

IEC 1

Green catalysis with alternative feedstocks

Graham J. Hutchings, *School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom, Fax: +4402920874059, hutch@cf.ac.uk*

The production of biodiesel can lead to the generation of large quantities of by-product glycerol. This is a highly functionalised feedstock that can be used to make a range of useful products by oxidation. This presentation will discuss some of these possibilities and specifically present data for the oxidation of glycerol using supported gold and gold palladium nanoparticles, using both batch and continuous flow reactors

IEC 2

New biofuels based on biobutanol: NAVY jet fuels and more

Michael Wright¹, *Vincent Homer*², *Andrew Guenther*¹, *William Hickle*¹, and *Benjamin Harvey*³. (1) NAVAIR Research Department, US NAVY, China Lake NAWCWD, China Lake, CA 93555, Fax: 760-939-1617, michael.wright@navy.mil, (2) NAVAIR Fire Science Department, US NAVY, China Lake, CA 93555, (3) Research Department, Chemistry Division, NAVAIR-NAWCWD, China Lake, CA 93555

The NAVY is interested in developing fuel sources that possess zero net carbon dioxide emissions and can satisfy mission critical needs. The latter are based on fuel performance and physical characteristics of the jet fuels. Our program has focused on, and been successful in, developing both diesel and JP (i.e. jet) fuels based on biobutanol. In the talk, we will discuss performance values, physical characteristics, and the subsequent chemistries used to convert the biobutanol to full performance JP-8 equivalents. These new fuels are based on the feedstock of biobutanol with selected 100% bio-based products for adjusting lubrication values to meet OEM specifications.

IEC 3

Eastman Chemical Company's chemicals from coal program: The first quarter century

Joseph R. Zoeller, *Research Laboratories, Eastman Chemical Company, P.O. Box 1972, Kingsport, TN 37662-5150, Fax: 423-229-4558, jzoeller@eastman.com*

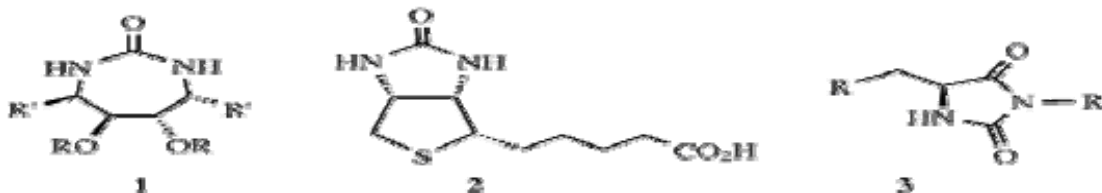
While there has been a resurgent interest surrounding alternatives to petroleum and natural gas as feedstocks for the chemical industry, especially in the transformation of coal to chemicals, this has been a continuing interest at Eastman in the period 1975-2000. After the first oil crises of the 1970's, Eastman turned its attention to local coal as a means to generate syngas as a primary chemical feedstock resulting in the commercialization of the first modern chemicals from coal facility in 1983. This facility is currently producing methanol, methyl acetate, acetic acid, and acetic anhydride. However, while less publicized, the effort continued through the year 2000, albeit at a significantly reduced level. As a consequence, Eastman developed yet to be commercialized technologies for the production of additional chemicals from syngas including vinyl acetate, acetaldehyde, propionic acid, propionic anhydride, methacrylates, and acrylates. As Eastman and the rest of the industry reenergize the programs to look at alternative resources, including coal, it is worthwhile to look back at these efforts since they represent models for transitioning from petroleum feedstocks to a coal based syngas feedstock in order to produce key chemicals for the US chemical industry.

IEC 4

Catalytic oxidative carbonylation of diamines to cyclic ureas

Lisa McElwee-White, Ampofo K. Darko, Seth Dumbris, and F. Chris Curran, Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611-7200, Fax: 392-846-0296, lmwhite@chem.ufl.edu

Catalytic carbonylation provides an alternative to phosgene or phosgene derivatives such as 1,1-carbonyldiimidazole for the conversion of amines to ureas. Primary and secondary amines can be catalytically carbonylated to ureas using $W(CO)_6$ as catalyst, I_2 as the oxidant, and CO as the carbonyl source. Tolerance of a wide variety of functional groups makes this method suitable for highly functionalized substrates. This method has been used in the preparation of the core structure (1) and derivatives of the HIV protease inhibitors, DMP 323 and DMP 450. Other targets to be discussed include biotin (2) and hydantoin derivatives (3).



IEC 5

By-product synergy: Dow Chemical's successful experience

Qingzhong Wu, *Environmental Technology Center, The Dow Chemical Company, 21255 Hwy1, Plaquemine, LA 70765, qwu@dow.com*

By-product synergy (BPS), sometimes also referred to as industrial symbiosis (IS), is the practice of achieving synergy among diverse industries to match generators of secondary materials (co-product, by-product and even “waste”) with potential users. The ultimate result is a reduction of the total environmental footprint.

Dow Chemical has taken a leadership role on studying and implementing BPS, both within Dow by its BPS team and externally under the framework of United States Business Council for Sustainable Development (USBCSD). It is a growing success within the company. This paper elaborates Dow Chemical's history of waste management, its movement to BPS/IS, its vision and mission on BPS and status quo of BPS activities. The BPS work process, developed and implemented by Dow, that provides guidelines for the BPS practices is discussed. This paper is intended to foster wide practice of BPS by sharing and leveraging Dow Chemical's experience and learnings. In order for by-product synergy to succeed, it is suggested that efforts should focus on (1) follow the principles of locality, diversity and gradual change; (2) try to cultivate a cultural change; and (3) constantly and conscientiously realize the challenges and barriers and work out countermeasures to address or remove the barriers.

IEC 6

Pyrolysis characteristics of pharmaceutical sewage sludge and brown coal

Liguo Zhang, *School of Municipal and Environmental Engineering, Harbin Institute of Technology, No. 202 Haihe Road, Harbin, China, Fax: NA, zhang1li2guo3@163.com, Chongwei Cui, Department of Environmental Engineering, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China, Jun Yin, Department of environmental Engineering, Jilin Architectural and civil Engineering Institute, Changchun 130021 NA, China, and Lei Liu, Department of Environmental Engineering, Jilin Architectural and Civil Engineering Institute, Changchun 130021 NA, China*

Pyrolysis provides a potential alternative method for treating pharmaceutical sewage sludge. The aim of the present work is to investigate pyrolysis characteristics of sewage sludge together with brown coal by the methods of thermogravimetry (TG) and differential thermal analysis (DTA). The pyrolysis tests were carried out at a constant heating rate of 10 0C/min in the temperature range of 20-800 0C. According to the pyrolysis data, activation energy and pre-

exponential factor were calculated, and the universal integral method was used to ascertain the optimal reaction mechanism of pyrolysis. The results indicate that the pyrolysis process of dried pharmaceutical sludge is divided into three phases: moisture loss(43.5-169.5 0C), volatile matter loss(166.5-416.39 0C) and fixed carbon loss (469.39-670.6 0C). Caloric energy of sludge pyrolysis is mostly released from fixed carbon, and partially released from volatile matter. Based on the pyrolysis kinetics of non-isothermal and heterogeneous system, nucleation and growth is the most probable mechanism of pyrolysis for pharmaceutical sludge and sample 1. No.13 and No.15 functions in integral forms are in the same series, which may suggest that there exists no apparent interaction between sludge and coal during the pyrolysis

IEC 7

Properties of partially biodegradable laminated LDPE - starch blend films

Asim Kumar Jana, Department of Biotechnology, National Institute of Technology, Jalandhar 144011, India, janaak@nitj.ac.in, Sangeeta Garg, Department of Chemical Engineering, National Institute of Technology, Jalandhar 144011, India, and Sarabjit Singh, Department of Applied Physics, National Institute of Technology, Jalandhar 144011, India

There has been an urgent need for the development of modified plastics or substitutes, to enhance the biodegradability and to lessen the dependency on the petroleum resources. One of the viable alternatives to accelerate the degradation and to guarantee at least partial biodegradation is the addition biodegradable agricultural feed stocks. LDPE-starch blend films offer an elegant approach to meet the requirements of responsible and ecologically sound utilization of resources and ultimate disposability. However, the blending of the hydrophilic starch and hydrophobic LDPE are not compatible in nature and have poor surface adhesion leading to phase separation during the processing of the blend film. The mechanical properties of the films deteriorate rapidly with the increase in starch concentrations. With the objectives to enhance the mechanical properties at higher starch content i.e. improved biodegradation properties, laminated films of the LDPE-starch blend film laminated on both sides of the LDPE films have been studied in the present paper. The concentration of the starch in the blend films were varied upto 15 %. Mechanical properties of the films were measured to see the effect of starch on tensile strength, % elongation, melt flow index and burst strength with respect to LDPE films. It was observed that the tensile strengths were higher for laminated films than the individual blend films but the % elongation was lower for the laminated film. Addition of starch increased the burst strength of all the films and the rate of increase was higher for the laminated films. The melt flow index decreased with the addition of starch in the blend film but for the laminated film melt flow index increased. All the

results have been explained in light of the compatibility of the blend, effect of the plasticizer, characteristics of the single and laminated films.

