the highest surface area for a disordered structure was that of carbon (2,030 m²/g), and for an ordered structure was that of zeolite Y (904 m²/g). More recently we, and others⁶, have reported crystals of metal-organic frameworks (MOFs) with similar or somewhat higher surface areas. Despite this progress and the critical importance of high surface area to many applications involving catalysis, separation and gas storage, no strategy has yet been outlined to answer the question of what the upper limit in surface area for a material is, and how it might be achieved. Here we present a general strategy that has allowed us to realize a structure having, by far, the highest surface area reported to date. Specifically, we report on the design, synthesis and properties of crystalline Zn₄₀(BTB)₂ (BTB = 1,3,5-benzenetribenzoate), a new metal-organic framework (named MOF-177) with a surface area of 4,500 m²/g. We also show that MOF-177 combines this exceptional level of surface area with an ordered structure that has extra-large pores capable of binding polycyclic

organic guest molecules—attributes heretofore unrealized in one material. We expect such materials to provide means of storing and releasing gases such as hydrogen and methane into fuel cells.

267.

SOLID STATE COORDINATION CHEMISTRY OF METAL-ORGANIC/MOLYBDOPHOSPHONATE HYBRID MATERIALS. *Jon Zubieta, Eric M. Burkholder, and N. Gabriel Armatas, Department of Chemistry, Syracuse University, 111 College Place, Center for Science and Technology, Syracuse, NY 13244, Fax: 315-443-4070, jazubiet@syr.edu*

A building block approach, based upon phosphomolybdate clusters, organic tethers and secondary metal-organic subunits as design elements, allows the rational design of one-, two- and three-dimensional hybrid materials. The structural determinants include the tether length of the diphosphonate ligand, the coordination preferences of the secondary metal and the identity of the ligand to the secondary metal, as well as variables associated with the hydrothermal domain, such as temperature, pH and stoichiometries. Representative structures of general compositions $[M_2(\text{tpyprz})(\text{H}_2\text{O})_x]_n[\text{Mo}_7\text{O}_{24}(\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3)_m]$ ($M = \text{Co, Ni, Cu}$; tpyprz = tetra-2-pyridylpyrazine; $n = 1$ to 10) will be presented, and their TGA profiles, thermo-crystallography and magnetic properties will be discussed. The sorptive properties of selected materials will be presented.

268.

CHARGE-DRIVEN ASSEMBLY OF SILICA NANOPARTICLES AND SALT-BRIDGED POLYAMINE-AGGREGATES FORMING MICROSHELLS. *Rohit K. Rana¹, Vinit Murthy¹, and Michael S. Wong². (1) Department of Chemical Engineering, Rice University, 6100 Main St., MS-362, Houston, TX 77251-1892, Fax: 713-348-5478, rkrana@rice.edu, (2) Department of Chemical Engineering and Department of Chemistry, Rice University*

Assembly of nanoparticles by organic superstructures has been of recent interests to fabricate inorganic structures with controlled morphologies. In this work we describe a detailed mechanistic study on a self-assembly process that leads to the formation of silica microspheres utilizing nanoparticles as building blocks and polyamines as the structure-directing agent. In the presence of multivalent counter-anions, salt-bridging of polyamines generates structured aggregates. Then the silica nanoparticles driven by a charge-interaction assemble themselves surrounding these spherical aggregates forming microspheres within seconds under mild conditions (near neutral pH, ambient temperature and pressure). The microspheres thus formed have spherical morphology with an empty or polyamine-filled core depending upon the counterion used. The size of the microsphere can be controlled by varying the polymer chain-length or aging the solution of polyamine and counterion mixture for various times.

269.

RECENT ADVANCES IN THE SYNTHESIS OF F-METAL CONTAINING ORGANIC/INORGANIC HYBRID MATERIALS. *Christopher L. Cahill, Department of Chemistry, The George Washington University, 725 21st Street NW, Washington, DC 20052, cahill@gwu.edu*

Our efforts have recently focused on the synthesis of open-structured oxide and metal-organic-framework (MOF) materials containing f-metals (e.g. Ln^{3+} , U(V)/U(VI)). As such, we have succeeded in producing (hydrothermally) a number of U-oxide materials with topologies related to those of mineral structures. Further, controlled redox in this system gives rise to mixed valence U(V)/U(VI) materials— a rare example of a pentavalent uranium species owing to its tendency to disproportionate in solution.

On a separate front, synthesis of Ln-MOFs has proceeded by two novel routes: 1) the use of heterofunctional ligands to produce heterometallic frameworks and 2) the use of non-coordinating structure directing molecules in addition to the MOF 'linker' species to produce templated topologies. Presented will be a survey of recent results exemplifying these approaches, as well as the resulting thermal and luminescent properties of these materials.

270.

HOMOGENEOUS HYBRID MIXTURES OF POLYMERS AND INORGANIC SALTS AS PRECURSORS IN A NOVEL SYNTHETIC PATHWAY TO MULTIMETALLIC OXIDES. *François Rullens, Dept. of Chemistry, Chemistry of Inorganic and Organic Materials, Catholic University of Louvain, Place Louis Pasteur, 1/3, Louvain-la-Neuve B-1348, Belgium, Fax: 32-10-472 330, rullens@chim.ucl.ac.be, Andre Laschewsky, Division Water-Based Polymers and Colloids, Fraunhofer-Institut für Angewandte Polymerforschung, and Michel Devillers, Chemistry Dept, Chemistry of Inorganic and Organic Materials, Catholic University of Louvain*

A novel approach based on the use of hybrid mixtures between inorganic salts and functionalized polymer matrices is described as a promising alternative pathway to synthesize multimetallic oxides. This strategy is applied, in a catalytic context, to the preparation of simple Ni, Co, Mn and mixed Ni-Co and Mn-Co molybdates. For that purpose, polymers resulting from the association of monomers bearing carboxylic acid (maleic or maleamic acids) or amine moieties (diallylammonium or diallylamines with alkyl chains of different lengths) have been designed and synthesized. These soluble polymers stabilize the inorganic species generated in solution from $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{MoO}_4$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ under various pH conditions. Interactions between these species and the polymer matrices have been studied in solution (using UV-vis-NIR) as well as in the solid state (using XRD and DR-UV-vis). In many cases, homogeneous hybrid mixtures, exhibiting or not a supramolecular arrangement in the solid state, could be obtained in a given pH range. The thermal behaviour of these new catalysts precursors has been evaluated by TGA, and the corresponding simple or mixed oxides have been obtained upon calcination at 600°C. Characterization of the final materials by XRD and Raman spectroscopy indicates that the α as well as the β -phase of the molybdates is formed, depending on the metal composition and the polymer used. The Ni-Co and Mn-Co molybdates prepared appear to be solid solutions of the α and/or β phases of the simple NiMoO_4 , and CoMoO_4 and MnMoO_4 compounds.

271.

STUDY OF DROPLETS, ONE BY ONE, USING MICROFLUIDIC DEVICES. *D. A. Weitz, Dept. of Physics, Harvard University, McKay Laboratory, 9 Oxford Street, Cambridge, MA 02138*

Microfluidic devices offer the possibilities of precision control over fluid flow. They are typically used to control the flow of single fluids or mixtures of miscible mixtures. However, they also offer the potential of producing more complex fluid structures. This talk will discuss the use of microfluidic devices to produce and study droplets of one fluid in a second. The droplets can be produced and studied one by one, enabling precision control over the structure and make-up of each drop, and allowing the formation of new complex fluid structures.

272.