IEC 8

Corrosion inhibition studies of moringa oleifera lam extract on mild steel and copper in hydrochloric acid solution

Sunday O. Ajeigbe, *Department of Science Laboratory Technology, Federal Polytechnic, PMB 55, Bida, Niger 921001, Nigeria, sunchem2002@yahoo.com, Evans C. Egwim, Department of Biochemistry, Federal University of Technology, Minna 921001, Nigeria, and J. O. Okafor, Department of Chemical Engineering, Federal University of Technology, Minna 921001, Nigeria*

Corrosion inhibition of crude extract of Moringa oleifera lam leaves extract was studied on mild steel and copper coupons in different concentrations of hydrochloric acid at the temperature range of 303 to 323K using weight loss techniques. Corrosion inhibition efficiency (CIE) on both metals increased with increasing concentration of the acid. However, temperature studies revealed a decrease in the CIE with increase in temperature. Kinetics and thermodynamic treatments of the results yielded activation energies, and other thermodynamic parameters, therefore, a physical adsorption mechanism is proposed for the inhibition process. The adsorption characteristics of the inhibitor were approximated by Freundlich isotherm. Corrosion inhibition using extract of Moringa oleifera lam is a promising alternative for synthetic organic corrosion inhibitors owing to its low toxicity, environmental acceptability, availability, renewability, effectiveness and potentially low cost.

IEC 9

Nanocrystal based solar cells

A. Paul Alivisatos, *Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, alivis@berkeley.edu*

This talk will describe the potential advantages as well as the many difficulties which must be overcome if we are to make future generation solar cells using nanoscale materials. Nanoscale PVs have the possibility of being manufactured on an enormous scale. They also offer the possibility of harnessing new physics which arises in dimensionally controlled systems to control energy dissipation. Yet, nanoscale systems have high surface areas with many potential trap sites and present difficulties for how to spatially organize electrical transport pathways. These issues will be illustrated with recent experiments utilizing colloidal inorganic semiconductor nanocrystals.

IEC 10

Metal–organic frameworks: Prospective industrial applications

Ulrich Mueller, BASF Aktiengesellschaft, GCC/Z M301, Ludwigshafen 67056, Germany, ulrich.mueller@basf.com

The generation of metal–organic-framework (MOF) enables the tailoring of novel solids with regular porosity. Since the discovery of this new family of nanoporous materials and the concept of reticular design, several hundred different MOF are known. The self-assembly of metal ions, which act as coordination centers, linked together with a variety of polyatomic organic bridging ligands, results in tailorable nanoporous host materials as robust solids with high thermal/mechanical stability.

With sufficient samples now being available, the testing of metal–organic frameworks in fields of catalysis and gas processing is exemplified. Report is given on the catalytic activation of alkynes. Removal of impurities in natural gas, pressure swing separation of rare gases and storage of hydrogen will underline the prospective future industrial use of MOFs in gas processing. Comparison is made to state-of-art applications in order to outline possibilities which might be superior by using MOFs.

IEC 11

Artificial photosynthesis: Combining technology with biology for efficient solar energy conversion

Thomas A. Moore, Ana L. Moore, Devens Gust, Michael Hambourger, Gary F. Moore, Amy Keirstead, and Miguel Gervaldo, Center for Bioenergy and Photosynthesis, Department of Chemistry & Biochemistry, Arizona State University, Tempe, AZ 85287-1604, Fax: 480-965-2747, tmoore@asu.edu

Provided significant challenges can be met, solar powered, bio-inspired constructs can contribute to renewable energy resources to meet human energy needs. The central challenge is reversing the combustion process by efficient water oxidation and reductive synthesis of CO₂ to fuels. Nature's catalysts direct these oxidation/reduction reactions along coordinates that have low activation barriers and almost no side reactions. In principle, these reactions can be driven by electricity provided by sustainable sources. In order to accomplish this, it will be necessary to switch nature's catalysts from their usual source of redox potential - electron/proton carrying redox species - to emf at appropriate electrical potentials. Taking a step in this direction, we have assembled a hybrid system in which a porphyrin-sensitized Grätzel-type nanoparticulate wide band gap

semiconductor photoanode is used as an interface between emf and redox potential for the photochemical reformation of biomass to hydrogen.

IEC 12

Inorganic nanowires for energy conversion

Peidong Yang, *Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, p_yang@berkeley.edu*

Nanowires are of both fundamental and technological interest. They represent the critical components in the potential nanoscale electronic and photonic device applications. The vapor-liquid-solid crystal growth mechanism has been utilized for the general synthesis of nanowires of different compositions, sizes, and orientation. Precise size control can be readily achieved using metal nanocrystals as the catalysts. Achieving high level of synthetic control over nanowire growth allows us to explore some of their very unique physical properties. It was discovered that the thermoconductivity of the silicon nanowires can be significantly reduced, pointing to a very promising approach to design better thermoelectrical materials. In addition, semiconductor nanowire arrays can also be used as potential substrates to achieve high energy conversion efficiency in photovoltaics.

IEC 13

Self-assembled bulk heterojunction nanomaterials for low cost solar cells

Alan J. Heeger, *Department of Physics, Department of Materials, University of California, Santa Barbara, University of California, Santa Barbara, CA 93106-9530, Fax: 805-893-4755*

I will summarize recent progress on the performance of “plastic” solar cells fabricated from self-assembled bulk heterojunction nanomaterials comprised of semiconducting polymers and fullerenes. The role of processing additives such as alkane-dithiols in controlling the nanomorphology will be discussed. The improved nanoscale morphology facilitates mobile charge carrier generation, charge transport to, and charge collection at the electrodes.

IEC 14

Use of nanoscale zero-valent iron for groundwater remediation from theory to technical maturity

Rehan Baig¹, **Michael Borda²**, and **Florin Gheorghiu¹**. (1) *Golder Associates Inc, 200 Century Parkway, Suite C, Mt. Laurel, NJ 08054, Fax: 856-793-2006, rbaig@golder.com*, (2) *Golder Associates Inc, Mount Laurel, NJ 08054*

Zero-valent iron has been used to remediate many organic contaminants, which can be completely reduced to non-toxic compounds such as ethene and ethane. Nano-scale zero-valent iron (NZVI) particles have been shown to be more reactive and extremely effective by virtue of their increased surface area compared to granular coarser iron particles and the ability to distribute the particles directly into contaminant plumes. Initially, Golder Associates implemented this technology at a pharmaceutical facility in Research Triangle Park, North Carolina. The results of this application showed rapid treatment of chlorinated solvents to below drinking water standards. Golder Associates has since conducted numerous in-situ pilot tests in fractured bedrock and porous media aquifers. Results have demonstrated the ability to rapidly reduce contaminant mass while concurrently conditioning the aquifers for more effective bioremediation. The rapid reaction rate and small particle size facilitates expeditious primary treatment in source areas and dissolved plumes, thereby substantially shortening overall remediation timeframes for otherwise recalcitrant groundwater plumes. A few challenges of this promising technology are to maintain nanoparticles quality and to ensure and control proper spread of nanoparticles into porous media. From research to field trials and full scale applications, this presentation will provide an overview on how this technology was developed to reach full technical and commercial maturity.

IEC 15

PBDE degradation with zero-valent bimetallic systems

Kathleen Carvalho, *Environmental Science, University of South Florida St. Petersburg, 140 7th Ave South, St. Petersburg, FL 33701, carvalho@stpt.usf.edu*, **Lukasz Talalaj**, *Environmental Science, University of South Florida, St. Petersburg, FL 33701*, and **Robert DeVor**, *Department of Chemistry, University of Central Florida, Orlando, FL 32816-2366*

Polybrominated diphenyl ethers (PBDEs) are a group of widely used brominated flame retardants. Due to their extensive use, increasing levels of PBDEs have been found in humans, fish, birds, marine mammals, sediments, house dust, air, and supermarket foods. As a new environmental pollutant, a feasible in-situ remediation method is needed. In situ remediation methods for PCBs have been developed at UCF using palladium/magnesium bimetal created by mechanical alloying. A thorough investigation of PBDE-47 with this bimetal pair was performed. The bimetal was very reactive with 92% reduction of PBDE-47 within 36 hours. This presentation will focus on the kinetic studies as well as byproduct identification.

IEC 16

Reductive degradation of halogenated organics in groundwater with nanoscale zero-valent iron

Teik-Thye Lim, Bao-Wei Zhu, and Jing Feng, School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, Singapore, Fax: 65-67910676, cttlim@ntu.edu.sg

Zero-valent iron (ZVI) technology is a promising treatment method to deal with halogenated organic compounds (HOCs) in groundwater. Nanoscale ZVI and ZVI based bimetallic (Pd/ZVI and Ni/ZVI) particles were synthesized by the wet chemical reduction method with sodium borohydride as the reductant. The products were characterized by applying various analytical techniques (BET, XRD, SEM, TEM and XPS). The particle sizes were smaller than 100 nm as observed with TEM, and the BET surface area was about 30 m²/g which is over one order higher than that of the commercial micro-scale ZVI.