EFFECT OF SURFACTANTS ON DROP DETACHMENT: VISCOUS DROPS IN VISCOUS LIQUIDS. *Fang Jin¹, Nivedita Gupta², R. Balasubramaniam³, and Kathleen J. Stebe¹. (1) Department of Chemical & Biomolecular Engineering, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218, Fax: 410-516-6292, fjin1@jhu.edu, kjs@jhu.edu, (2) Department of Chemical Engineering, University of New Hampshire, (3) National Center for Microgravity Research on Fluids and Combustion, NASA John H. Glenn Research Center*

Drop detachment is of fundamental interest in understanding topological transitions, and of applied interest in the creation of dispersions or in microfluidics devices. When a viscous drop detaches in a viscous fluid, it evolves to form a distended drop which detaches via the rapid formation and pinching of a neck. Neck formation and pinch-off are self-similar, governed locally by the balance of capillary and viscous stresses. In creeping flow, this regime has been predicted by scaling arguments, verified in experiment and demonstrated using boundary integral simulations. Here, the effects of surfactants on drop pinch-off are studied in the low Reynolds number regime. Using a volume of fluid code with a front tracking scheme, we recover and extend prior results for surfactant-free interfaces. For insoluble surfactants, describing the surface tension with a surface equation of state which accounts for the upper bound on surfactant concentrations in a monolayer, we show that surfactants can alter the gross shape of a drop prior to neck formation, but that the necking dynamics retain the self-similar dynamics of the clean interface. For soluble surfactants with very

fast kinetics of surfactant exchange, the drop dynamics are indistinguishable from the clean case. For slower exchange kinetics, at sufficiently high concentration, new self-similar shapes emerge. Finally, regimes are identified in which the pronounced accumulation of surfactant in the neck region prevents it from contracting, and favors a transition from dripping to jetting modes.

273.

IN SITU FLUID STUDIES IN MULTI-WALLED CARBON NANOTUBES. *Yury Gogotsi¹, Maria Pia Rossi², Nevin Naguib¹, Haihui Ye¹, Almila G. Yazicioglu³, and Constantine Megaridis³.* (1) Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street, Bldg. 27-437, Philadelphia, PA 19104, gogotsi@drexel.edu, (2) Materials Science and Engineering, Drexel University, (3) Department of Mechanical and Industrial Engineering, University of Illinois at Chicago

The processes that govern fluid transport in pipes are well understood for diameters in the range of micrometers and above. As diameters diminish, the role of surface tension and capillarity vary. A basic understanding of such forces is urgently needed for the technological application of carbon nanotubes (CNT, 1-50 nm inner diameter) and nanopipes (CNP, 50-300 nm inner diameter). Liquid/vapor distribution in CNT, interaction of fluids with tube walls and the effect of hydrothermal treatment on the surface chemistry of CNT have been investigated in situ using ESEM and TEM. We are developing a research program that will thoroughly explore the various aspects of phase interfacial and behavior of aqueous fluids in different nanotube situations, and fluid behavior and chemical modification of Hydrothermal CNT and CVD-grown CNP have been investigated. Finally, we will discuss nanotube-based nanofluidic devices, which may find applications like cellular probes, lab-on-a-chip manufacturing and electrochemical cells.

274.

CAPILLARY MICROFLUIDICS FOR RECOGNITION OF DNA HYBRIDS. *Konstantin Kornev¹, Gerardo Callegari¹, Olga Amosova², and Alexander V. Neimark¹.* (1) Center for Modeling and Characterization of Nanoporous Materials, TRI/Princeton, 601 Prospect Avenue, PO Box 625, Princeton, NJ 08542-625, Fax: 609-683-7149, kkornev@triprinceton.org, (2) Department of Molecular Biology, Princeton University

In conventional microfluidic devices, fluid is pumped by applying either pressure, or temperature gradient, or voltage. We present a new principle of controlled transport of minute quantities of fluids at micro- and nanoscale. This principle is based on the phenomenon of spontaneous absorption of wetting fluids by porous materials. Capillarity facilitates the droplet self-propulsion without the need for external forces. Fluid velocity may be as fast as 100 cm/s. Droplets can be as small as 10 microns in diameter. In this study we investigate spontaneous absorption of DNA solutions by capillaries and nanofibrous webs. A systematic experimental analysis of the droplet absorption by microcapillaries was done on a special optical electronic measuring system employing aqueous solutions of different forms of lambda-DNA and DNA with complex sequences. CMOS camera was used to film the meniscus propagation and droplet dynamics on the millisecond scale. The capillarity-driven absorption of microdroplets allows us to differentiate the viscoelastic response of single-stranded and double stranded DNA, which have different stiffness. The relaxation time of different forms of DNA is estimated from a theoretical model of flow of viscoelastic solutions into capillaries. The proposed method can be utilized for DNA characterization and sequencing in short time intervals on the microchip level.