In our study, carbon tetrachloride (CTC), chloroform (CF), carbon tetrabromide (CTB), bromoform (BF), and chlorobenzenes (CBs) were chosen as target compounds. Batch reduction experiments were conducted with the two different types of the nanoscale bimetals (Ni/ZVI and Pd/ZVI) as well as with the nanoscale ZVI. All the target compounds were degraded quickly with the half-time ranging from several minutes to hours, in which CF is the most refractory one with a half-time of 20 h as degraded with ZVI. All the reactions followed the pseudo-first order kinetics. The reaction rate constants for various particles followed the order of Pd/ZVI > Ni/ZVI > ZVI. Chlorinated benzenes could not be dechlorinated by ZVI alone. Interestingly, the reaction rate tended to increase as the number of chlorine atoms attached to carbon increases, which was exactly contrary to what occurred in the dechlorination of chlorobenzenes.

To evaluate the potential field application of the synthesized materials, influences of matrix effects (including anions, surfactants, and natural organic matters (NOMs), which might exist in groundwater) were investigated. Results showed that most factors (such as anions of SO₄²⁻, CO₃²⁻, ClO₂⁻, SiO₄²⁻, and some surfactants) had insignificant influences on the degradation reactions. The effects of particle ageing on its reactivity will be also discussed in this paper.

IEC 17

Electrokinetically enhanced removal and degradation of subsurface pollutants using nanosized Pd/Fe slurry

Gordon Yang, *Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, Fax: 886-7-5254407, gordon@mail.nsysu.edu.tw*

In this work a hybrid technology combining the injection of the slurry of palladized nanoiron (PNI) and electrokinetic remediation process was used to mimic the removal and degradation of trichloroethylene (TCE) and nitrate in the subsurface environment. Laboratory-prepared palladized nanoiron was characterized to be in the range 50-80 nm with a specific surface area of 101 m²/g. PNI was further stabilized using 1 vol% polyacrylic acid as a dispersant. The nanosized Pd/Fe slurry thus prepared was then used to evaluate the treatment efficiency of combined technologies of the injection of the slurry of PNI and electrokinetic remediation process in treating TCE- or nitrate-contaminated loamy sand in horizontal columns. The initial TCE concentration in soil ranged from 160-181 mg/kg, while nitrate concentration was 7316 mg/kg. Test conditions used were: (1) electric potential gradient: 1 V/cm; (2) daily addition of 20 mL of the slurry of PNI (2.5 g/L and 4.0 g/L for the cases of TCE and nitrate, respectively) to the electrode reservoir(s); and (3) reaction time: 6 days. The addition of PNI slurry to the anode reservoir yielded the lowest residual TCE concentration in soil, namely about 92.5% removal of TCE from soil. The residual TCE concentration in the cathode reservoir was about 8 mg/L. Although the addition of PNI slurry to the cathode reservoir could completely degrade TCE therein, its residual TCE in soil was up to 29.0%. In the case of nitrate decontamination, by injecting nanosized Pd/Fe slurry into the anode reservoir of the EK system, an efficiency of over 99% nitrate removal and degradation for the entire system was achieved. The cathode reservoir, however, was found to be the worst injection position. Chemical reduction of nitrate would occur mostly in the anode reservoir where nanosized Pd/Fe bimetal existed.

IEC 18

Small particle size magnesium in one-pot Grignard-Zerewitinoff reactions: Kinetics of and practical application to reductive dechlorination of persistent organic pollutants

Volker Birke, *Koordinierung BMBF-Forschungsverbund RUBIN, Leuphana Universität Lüneburg, Projektbüro: Steinweg 4, D-30989 Gehrde, Lüneburg, Germany, Fax: 05108-9217-39, birke@uni-lueneburg.de*

Ball mills can be utilized as mechanochemical (MC) reactors for producing micro- and/or nano-sized base metals which accomplish simultaneously, i.e., during permanently milling, rapid reductive dechlorinations of added various hazardous polychlorinated compounds to their parent hydrocarbons in high yields at room temperature in a one-pot reaction. For instance, polychlorinated biphenyls

(PCBs) are dechlorinated to harmless chloride and biphenyl by applying alkali or alkaline-earth metals, aluminum, or iron, plus a low acidic hydrogen source.

Regarding magnesium and amines, resp., a kinetic study, employing dichloro- or monochlorobenzene as the model pollutant, reveals that one-pot Grignard-Zerewitinoff reactions most likely occur. A specific, coupled system of ordinary differential equations (ODE), i.e., rate equations representing single steps of the entire mechanism, could successfully be fitted simultaneously to various data sets gathered through different degradation experiments.

IEC 19

A proposed mechanism for the radical dechlorination of PCBs using microscale MgPd in methanol

Robert DeVor¹, Phillip Maloney¹, Cherie L. Geiger¹, Christian A. Clausen¹, Seth Elsheimer¹, and Kathleen Carvalho². (1) Department of Chemistry, University of Central Florida, 4000 Central Florida Blvd., Orlando, FL 32816-2366, Fax: 407-823-2252, cgeiger@mail.ucf.edu, (2) Environmental Science, University of South Florida St. Petersburg, St. Petersburg, FL 33701

Mechanically alloyed palladized magnesium has successfully been shown to dechlorinate polychlorinated biphenyls (PCBs). A variety of single congener studies have been performed in an attempt to deduce the reaction mechanism by which the dechlorination occurs in methanol. Monochlorinated congener (PCB-1, PCB-2, PCB-3) studies in both methanol and water (9:1 water:methanol) show different relative rates of dechlorination, suggestive of solvent specificity in the mechanism. Also suggestive of solvent specificity is that different final products are seen in both solvents. Use of isotopically labeled methanol-d in the degradation of PCB-151 has indicated that hydrogen exhibits a primary kinetic isotope effect ($k_h/k_d > 2$), indicating that it is involved in the rate-determining step of the reductive dehalogenation process. Based upon experimental data, a free-radical substitution similar to that of an SRN1 mechanism is proposed, where atomic hydrogen abstracts chlorine from the PCBs in a homolytic bond-cleavage. An aryl radical would be produced which can then be attacked by a second hydrogen radical in a termination step. Subsequent dechlorination can continue in this manner until biphenyl is reached, at which point the degradation would be halted.

IEC 20

Degradation of chlorinated organics from water by membrane-based nanosized metallic systems and by hydroxyl radical reaction

Dibakar Bhattacharyya¹, Jian Xu¹, Leonidas Bachas², Saurav Datta³, and Y Tee¹. (1) Department of Chemicals & Materials Engineering, University of Kentucky, Lexington, KY 40506, db@engr.uky.edu, (2) Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, (3) Chemical and Materials Engineering, University of Kentucky, Lexington 40506

Groundwater contamination with chlorinated organics is quite widespread in various locations. We have successfully evaluated highly effective methods for the destruction of toxic, chlorinated organics through comprehensive mechanistic probing of both oxidative (free-radical reaction pathways) and reductive (zero-valent nanoscale metals) dechlorination systems. For oxidative pathway Fe(II), a chelate (citric acid or gluconic acid), and hydrogen peroxide are needed for free radical production. Highly effective dechlorination was obtained with TCE (trichloroethylene), TCP (trichlorophenol), and selected PCBs. Both H₂O₂ and gluconic acid were generated by reacting glucose in membrane pore nanodomain by immobilizing Glucose oxidase enzyme in layer-by-layer assembled poly-electrolytes.

Work involving reductive dechlorination involved the use of bimetallic (Fe/Ni, and Fe/Pd) nanoparticle systems, both membrane-supported and direct aqueous-phase synthesis. The significant findings are: (1) direct synthesis of bimetallic nanoparticles with controlled diameters < 40 nm using membrane-based supports derived from polyligand functionalization and ion exchange, and phase inversion synthesis, (2) demonstrated complete (with product and intermediates analysis) dechlorination of trichloroethylene (TCE) and selected PCBs by nanosized metals. High catalytic activity of Pd was confirmed by the low activation energy (experimentally evaluated) compared with other catalytic systems. Our lab group has quantified the hydrogen generation from the iron corrosion reaction. For both bimetallic systems, hydrogen generation by iron oxidation depends strongly on the surface coverage of the second metal. Based on these findings, it is likely that the primary step of the reaction mechanism associated with bimetallic dechlorination involves the generation of reactive hydrogen (H) by the primary metal (Fe). Active hydrogen then reacts with the chlorinated organic on the surface of the second-metal, which is typically a hydrogenation-promoting catalyst such as Pd or Ni.

This research is funded by the NIEHS-SBRP program and by KRCEE-DOE.

IEC 21

Degradation of TATP, TNT, and RDX using mechanically alloyed metals

Rebecca Fidler¹, Cherie L. Geiger¹, Christian A. Clausen¹, and Michael E. Sigman². (1) Department of Chemistry, University of Central Florida, 4000 Central Florida Blvd., Orlando, FL 32816, Fax: 407-823-2252,

*bekafidler@aol.com, (2) Chemistry / National Center for Forensic Science,
University of Central Florida, Orlando, FL 32826*

Mechanically alloyed metals have been explored for the catalytic reduction of the explosives triacetone triperoxide (TATP), trinitrotoluene (TNT), and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX). TNT and RDX have been found to contaminate soil and water near industrial production sites. Previous remediation techniques of TNT and RDX include phytoremediation, bioremediation, and exposure to iron catalysts. TATP, a peroxide explosive, has become more commonly used in terrorist acts due to both the ease of synthesis and availability of reagents. TATP is difficult to treat due to its sensitivity to heat and friction. Decomposition of TATP has been limited to thermal decomposition, as well as refluxing with SnCl₂ in toluene. Although these methods are effective in decomposing TATP, they do not provide an in situ method for safely managing TATP contamination.