275.

FLUID FLOW THROUGH CARBON NANOPIPES. *Maria Pia Rossi, Materials Science and Engineering, Drexel University, 3141 Chestnut Street, LEbow Building Room 344, Philadelphia, PA 19104, mpr22@drexel.edu, and Yury Gogotsi, Department of Materials Science and Engineering, Drexel University*

Fluidic properties of carbon nanotubes (CNT) are being studied for applications such as probes in nanofluidic devices. Using the environmental scanning electron microscope (ESEM), a dynamic in situ study of CNT/liquid interactions at high magnification has been done. As a result, hydrophilic and hydrophobic behavior of diverse types of CNT, including commercially-produced CNT, has been observed. What is more interesting, however, is that it has been possible to see water menisci inside CNT fabricated by chemical vapor deposition (CVD) because these are transparent under the ESEM electron beam, as shown in

Figure 1. From the measured contact angles, it is clear that these CNT are hydrophilic. In addition, rupture of these thin-walled CNT was observed inside the ESEM chamber as a result of rapid changes in pressure at constant temperatures. This has never been observed in the absence of liquid and is not the result of electron beam damage.

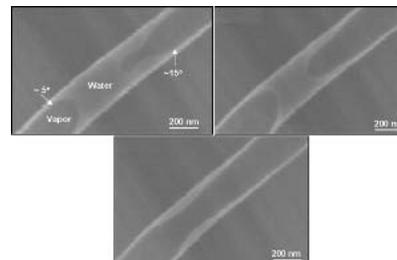


Figure 1. ESEM images of water menisci inside CVD-grown CNT as a result of pressure changes inside the chamber.

276.

EFFECT OF THE SYNTHESIS METHOD AND OF NIOBIA ON SUPPORTED Sb-V-O PROPANE AMMOXIDATION CATALYSTS. *Miguel A. Banares and M. O. Guerrero-Perez, CSIC-Institute of Catalysis, Marie Curie, 2, E-28049-Madrid, Spain, Fax: +34 915854760, mbanares@icp.csic.es*

The use of different Sb precursors for supported Sb-V oxide catalysts is investigated on alumina, niobia and silica support. These supports are impregnated with soluble vanadium precursor and with different antimony precursors at different Sb/V atomic ratios. The relevance of an intimate interaction between V and Sb is evaluated at different Sb/V atomic ratios. The nature of antimony precursor affect the interaction of antimony with vanadium and niobium, and tunes the competitive vanadium-niobium, vanadium-antimony and niobium-antimony interactions.

277.

BULK AND SUPPORTED SOLID SOLUTIONS OF NI-CO MOLYBDATES ON VARIOUS INORGANIC SUPPORTS: COMPARISON BETWEEN SOL-GEL AND IMPREGNATED CATALYSTS AND THEIR CATALYTIC ACTIVITY IN PROPANE OXYDEHYDROGENATION. *Andrea Maione¹, Patricio Ruiz², and Michel Devillers¹.* (1) Chemistry Dept, Chemistry of Inorganic and Organic Materials, Université Catholique de Louvain, place Louis Pasteur, 1/3, Louvain-la-Neuve B-1348, Belgium, Fax: (32) 10 47 23 30, devillers@chim.ucl.ac.be, (2) Unité de Catalyse et de Chimie des Matériaux Divisés, Université Catholique de Louvain