Laboratory scale tests were designed to measure the effectiveness of MgPd in degrading TATP, TNT, and RDX. TATP in solution has been found to undergo 96% degradation in 1.5 hours in the presence of the MgPd with a pseudo-first order rate constant. The major byproduct observed from the TATP degradation is acetone. TNT and RDX dissolved in water also exhibit pseudo-first order kinetic degradation with exposure to the MgPd. Other studies include using other mechanically alloyed metals, FeNi and FePd, for the degradation of TNT and RDX. MgPd and these other metals are also being tested to be used in combination with EZVM and BTS systems to help degrade TNT, and RDX to remediate contaminated water, soil, surfaces, and structures. Use of a MgPd in an emulsion consisting of active metal, oil, water, and surfactant, has been shown to absorb and degrade TATP crystals and remove 95% of TATP in aqueous media in 55 hours. The rate constants of the degradation of TNT and RDX as well as the degradation byproducts are being explored.

IEC 22

Environmental applications of nanocrystalline metal oxides

***Olga B Koper**, NanoScale Corporation, 1310 Research Park Dr, Manhattan, KS 66502, Fax: 785-537-0226, olga@nanoactive.com*

NanoActive materials are metal oxide aggregates that possess very large surface areas, defect-rich morphology, large porosities, and small crystallite sizes. This combination of properties results in extremely high reactivity including both enhanced reaction kinetics and large capacities. These materials have shown utility in both consumer and military applications. Of particular importance is the destructive adsorption of various toxic and odorous compounds, air and water filtration, as well as removal of heavy metals and sulfur species. In addition,

novel metal oxide formulations with the unique ability to neutralize toxic chemicals as well as biological organisms were developed. Several of oxides have been shown to possess considerable biocidal activity against the opportunistic pathogens *Staphylococcus aureus* and *Pseudomonas aeruginosa* with applications in antimicrobial paints and coatings. Consumer products based on these materials include chemical spill control systems and odor neutralization systems.

IEC 23

Application of nanoparticle technology for environmental cleanup at an industrial facility

Michael Corbin and Jeanna Wolters, Weston Solutions, 1400 Weston Way, Building 5-2, West Chester, PA 19380, Fax: 610-701-7401, M.Corbin@westonsolutions.com

This paper will present the field application of zero valent iron nanoparticle technology for remediation of groundwater at an operating industrial facility. The nano scale zero valent iron particles were prepared in a catalyst stabilized vegetable oil emulsion, which was applied to the chlorinated solvent contaminant source area in the groundwater. This source area had been studied and evaluated for over 20 years and remediation was not technically practicable. The solvent source, which was the location of a former wastewater lagoon, continued to feed a groundwater contamination plume extending $\frac{1}{4}$ mile off-site. A groundwater solute transport model was used to predict the decrease in future concentrations of chlorinated solvents in the groundwater plume after the source area was treated. Dissolved phase concentrations in the plume would meet regulatory requirements at the point of compliance.

Using this emerging technology, the nonaqueous phase source area in the groundwater was successfully treated and the chlorinated solvent degraded to benign byproducts within a year. Use of the nanoscale iron facilitated distribution of the zero valent iron particles into the silty clay soil pores using high pressure injection. The work was performed adjacent to active plant buildings and roadways with no loss of plant production. The paper will present the performance monitoring results in the groundwater following application including concentration trends of the source solvent and breakdown products. This nanoparticle technology offers significant promise for cleanup of many industrial sites impacted by chlorinated solvent nonaqueous phase liquids (NPLs) nationwide, which have been impracticable to remediate to date.

IEC 24

NZVI treatability study for a TCE source area at Alameda Point, CA

Gregory V. Lowry¹, **Tanapon Phenrat**¹, **Daniel Schoenfelder**¹, **Robert D. Tilton**², **Teresa Kirschling**², **Mark Losi**³, **June Yi**³, and **Steven Peck**⁴. (1) Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, Fax: 412-268-7813, glowry@cmu.edu, (2) Department of Chemical Engineering and Department of Biomedical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, (3) Geosciences, Tetra Tech, EC, Santa Ana, CA 92705, (4) Navy Base Realignment and Closure (BRAC) Program Management Office, San Diego, CA 92108

Several types of nanoscale zero-valent iron (NZVI) are commercially available for groundwater treatment. Site geochemistry affects NZVI reactivity, so site specific treatability studies are conducted to determine efficacy. This study compares six commercially available NZVIs and four types of ZVI-based materials for use as a TCE plume interception media. The objectives are to determine the rate of TCE dechlorination, propensity for formation of chlorinated byproducts, mass of TCE reduced/mass of ZVI (or total product mass) added, and the overall effect of ZVI addition on the site biogeochemistry in aquifer sediment and groundwater (40% solids) from a TCE-impacted groundwater site at Alameda Point, CA. TCE dechlorination was faster for NZVI than their micron-sized counterparts. TCE half-life time ranged from as little as 1.2 hr to as high as 89 hours for NZVI, and ranged from 200 hrs to 2000 hours for the plume interception ZVI a 2g/L. The reactive lifetime of the NZVI ranged from 3 days to ~30 days. Low levels of chlorinated intermediate compounds (c-DCE and 1,1-DCE) formed and degraded and were typically less than 1-2wt% of the initial TCE. Vinyl chloride was not detected. The ratio of mass of TCE reduced to mass of iron added measured at the end of the NZVI particle reactive lifetime ranged from as much as 1:17 to as little as 1:120. The addition of NZVI or ZVI increased the pH from 7.3 to 7.8, but the high alkalinity of the site groundwater limited the pH increase. NZVI addition did not decrease microbial diversity in the samples.

IEC 25

Using nanomaterials in risk management of environmental pollutants: An overview of recent advancements

Souhail R. Al-Abed, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26 W. Martin Luther King Dr, Cincinnati, OH 45268, Fax: 513-569-7879, al-abad.souhail@epa.gov

Persistent organic pollutants, known as POPs, are toxic substances released into the environment by human activities. Of all POPs released into the environment by human activity, polychlorinatedbiphenyl PCBs are among the most dangerous. They are highly toxic, causing death, disease, and birth defects

among humans and animals. These highly stable compounds can last for years or decades before breaking down. Characterization of how these contaminants reside in the sediments system and how to degrade them to harmless compounds in the environment will drastically reverse pollution trends in contaminated sediments. These organic contaminants usually have low solubility in water, and they are hydrophobic nature make them attached quite strongly to organic components of the sediments. We will present our findings using new innovative strategy based on sound science and fundamental understanding of PCBs degradation process using nanomaterials as reactive ingredients. Our approach consists of developing a suite of electrochemical and catalytic processes to degrade PCBs using nano-scale materials. These nanomaterials may be applied as ex-situ and/or in-situ scenarios. We are developing and testing the aforementioned methods using bench-scale, and pilot-scale approach. Future plans may extent to field testing and full scale applications.

IEC 26

Energy storage by water-splitting

Daniel G. Nocera, Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, Fax: 617 253-7670

Of the possible sustainable and renewable carbon-neutral energy sources, sunlight is preeminent. If photosynthesis can be duplicated outside of the leaf – an artificial photosynthesis if you will – then the sun's energy can be harnessed as a fuel. The combination of water and light from the sun can be used to produce hydrogen and oxygen. The hydrogen can then be combined with the oxygen in a fuel cell to give back water and energy. In the overall cycle, sunlight is converted to useful energy. This talk tackles the challenge of constructing a conversion device based on catalysts that capture holes and electrons to transform water into its chemical constituents: hydrogen and oxygen.

IEC 27

Architectural design, interior decoration, and 3-D plumbing en route to multifunctional nanoarchitectures—especially for energy storage and conversion

Debra R. Rolison¹, Jeffrey W. Long¹, Justin C. Lytle¹, Anne E. Fischer¹, Christopher N. Chervin¹, Katherine A. Pettigrew¹, Margret J. Geselbracht¹, and Matthew P. Saunders². (1) Code 6170, Surface Chemistry Branch, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375, Fax: 202-767-3321, (2) Surface Chemistry Branch, Naval Research Laboratory, Washington, DC 20375

Rate-critical applications, such as catalysis, sensing, separations, and especially power generation, require facile transport of molecules and charge carriers for high performance [1]. The fundamental processes that produce or store energy can now be rethought in light of architectural nanoscience, i.e., the design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks, including the use of “nothing” (void space) and deliberate disorder as design components. Aerogels and ambigels, which are sol-gel-derived ultraporos, aperiodic nanoarchitectures, unite high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of molecules. Response times to gas-phase analytes are >10 times faster than those of the same chemistry expressed as a xerogel or 3D templated mesoporous material. An architectural viewpoint provides a powerful metaphor to guide the chemist and materials scientist in the design of nanoarchitectures and in their physical and chemical transformation into multifunctional objects that yield high performance for critical technologies of the 21st century [2]. Interior decoration that imparts the multifunction necessary for electrochemical capacitors, 3D microbatteries, or fuels cells will be highlighted. [1] D.R. Rolison, *Science* **2003**, 299, 1698. [2] J.W. Long and D.R. Rolison, *Acc. Chem. Res.* **2007**, 40, 854.