Transition metal molybdates display a wide interest as heterogeneous catalysts for several selective oxidation processes, like for the oxidative dehydrogenation of light alkanes. In particular, Ni and Co molybdates are efficient catalysts for propane ODH, but the interpretation of their catalytic behaviour is sometimes difficult because of their well-known - but not always fully mastered- polymorphism. This work is devoted to a comparison between simple and mixed Ni-Co molybdates obtained as solid solutions, either as bulk phases or as dispersed phases on silica, alumina, magnesia, titania and zirconia. These supported catalysts were obtained either by impregnation (in all cases), or by sol-gel methods (all cases but titania and zirconia), starting with the corresponding alkoxides and metal nitrates. A mixed alumina-magnesia support of intermediate acidity prepared by the sol-gel method was also considered. The bulk and surface characteristics of these catalysts were investigated in detail with XRD, XPS, BET/BJH analysis of the adsorption/desorption curves, Raman and diffuse reflectance UV-vis spectroscopy. Contrary to the bulk catalysts prepared by the citrate method, where the β -phase was observed at high Co content only, stabilization of the β -phase of $Ni_{1-x}Co_xMoO_4$ was observed throughout the composition range in all supported catalysts prepared by the sol-gel method. Dispersion of the active phase was found to improve the propene productivity in comparison with bulk catalysts obtained by citrate or coprecipitation methods. Support effects related to the various acidities and the influence of the preparation method on the metal dispersion, textural properties and catalytic performances in propane ODH will be discussed.

278.

CHARACTERIZATION OF MIXED-METAL MOLYBDATE CATALYSTS FOR PROPANE AMMOXIDATION. *Peter de Santo Jr.*, *Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD 20899-8520, Fax: 00, peter.desanto@nist.gov, Douglas J. Buttrey, Department of Chemical Engineering, University of Delaware, and Robert K. Grasselli, Center for Catalytic Science and Technology, University of Delaware*

Our previous structural studies of crystalline phases in the MoVNBTeO catalyst system show that the channel structure of the active phase Mo₇8V₁2NbTeO₂₉ (M1) accommodates a partial occupancy of Te⁴⁺ in hexagonal and heptagonal channels parallel to the c axis. However, Te is not desirable in the commercial ammoxidation of propane to form acrylonitrile due to its volatility and possible deleterious effects on downstream processes. Other lone-pair Group 5 and 6 main group cations have been studied as alternatives for Te⁴⁺ in the mixed-metal molybdate catalyst using water-soluble reagents in a similar preparation method. Furthermore, the effective diameter of the heptagonal channels, which contain low occupancies (20%) of Te, is comparable to that found in the zeolites LTA and ZSM-5 used to for propane separation and cracking, respectively. Consequently, the unoccupied channels in M1 may trap propane and facilitate the formation of combustion products leading to lower selectivity. Comparison of M1 with the isostructural Cs_{0.7}Nb_{2.3}W_{2.7}O₁₄ phase suggests that Cs⁺ may be used to fill these channels and possibly reduce CO₂ formation. In addition, we have further investigated the location of Nb in the M1 structure using anomalous dispersion data at the Nb K edge.

279.

DC MAGNETRON SPUTTERED VANADIA CATALYSTS FOR OXIDATION PROCESSES. *M. Olea¹, I. Sack¹, V. Balcaen¹, G. B. Marin¹, H. Poelman², K. Eufinger², R. de Gryse², J. S. Paul³, B. F. Sels³, and Pierre A. Jacobs⁴.* (1) *Laboratorium voor Petrochemische Techniek, Department of Chemical Engineering, Ghent University, Krijgslaan 281, Ghent B-9000, Belgium, Maria.Olea@UGent.be,* (2) *Department of Solid State Sciences, Ghent University,* (3) *Centrum voor Oppervlaktechemie en Katalyse, KULeuven,* (4) *Department of Interphase Chemistry, KULeuven*

In order to deposit highly adhesive thin films, DC magnetron sputtering technique was chosen and two series of supported vanadia catalysts were prepared: a) direct deposition of vanadia onto a ZrO₂/SiO₂ carrier; b) deposition of vanadia onto a TiO₂ layer that was sputtered first onto carrier. The catalysts were characterized by XPS and ICP. A kinetic model for the reduction/reoxidation of the catalysts was proposed and kinetic parameters were estimated by regression of single-pulse responses obtained in a Temporal Analysis of Products setup. The catalytic performances for the oxidative dehydrogenation of isobutane were investigated by performing steady-state experiments in a fixed bed micro multi-tubular reactor. Preparation conditions such as intermediate heating between two depositions, final heating after vanadia deposition, temperature of the final heating and deposition time of the vanadia layer strongly influenced the physical properties of these catalysts, which, in turn had a strong influence on their chemical behavior.

280.

FROM TRANSITION METAL ION COMPLEXES TO SUPPORTED METAL OXIDE CATALYSTS: AN OPERANDO SPECTROSCOPIC STUDY. *Bert M. Weckhuysen,* *Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Sorbonnelaan 16, Utrecht 3508 TB, Netherlands, Fax: +31-30-2511027, b.m.weckhuysen@chem.uu.nl*

Support oxides, such as zeolites, silica and alumina, can be regarded as inorganic ligands influencing the electronic properties of supported transition metal oxides; and as a consequence, steering their catalytic performances. In this presentation, we will discuss the possibilities of operando spectroscopy to study the host-guest chemistry of transition metal ion complexes in zeolites as well as the effect of amorphous supports on well-dispersed transition metal oxides. The spectroscopic techniques of choice are UV-Vis, Raman, IR and XAFS.

281.

NANONETWORK ELECTRONIC CONDUCTIVITY IN OLIVINE COMPOSITES. *Linda Nazar¹, P. Subramanya Herle², Brian Ellis¹, and Young Ho Rho².* (1) *Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada, Fax: 519-746-0435, lfnazar@uwaterloo.ca,* (2) *Chemistry, University of Waterloo*

Efficient electron and ion transport is a critical issue in lithium metal phosphates, important as cathodes for lithium-ion batteries. Much recent interest has focused on olivine-type LiFePO₄. Although it is the most prominent member of the phosphate family owing to many promising characteristics, it suffers from very poor electronic conductivity (~ 10⁻⁹ S/cm). In this talk, we will report our findings on composite LiMPO₄ materials (M = Fe, Ni, Co, Mn), which demonstrate that low conductivity can be overcome by controlling surface reactivity. Carbothermal reduction of phosphates via reaction with residual carbon (< 2%), forms a metallic, magnetic phosphide nanonetwork created in-situ within the grain boundaries of the insulating LiFePO₄ nanocrystallites. An efficient electrical conduit is created that can be directly imaged by TEM, and gives rise to bulk conductivities up to 10⁻² S/cm. The carbothermal chemistry can be controlled through subtle variation of processing conditions and stoichiometry.

282.

POLYMER NANOCOMPOSITES FROM SILICA SUBSTRATES. *Thomas A. P. Seery¹, Isabelle L. Lagadic², Mark Jordi³, and rosette Guino¹.* (1) *Chemistry Department and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, Fax: 860-486-4745, seery@mail.ims.uconn.edu,* (2) *Department of Chemistry, University of Connecticut,* (3) *Polymer Program and Department of Chemistry, University of Connecticut*

Polynorbornene/silica nanocomposites were prepared from a variety of silicate substrates using surface initiated polymerization. This approach to polymer formation has been utilized for nanoparticles and nanowafers. These substrates are prepared with pendant norbornene moieties that may be further modified with ruthenium alkylidenes for the polymerization of tethered norbornenes. The nanoparticles are prepared via a multistep process and the nanowafers (a norbornene-functionalized magnesio-silicate) were synthesized via a one-step, direct and cost-effective co-condensation silylation process. Physical and structural characterization of these materials, before and after polymerization, was done using X-ray diffraction, infrared spectroscopy, thermogravimetric analysis and transmission electron microscopy. The 2-D nanocomposites serve as model systems and are comparable to nanocomposites of clay-like materials. Tailoring of the organic moieties allows for a wide range of applications due to controlled alteration of the physico-chemical properties.

283.

TETRAHEDRAL CHALCOGENIDE CLUSTERS AND OPEN FRAMEWORKS.