IEC 28

MOFs as molecular reservoirs for hydrogen, methane and carbon dioxide storage

Omar M. Yaghi, *Center for Reticular Chemistry at California NanoSystems Institute, Department of Chemistry & Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, CA 90095, Fax: 310-206-5891, yaghi@chem.ucla.edu*

Metal-organic frameworks are a new class of porous materials in which inorganic 'joints' are linked by organic 'struts' to give extended structures with surface areas greater than 5000 m²/g. Their ultra-high surface area is useful in storing hydrogen and natural gas for automobile fueling. Some members of the MOF family are ideally suited for the selective capture of carbon dioxide and its storage in voluminous quantities. The role that MOFs play in advancing technologies in the energy sector will be discussed.

IEC 29

Hydrogen from sunlight and water: The sustainable hydrogen economy

John A. Turner, *Hydrogen Technologies & Systems Center, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, John_Turner@nrel.gov*

The "Hydrogen Economy" is the production of hydrogen, its distribution and utilization as an energy carrier. The vision of hydrogen derived from water replacing fossil-derived energy carriers has been around for over 130 years. Hydrogen as an energy carrier, primarily derived from water, can address issues of sustainability, environmental emissions and energy security. Hydrogen can be the answer to one of the major issues facing America and most other countries in the world, how to supply a transportation fuel, an energy carrier to replace gasoline. It is important that we consider hydrogen in tandem with other technologies as an alternative to the once-abundant hydrocarbon resources on which our society depends. This talk will introduce sustainable energy systems, including fuel cell technology and discuss the vision, the barriers and possible pathways for the production and implementation of hydrogen into the energy infrastructure.

IEC 30

Electric power and hydrogen fuel generation from sunlight

Michael Graetzel, *Department of Chemistry, Swiss Federal Institute of Technology Lausanne, Laboratoire de Photonique et Interfaces, Station 6, Lausanne CH 1015, Switzerland, Fax: +4121 693 4111, michael.graetzel@epfl.ch*, and **Kevin Sivula**, *Department of Chemistry and Department of Chemical Engineering, University of California Berkeley, Berkeley, CA 94720*

The development of tools to control materials on the nanometer length scale has catalyzed the development of a new class of solar energy conversion devices. The prototype of this new family of devices is the dye-sensitized solar cell (DSC). These devices operate in an entirely different fashion than conventional silicon p-n junction devices as they achieve the separation of light harvesting and charge carrier transport. Continued research with DSC has resulted in devices with power conversion efficiencies over 11 percent and excellent stability. Nanostructured systems also show great promise for the generation of hydrogen from sunlight. Silicon doped alpha-Fe₂O₃ films are shown capable of an overall solar to chemical conversion efficiency of 4.2 percent in a tandem device using a DSC as a bottom electrode. These new technologies are both viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability, availability and environmental compatibility.

IEC 31

Effect of sequence on protein stability: A numerical study using water-explicit lattice models

*Bryan Patel¹, Pablo G. Debenedetti¹, Frank H. Stillinger², and Peter J. Rossky³.
(1) Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, Fax: 609-258-0211, pdebene@princeton.edu, (2) Department of Chemistry, Princeton University, Princeton, NJ 08544, (3) Department of Chemistry & Biochemistry, University of Texas at Austin, Austin, TX 78712*

The stable functional conformation of a protein depends entirely on the primary sequence of amino acids. This native structure is stable within a limited span of temperatures, pressures, and solvent conditions, and in globular proteins is stabilized by the formation of a hydrophobic core from which water is largely excluded. Few of the existing theoretical and computational investigations of protein stability treat water explicitly or are concerned with cold- or pressure-induced unfolding of proteins. We present simulations of a water-explicit heteropolymer protein model that exhibits heat-, cold-, and pressure-induced unfolding. We have developed a lattice model of a hydrophobic homopolymer in a hydrogen-bonding solvent [1]. The model solvent displays many of water's thermodynamic anomalies, including a temperature of maximum density [2]. We have extended the model by incorporating both hydrophobic and polar monomers in the protein alphabet. Density of States simulations [3] of this model reproduce key features of experimentally-determined protein stability curves in the pressure-temperature plane. We explore the dependence of protein stability on the heteropolymer sequence, and identify specific patterns associated with thermal and mechanical stability. We also examine the effect of point mutations on the stability of individual sequences.

IEC 32

Direct numerical simulation of emulsion flow through porous media

Robert H. Davis and Alexander Z. Zinchenko, Department of Chemical Engineering, University of Colorado, Campus Box 424, Boulder, CO 80309-0424, Fax: 303-492-4341, robert.davis@colorado.edu

The flow of an emulsion containing drops or bubbles through a porous medium has practical applications in biology, engineering and geology. Of fundamental importance are the relationships between pressure drop and flow rates of the dispersed and continuous phases, and the conditions where the drops or bubbles become trapped within the porous medium. These issues are particularly challenging when the drops or bubbles have sizes close to or larger than the pores, in which case an effective-medium approach fails.

This talk presents direct numerical simulations of emulsion flows through a porous medium modeled as a granular bed at low Reynolds number, using boundary-integral methods. A model problem is considered first, where a single drop squeezes between two or more solid obstacles. It is shown that the drop becomes trapped when the capillary number (representing the ratio of viscous and interfacial forces) is below a critical value and the drop is not able to deform sufficiently to pass through the constriction. Subsequently, an efficient, multipole-accelerated algorithm was used for dynamical simulations of many nonwetting deformable drops squeezing through a granular medium comprised of fixed spheres in lattice formation or distributed randomly in a periodic box. A large number of boundary elements per surface is needed, because of the lubrication sensitivity of drop-solid interactions. Surprisingly, away from the critical condition, the dispersed phase may have higher average velocity than the continuous phase. This result is due to steric exclusion of the drops from the slow-moving streamlines near the solid surfaces. Near the critical condition, however, the average velocity of the dispersed phase is reduced as the drops become trapped (or nearly so) in the narrow spaces between the particles comprising the granular medium.

IEC 33

Predicting the thermodynamic properties of unusual chemicals

Stanley I. Sandler, *Department of Chemical Engineering, University of Delaware, Center for Molecular and Engineering Thermodynamics, Newark, DE 19716, Fax: 302-831-4466, sandler@che.udel.edu*

To design processes to destroy unusual chemicals, or to estimate their fate and transport in the environment, it is necessary to have information on their thermodynamic properties. However, and especially for dangerous substances, such information may not be available. Here we discuss the use of quantum mechanical methods to predict the vapor pressure, Henry's law constants, activity coefficients and octanol-water partition coefficients of chemical warfare agents, PCBs and steroidal drugs.

IEC 34

Solvatochromism and antisolvent behavior in ionic liquid/organic/CO₂ systems

Berlyn R. Mellein and Joan F. Brennecke, *Department of Chemical and Biomolecular Engineering, University of Notre Dame, 180 Fitzpatrick Hall, Notre Dame, IN 46556, Fax: 574-631-8366, jfb@nd.edu*

Ionic Liquids (ILs) are an important new class of solvents that have potential for many different applications. The ability to separate products and impurities from ILs remains an important issue. Ionic and organometallic compounds are especially difficult to separate from ILs. However, CO₂ can be used as a separation aid. Previously, we have shown that CO₂ is a successful antisolvent for separating salts from ILs, but only in the presence of a cosolvent. Here we use CO₂ as a gas antisolvent to induce the nucleation of a solute that is a solid, ionic, organometallic copper compound. The ease of separation depends on the donor number (ability to donate an electron pair) of the organic cosolvent used. The copper compound was chosen because it is a solvatochromic probe indicative of donor number. Solvatochromic studies of complementary IL/organic/CO₂ systems are used to further explain this behavior.

IEC 35

Ruben Carbonell at UC Davis: Reflections on connections

Steve Whitaker, Department of Chemical Engineering and Materials Science, UC Davis, 1 Shields Avenue, Davis, CA 95616-5294, whitaker@mcn.org

Under the best of circumstances, the central core of any academic program consists of a continuous evolution of concepts and a continuous development of skills. When concepts and skills are scattered across departments with different missions and faculty with different points of view, students are often confronted with what appears to be a problem in chaos theory. In this presentation, I want to provide one example of how Ruben Carbonell avoided chaos and created order in an important part of every chemical engineering curriculum.

IEC 36

Adhesion of micron-/nanoscale particles to surfaces in microelectronics manufacturing

Ravi Jaiswal, Gautam Kumar, Caitlin Kilroy, Dave Balachandran, and Steve Beaudoin, School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47906, sbeaudoi@purdue.edu

Micron-/nano-scale particle contaminants adhering to substrates of interest in microelectronics manufacturing pose a significant challenge. Particles on this size scale may have highly unusual geometry and roughness, and the substrates themselves may have surface patterns with characteristic dimensions on the length scale of the particles. The National Technology Roadmap for Semiconductors indicates that there are currently no manufacturable solutions for particle removal in many key future applications, including front end of the line

(FEOL) manufacturing and on extreme ultraviolet (EUV) photomasks. Effective removal of contaminants in these settings without damage to the underlying substrate requires knowledge of the adhesion force between the contaminant particles and the substrates. In this current work, an experimental and a continuum-based theoretical study will be presented for systems involving micron- to nano-scale particles and homogeneous and patterned substrates relevant to the microelectronics industry.

IEC 37

Cellular-scale hydrodynamics

***Howard A. Stone**, Division of Engineering & Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, Fax: 617-495-9837, has@deas.harvard.edu*

We describe several microfluidic approaches for cellular-scale hydrodynamics. In particular, (i) we consider the influence of shear stress on the kinetics of ATP release from red blood cells that flow through constrictions, (ii) we demonstrate a microfluidic technique for measuring Michaelis-Menten rate constants, which should be broadly applicable to enzymatic reactions, and investigate the idea using experiments, numerics, and scaling arguments, and (iii) we present an electrohydrodynamic technique for separating by size giant unilamellar vesicles in polydisperse suspensions. These projects have in common the use of hydrodynamic principles to explore quantitatively new questions in mechanotransduction, nonlinear chemical kinetics, and separations.

IEC 38

3M's legacy of innovation

***Wayne Maurer**, Abrasive Systems Division, 3M, 3M Center, 251-2B-11, St. Paul, MN 55144, Fax: 651 737-4087, wmaurer1@mmm.com*

The 3M™ Trizact™ Structured Abrasive story begins with 3M's century-long innovative culture. This presentation will cover some of the key features of 3M's history, structure, technologies and principles that enable uncommon connections to be transformed into innovative solutions solving customer problems. In addition, an overview of 3M's current business, technology platforms and

products will be covered, with a special emphasis on 3M's Abrasive business.

IEC 39

3M™ Trizact™ structured abrasives - part I

Stan Collins, *Abrasives Systems Division, 3M - Retiree, 3M Center, 251-2B-11, St. Paul, MN 55144, Fax: 651-737-4087, sbcollins@cpinternet.com*

A high-powered multidisciplined team armed with promising laboratory results and exciting market potential was challenged with reinventing 3M's 100 year-old abrasive product line. This talk discusses how the team encouraged innovation and leveraged corporate resources to launch

revolutionary new products.

IEC 40

3M™ Trizact™ structured abrasives - part II

Scott R. Culler, *Abrasive Systems Division Lab, 3M, 3M Center, 251-2B-11, St. Paul, MN 55144, Fax: 651-737-4087, srculler1@mmm.com*

This presentation continues the 3M™ Trizact™ Structured Abrasive story. Examples of how the chemistry, microreplication patterns and composite technology combine to control the grinding performance of these new-to-the-world abrasives will be described. The features, advantages

and benefits of Trizact™ structure abrasives will be discussed along with special emphasis on how these unique abrasives provide a substantial benefit to 3M's customers.

IEC 41

The next generation of 3M™ Trizact™ structured abrasives

Louie Moren, *Abrasive Systems Division Lab, 3M, 3M Center, 251-2B-11, St. Paul, MN 55144, Fax: 651-737-4087, lmoren1@mmm.com*

Integrating technologies is a key component of 3M innovation. Leveraging the strengths of 3M's broad array of technologies resulted in the development of novel macroreplicated abrasives that have enabled 3M to pursue new abrasive market applications outside the scope of the original microreplicated Trizact™ structured abrasives. This discussion reviews the technology combinations,

customer needs and practical solutions that extend the Trizact™ structured abrasive technology into the next decade.

IEC 42

Engineered drug therapies enabled by fabrication processes from the electronics industry

Joseph DeSimone, Department of Chemistry and Pharmacology, University of North Carolina at Chapel Hill, B-5 Venable Hall, Department of Chemical and Biomolecular Eng, NC State University, Raleigh, NC 27695-7905, Chapel Hill, NC 27599, Fax: 919-962-5467, desimone@unc.edu

To translate promising molecular discoveries into benefits for patients, we are taking a pharmacoengineering systems approach to develop the next generation of delivery systems with programmable multifunctional capability. A key strategy is to apply manufacturing technologies from the microelectronics industry to fabricate polymeric delivery systems that are capable of multiple functions. A novel method for the fabrication of organic particles on the order of tens of nanometers to several microns will be described. Our imprint lithographic technique called PRINT (Particle Replication In Non-wetting Templates), takes advantage of the unique properties of elastomeric molds comprised of a low surface energy perfluoropolyether network, allowing the production of monodisperse, shape-specific nanoparticles from an extensive array of organic precursors. This engineered nature of particle production has a number of advantages over the construction of traditional nanoparticles such as liposomes, dendrimers, and colloidal precipitates. The nature of the PRINT technology takes drug delivery for the first time into the uncharted realm of engineered drug therapies given its á la carte approach and versatility. PRINT allows for the precise control over particle size (20 nm to >100 micron), particle shape (spheres, cylinders, discs, toroidal), particle composition (organic/inorganic, solid/porous), particle cargo (hydrophilic or hydrophobic therapeutics, biologicals, proteins, oligonucleotides, siRNA, imaging agents such as MR contrast agents, positron emitters), particle modulus (stiff, deformable) and particle surface properties (Avidin/biotin complexes, targeting peptides, antibodies, aptamers, cationic/anion charges, Stealth PEG chains). Key therapeutic parameters such as bioavailability, biodistribution, and target-specific cell penetration can be simultaneously designed into a therapy. Extensive in vitro and in vivo studies have begun focused on fundamental cellular uptake and intra-cellular trafficking of particles; in vivo biodistribution as a function of size, shape, surface chemistry and deformability; and in vivo tissue and cellular targeting for autoimmune disease treatment and cancer treatment and diagnosis (PET/CT, MR).

IEC 43

High throughput synthesis and screening for protein adhesion during membrane filtration

*Mingyan Zhou¹, Hongwei Liu², James E. Kilduff³, Daniel G. Anderson⁴, Robert Langer⁵, and **Georges Belfort²**. (1) Civil and Environmental Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180-3590, Fax: 518-276-6360, zhoumy@rpi.edu, (2) Howard P. Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180-3590, Fax: 518-276-4030, (3) Department of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, (4) Center for Cancer Research, Massachusetts Institute of Technology, Boston, MA 02139, (5) Department of Chemical Engineering and Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, MA 02139*

Since surface science has not yet developed to the point that allows prediction of the surface or functional characteristics needed to reduce protein fouling. Hence, few new polymers have been used for membrane production. What is urgently needed is a fast, efficient and reproducible process to allow quick selection of the best polymer, and subsequent analysis of its mechanism of action to gain understanding for future design of surfaces for membrane and other separations.

Here, we offer a high throughput platform (HTP) together with our patented photo-induced graft polymerization (PGP) method to the facile modification of commercial poly(ether sulfone) (PES) membranes. The novel method is inexpensive, fast, simple, reproducible and scalable. It can quickly produce large libraries of candidate surfaces from a library of monomers, and can quickly identify the surfaces having the surface or functional characteristics that optimize filtration of a specific feed stream. The HTP-PGP approach can also optimize grafting and filtration conditions.

A library of surfaces using commercially-available monomers was produced and evaluated by our HTP-PGP method. Several high-performance surfaces were identified using two different proteins (lysozyme & RNase A) as foulants for the evaluation of adhesion during membrane filtration.

IEC 44

Design of pharmaceutical nanoparticles for enhanced therapeutics

***Keith P. Johnston**, Joshua Engstrom, Jasmine Tam, Michal Matteucci, Andrea Mazuski, and Robert O. Williams, Department of Chemical Engineering, Center for Nano- and Molecular Science and Technology, Texas Materials Institute, University of Texas at Austin, Austin, TX 78712*

The size and unique surface properties of pharmaceutical nanoparticles offer substantial therapeutic benefits in dissolution and controlled release. These properties may be designed with novel precipitation processes including controlled precipitation with an antisolvent, spray freezing into liquid nitrogen and thin film freezing. For poorly water soluble drug nanoparticles, high surface areas and stable amorphous polymorphs enhance thermodynamic and kinetic properties of dissolution. Smart surfactants are being designed to: (1) control particle nucleation, growth and stabilization, and (2) facilitate in vitro and in vivo wetting and dissolution behavior in the GI tract or lungs. Stable protein nanoparticles on the order of 100 to 500 nm offer new opportunities for controlled release in parenteral and pulmonary delivery. Protein aggregation is largely avoided by minimizing the time of exposure to air-water and glass-water interfaces. The particle size is controlled by manipulating the nucleation and growth rates, as a function of the droplet/film geometry and cooling rate.