Pingyun Feng¹, Nanfeng Zheng¹, and Xianhui Bu². (1) *Department of Chemistry, University of California at Riverside, Pierce Hall, Riverside, CA 92521, Fax: 909-787-4713, pingyun.feng@ucr.edu,* (2) *Department of Chemistry and Biochemistry, California State University*

The self-assembly of multi-series of metal chalcogenide tetrahedral clusters will be presented. These single-sized tetrahedral clusters act as building blocks in the formation of well-ordered superlattices from zero to three dimensions. Tetrahedral clusters can be crosslinked directly to produce purely inorganic frameworks or by multidentate organic ligands to form inorganic-organic hybrid frameworks. A number of main-group and transition metals have been incorporated into the tetrahedral clusters to allow the modification of structural and physical properties. The structural analysis based on single crystals reveals detailed information that could serve as a basis for the elucidation of larger colloidal nanostructures. The unique physical properties such as porosity, photoluminescence, tunable bandgap, and fast ion conductivity together with their potential applications will be discussed.

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SYNTHESIS OF TITANIUM DIOXIDE PARTICLES IN THE PRESENCE OF ALKYLTRIMETHYLAMMONIUM SALTS AND THEIR PHOTOCATALYTIC ACTIVITY. *Hirobumi Shibata, Tatsuya Mukai, Takahiro Ohkubo, Hideki Sakai, and Masahiko Abe, Faculty of Science and Technology, Tokyo University of Science, 2641, Yamazaki, Chiba 278-8510, Japan, Fax: +81-4-7122-1442, j7203703@ed.noda.tus.ac.jp*

Titanium dioxide (TiO₂) is known as an n-type semiconductor that can be applied for a photocatalyst capable of decomposing environmentally hazardous materials under UV light irradiation. In this study, sol-gel synthesis of TiO₂ was carried out in the presence of alkyltrimethylammonium bromides and the effect of the alkyl chain length of the quaternary ammonium salt on crystallinity, pore structure and photocatalytic activity was investigated. Cetyltrimethylammonium bromide (CTAB), titanium oxysulfate-sulfuric acid (TiOSO₄) were used as a quaternary ammonium salt and TiO₂ precursor, respectively. TiO₂ particles were synthesized by stirring the mixture composed of CTAB, TiOSO₄ and water. In the low-angle XRD pattern of the obtained particles, a sharp diffraction peak assigned to uniform mesoporous structure was observed. The particles after calcination at 450°C showed photocatalytic activity under both UV and visible light irradiation. The influence of addition of tetramethylammonium bromide on the crystallinity and photocatalytic activity will be also presented.

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SYNTHESIS AND CHARACTERIZATION OF MIXED METAL OXIDE-POLYMER COMPOSITES WITH SPHERICAL MORPHOLOGIES. *Suresh Valiyaveetil and Sindhu Swaminathan, Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore, Fax: (65) 779 1691, chmsv@nus.edu.sg*

Synthesis and characterization of ferrite-polymer composites based on nickel ferrite or nickel zinc ferrite and a hydrophilic polymer such as polyhydroxylated methyl methacrylate (PHPMMA) or polyvinyl alcohol (PVA) with spherical morphology is reported. The ferrite filler was synthesized via nitrate-citrate autocombustion method. The composite samples were prepared by direct mixing of the ferrite powder with polymer solution followed by sonication. X-ray powder diffraction patterns indicate crystalline nature of the filler and composite particles. Effect of weight percentage of the ferrite filler on the physical and thermal properties of the composite was investigated. Electron microscopic investigation revealed spherical morphology and an average size for the filler between 30-40 nm and for composite c.a. 86 nm. Nature of dispersion of the filler in the polymer matrix was analyzed using EDAX and FTIR spectroscopy. The percentage of magnetization induced in composites with the polyhydroxylated methyl methacrylate (PHPMMA) was higher than that obtained from PVA based composites. It is established that the hydroxyl groups on the polymer backbone played an important role in controlling the structure-property relationship of the composite materials.