IEC 45

Investigation of chemical selective displacers using robotic high throughput screening, SPR, NMR and MD simulations

*C. Morrison, S. McCallum, R. Godawat, J. Moore, S. Garde, and **Steven Cramer**, Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, Fax: 518-276-4030, crames@rpi.edu*

High throughput screening was employed in concert with several analytical techniques to identify and evaluate the behavior of chemically selective displacers for protein purification in ion exchange systems. A robotic liquid handling system was adapted to efficiently carry out this parallel batch screen of selective displacers on multiple protein pairs. The results identified potential selective displacers and important functional group chemistries and also indicated that this selectivity was due primarily to the selective binding between the displacer and targeted proteins. Nuclear Magnetic Resonance was then conducted on several protein/displacer mixtures verifying the binding of the selective displacers to targeted proteins and the location of the binding event. Surface plasmon resonance experiments and molecular dynamic simulations were also carried out to corroborate the NMR results. This proof of concept study shows that more specific selectivities may also be possible by utilizing affinity based selective displacers for explicit protein systems.

IEC 46

Properties of affinity membranes for h-IgG purification

Cristiana Boi¹, Simone Dimartino¹, Ruben G Carbonell², and Giulio C. Sarti¹. (1) Department of Chemical Engineering, Mining and Environmental Technologies, Università di Bologna, viale Risorgimento 2, Bologna 40136, Italy, Fax: +39 051 581200, giulio.sarti@mail.ing.unibo.it, (2) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695

Different affinity membranes have been tested for the capture step of monoclonal antibody production. The study has been performed using affinity membranes specifically obtained using cellulose based as well as polyethersulfone based substrates, modified by using different ligands, including protein A mimetic ligands and a specific sequence of six peptides recently selected by in NCSU laboratories; a new protein A membrane as well as a commercially available protein A membrane were also considered. The membranes have been characterized and compared in terms of their ligand densities, binding capacities, ligand utilization and selectivity for the target antibody. Breakthrough performances have been evaluated together with recovery and concentration factors for the most promising membranes. Model simulations of the affinity cycle is also considered, including convection, diffusion and multi-component adsorption to simulate the adsorption, washing and elution steps. Results of the simulation have been compared with the experimental data, giving a good description of the affinity cycle.

IEC 47

Reckoning protein physical stability in terms of tendency to self associate

Todd Przybycien, Department of Biomedical Engineering and Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213, Fax: (412) 268 7139, todd@andrew.cmu.edu

The aggregation of pharmaceutical proteins is a significant concern in processing, storage and delivery operations. Real-time and accelerated stability studies can provide helpful information on tendency to aggregate under specific conditions, but take "real-time" to execute and use elevated temperatures that do not represent anticipated solution condition, respectively. We have used self-interaction chromatography (SIC) to provide insight into the tendency of proteins to self-associate in terms of second virial coefficients and corresponding equilibrium unfolding studies to provide insight into tendency to unfold in terms of unfolding free energies. We have further used these second virial coefficients and unfolding free energies to inform a lumped kinetic model for protein aggregation that can be compared to real-time and accelerated stability data. We report on our comparison of model predictions to physical stability data for two model pharmaceutical proteins, bovine growth hormone and human growth hormone.

IEC 48

The influence of diffusion on energy metabolism and cellular organization in skeletal muscle

Bruce R Locke¹, Santosh Dasika¹, Stephen T. Kinsey², and Kristin M. Hardy².
(1) Department of Chemical and Biomedical Engineering, Florida State University, FAMU-FSU College of Engineering, 2525 Pottsdamer St., Tallahassee, FL 32310, locke@eng.fsu.edu, (2) Department of Biology and Marine Biolog, University of North Carolina at Wilmington, Wilmington, NC 28403-5915

Skeletal muscle, a vital component of animals with vertebrae, is an excellent system to analyze within the framework of multiple chemical reactions coupled with diffusion in a complex, well organized, environment. The function of skeletal muscle is directly related to the relative amounts and distribution of the space allocated for aerobic metabolic capacity (mitochondria) and contractile capacity (myofibrils and sarcoplasmic reticulum). The influence of diffusion on reaction rates increases as either the diffusion distance or rate of aerobic ATP demand increases. Since diffusion distances in animal cells can range from <1 to several hundred μm , and ATP demand varies from <0.1 to >2000 $\mu\text{moles g}^{-1} \text{min}^{-1}$, it is possible that diffusion may set an upper limit on aerobic metabolic rate, which may ultimately constrain animal function. This work focuses on consideration of both oxygen and phosphate metabolites within skeletal muscle cells using the effectiveness factor and the method of volume averaging to characterize the relationship between diffusion distance and ATP turnover rate.

IEC 49

Managing the risks from blood-associated TSE infectivity with prion affinity ligands

Robert Rohwer¹, Luisa Gregor², Brian C. Lambert¹, Ruben G Carbonell³, Patrick V. Gurge⁴, David Hammond⁵, Julia Lathrop⁶, Peter Edwardson⁷, and Steve J. Burton¹. (1) Department of Neurology, University of Maryland at Baltimore, 10 N. Greene Street, Baltimore, MD, MD 21201, Fax: 410-605-7959, rrohwer@umaryland.edu, (2) Medical Research Service 151, Veterans Affairs Medical Center, Baltimore, MD 21201, (3) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, (4) Department of Chemical and Biomolecular Engineering, ProMetic Life Sciences and NC State University, Mont-Royal, QC H4P 2L7, Canada, (5) American Red Cross, (6) Prolias, Laytonsville, (7) ProMetic Life Sciences, Mont-Royal, QC H4P 2L7, Canada

Since 1996 there have been over 200 cases of a distinctive variant (vCJD) of a rare human TSE called Creutzfeld-Jakob disease (CJD) that are almost certainly BSE infections of humans. To date there have been four recognized cases of secondary transmission of vCJD in humans by transfusion. Based on our earlier quantitative studies of the titer and distribution of TSE infectivity in rodent blood we began development of a removal strategy for all forms of the human prion protein, infected and uninfected, based on prion protein affinity ligands that we selected by high-through-put screening of combinatorial ligand libraries. Those ligands that performed best were tested for their ability to remove TSE infectivity using animal bioassays. By spiking human red blood cells with brain-derived preparations of TSE infectivity, we were able to show that the capacity of the resins far exceeded the mass of prion protein expected for a single 500ml unit of blood. By challenging the resins with whole blood collected from rodents during symptomatic infection with TSE, we demonstrated removal of relevant, blood-associated infectivity to the limit of detection. Several of these ligands are now being developed into devices for removing TSE infectivity from red blood cells collected for transfusion, and for removal of TSE infectivity from plasma derivatives prepared as human therapeutics.

IEC 50

Catalytic dechlorination of gas-phase perchloroethylene under mixed redox conditions

A. Eduardo Sáez¹, E. Rupp¹, R. G. Arnold¹, EA. Betterton², and S. Gao². (1) *Department of Chemical and Environmental Engineering, University of Arizona, Harshbarger, Rm. 108, University of Arizona, Tucson, AZ 85721, esaez@engr.arizona.edu,* (2) *Department of Atmospheric Sciences, University of Arizona, Tucson, AZ 85721*

Remediation of groundwater and soils contaminated with chlorinated organics, such as perchloroethylene (PCE), is commonly undertaken using soil-vapor extraction followed by adsorption on activated carbon. Our research has focused on developing a destructive technology based on conversion of the contaminants to harmless products on an alumina-supported Pt/Rh catalyst. Direct oxidation of chlorinated organics requires relatively high temperatures and may produce highly toxic oxygenated products, while reductive hydrodechlorination is generally ineffective due to catalyst deactivation. Our experiments show that redox environments provide stable reactor operation and prevent catalyst deactivation. We hypothesize that PCE reduction precedes oxidation reactions, and that the importance of oxidation lies in elimination of intermediates that would otherwise poison the catalyst. The technology has been deployed at pilot scale at a local Superfund site in Tucson, Arizona. The reactor has been operated continuously for almost a year with total elimination of chlorinated organics without change in catalyst performance.

IEC 51

Continuous polymerization in supercritical carbon dioxide

George W. Roberts¹, T. Liu¹, T. S. Ahmed¹, and Joseph DeSimone². (1) Department of Chemical and Biomolecular Engineering, North Carolina State University, CB#: 7905, Raleigh, NC 27695-7905, Fax: 919-515-3465, groberts@eos.ncsu.edu, (2) Department of Chemistry and Pharmacology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599

Supercritical carbon dioxide (scCO₂) is a low-cost, environmentally-friendly medium for carrying out polymerization reactions. A number of chain-growth and step-growth polymers have been synthesized in scCO₂, primarily in small batch reactors. Only a few polymerizations have been carried out continuously in scCO₂, despite the practical and scientific advantages of continuous operation.

Poly(vinylidene fluoride), poly(acrylic acid), and poly(vinylidene fluoride-co-hexafluoropropylene) have been synthesized in scCO₂ using a continuous stirred-tank reactor (CSTR). The first two polymers are formed via precipitation polymerization. The copolymer can be formed by either precipitation or solution polymerization, depending on the CO₂ pressure, monomer concentration, molecular weight, and hexafluoropropylene content.

The effects of reaction conditions on the polymerization rate and the molecular weight distribution were studied for the three polymer systems. The behavior of the polymerization rate and the evolution of molecular weight was distinctly different for acrylic acid than for the fluoromonomers. The differences suggest differences in the mechanisms of polymerization.

IEC 52

Epoxidation of light olefins in olefin-expanded liquid phases

Hyun-Jin Lee¹, Madhav Ghanta¹, Daryle H. Busch², and **Bala Subramanian¹**. (1) Department of Chemical and Petroleum Engineering, University of Kansas, Center for Environmentally Beneficial Catalysis, Lawrence, KS 66047, bsubramanian@ku.edu, (2) Department of Chemistry and Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66047

Novel homogeneous catalytic process concepts for propylene oxide and ethylene oxide manufacture will be presented and discussed. It is shown that these commodity products may each be formed under very mild conditions (ambient temperature and total pressure on the order of tens of bars) at high selectivity (99% or greater) by reacting the appropriate olefin in a single liquid phase

containing methyl trioxorhenium as the catalyst and hydrogen peroxide as the oxidant. Enhancing the availability of the gaseous substrate in the liquid phase is key to increasing the overall reaction rate. This is done by choosing the appropriate solvent, pressure and temperature conditions based on knowledge of the phase behavior of the reaction mixture. The new processes utilize benign components, produce little or no waste compared to their commercial counterparts, and the catalyst exhibits good durability. Economic and environmental impact analyses will be presented to assess the potential for commercialization.

IEC 53

Filtered two-fluid models for fluidized gas-particle suspensions

*Yesim Igci and **Sankaran Sundaresan**, Department of Chemical Engineering, Princeton University, A315 Engineering Quadrangle, Princeton, NJ 08544, sundar@princeton.edu*

Gas-particle flows exhibit large fluctuations in velocities and local suspension density. In riser flows, these fluctuations are associated with the random motion of the individual particles and with the chaotic motion of particle clusters, which are repeatedly formed and broken apart. These clusters occur over a wide range of length scales and their dynamics span a broad range of time scales. This broad range of scales has made it difficult to construct efficient flow models required for practical analysis of flows in large fluidized beds and risers. In this paper, we construct filtered hydrodynamic models for such systems and determine the associated constitutive models by filtering results obtained from highly resolved simulations of fluidized suspensions in a periodic domain. We also demonstrate that the filtering process does indeed erase the small scale structures and allow grid size-independent solutions at much lower grid resolutions than the underlying kinetic theory based model.

IEC 54

Numerical simulation of aerated-liquid and supercritical injection of hydrocarbon fuels

***Jack Edwards**, Department of Mechanical and Aerospace Engineering, NC State University, Campus Box 7910, Raleigh, NC 27695-7910, jredward@ncsu.edu*

Regenerative fuel cooling is being used as an enabling technology for next-generation propulsion systems for high speed (>Mach 5) flight. The heating load is partially absorbed by the endothermic fuel, inducing a transition from a liquid

phase to a supercritical-fluid phase. The injection of the fuel into the combustor involves the expansion of the supercritical fluid through a small orifice, which may be accompanied by liquid droplet formation, turbulent mixing, and shock waves. This paper will survey recent work in simulating the injection of supercritical fuels through solution of the Navier-Stokes equations governing a multi-phase mixture of fluids. Results will also be presented for aerated-liquid atomization, which is used to accelerate the primary breakup of the fuel stream. Work performed with Dr. Carbonell on the use of the RESS process for depositing polymeric coating materials led directly to these capabilities, and this connection will be specifically highlighted in the paper.

IEC 55

Photocatalysis: A retrospective view after three decades

David F. Ollis, Department of Chemical and Biomolecular Engineering, North Carolina State University, 911 Partners Way, Raleigh, NC 27695-7905, Fax: 919-515-3465, ollis@eos.ncsu.edu

The white paint pigment, titanium dioxide, has been widely studied for photocatalytic applications in water treatment and decontamination, air purification, and self-cleaning windows and walls. While only 24 papers in photocatalysis appeared worldwide in 1978, more than 2,000 were published in 2007. We survey our contributions over this interval to the photocatalysis application areas noted above, as well as the more fundamental considerations of catalyst definitions, reaction kinetics and mechanisms, and catalyst deactivation and regeneration. While the range of proposed commercial applications for the ambient temperature photocatalysis is remarkably broad, the fierce remaining challenges of optimal photoreactor design, efficient photon capture and utilization, and catalyst deactivation and regeneration all indicate that progress in photocatalysis has "miles to go" before it can rest on commercial successes.

IEC 56

Using the tunable properties of gas expanded liquids to control nanoparticle deposition and separation processes

Christopher B. Roberts, Steven R. Saunders, Kendall M. Hurst, and W. Robert Ashurst, Department of Chemical Engineering, Auburn University, 210 Ross Hall, Auburn, AL 36849-5127, Fax: 334-844-2063, croberts@eng.auburn.edu

A novel process will be described that utilizes the pressure tunable physico-chemical properties of CO₂ gas expanded liquid solutions to size selectively

precipitate and fractionate polydisperse metal and semiconductor nanoparticle dispersions into multiple narrow size populations. Our work demonstrates that ligand stabilized nanoparticles can be size selectively precipitated by simply controlling the addition of compressed CO₂ antisolvent to an organic nanoparticle dispersion. This tunable gas expanded liquid approach allows for rapid and efficient size separation while also reducing organic solvent usage. The efficacy of this process has been demonstrated with several types of metal and semiconductor particles at process scales ranging from microliters to >100 milliliters of an organic nanoparticle dispersion. In addition, this gas expanded liquid driven nanoparticle deposition process has been utilized to create ordered thin films and arrays of nanoparticles on device surfaces, such as MEMS devices, without the detrimental interfacial dewetting effects inherent to liquid evaporation driven nanoparticle deposition techniques.

IEC 57

Nucleation kinetics in reactive precipitation

Donald J. Kirwan, Department of Chemical Engineering, University of Virginia, 102 Engineer's Way, Charlottesville, VA 22904, Fax: 434 982 2658, djk@virginia.edu, and Jason M. Gillian, GlaxoSmithKline, Research Triangle Park, NC 27709

Reactive crystallization is employed in pharmaceutical processing to produce high supersaturation resulting in rapid nucleation and the production of fine particles. However, the time scale of liquid mixing is often comparable to the nucleation induction time, and both are often orders-of-magnitude longer than the half-life of the chemical reaction, making analysis and control of the precipitation process challenging. We have developed three techniques for nucleation measurements using opposed jet Y-mixers with well-characterized mixing times as small as 5 ms. Light scattering and turbidity are used to detect particles at a given residence time in an observation tube following a Y-mixer. In the continuous flow mode induction times between ~10 and ~100 ms are measurable while in the stopped flow mode, induction times greater than 100 ms can be determined. The third technique uses a double Y-mixer where the second mixer quenches the precipitation after a given residence time prior to particle counting to provide a direct measure of nucleation rate. The acid precipitation of benzoic acid and the sodium acetate precipitation of voriconazole (free base) were the model systems studied.

Under good mixing conditions the measured induction times and nucleation rates agreed with one another, and their supersaturation dependence followed classical nucleation theory. Experiments testing the effects of reactant ratio showed little effect on nucleation in both systems. Experiments with poorer initial mixing showed lower nucleation rates for benzoic acid; but, paradoxically, they

resulted in higher nucleation rates for voriconazole. Our previously-developed and validated eddy growth model for mixing was adapted to the reactive precipitation case, and it was found to quantitatively capture most of the observed experimental effects. The unusual behavior of voriconazole was attributed to a combined anti-solvent and reaction effect in this precipitation process.

IEC 58

Pathway leading from supersaturated solution to solid crystal studied by small angle X-ray scattering

Deniz Erdemir, Department of Chemical and Biological Engineering, Illinois Institute of Technology, 10 West 33rd Street, Chicago, IL 60616, Fax: 312-567-7018, and Allan S. Myerson, Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616

Solution crystallization is one of the most important unit operations used in wide range of industries, therefore it is necessary to control the crystallization process to obtain products with desired and reproducible properties. The early stages of crystallization, called nucleation, plays a decisive role in determining these properties, so higher levels of control over crystallization can not be achieved without understanding the fundamentals of nucleation. However, the mechanism of nucleation is still not well understood. This talk will summarize the findings of small angle x-ray scattering (SAXS) studies performed on glycine over the last five years with the aim of developing a comprehensive picture of nucleation of small organic molecules from supersaturated solutions. The major findings include the nucleation of glycine crystals via a two-step mechanism, in which the formation of a liquid-like cluster is followed by the organization of such cluster into a lattice, and a direct link between the molecular assembly process in supersaturated solutions and the final solid form.

IEC 59

Understanding additive effects on crystallization, polymorphic transformation and solubility

Stephen Byrn, Charles B. Jordan Professor and Head of the Department of Industrial and Physical Pharmacy, Purdue University, West Lafayette, IN 47907, sbyrn@purdue.com, and EunHee Lee, Industrial and Physical Pharmacy, Purdue University

Crystallization of the mefenamic acid in the presence of a structurally related compound allows isolation of single crystals of the metastable form for the first

time. This result is explained by the fact that an additive inhibits the nucleation of the stable form and thus allows the metastable form to grow by kinetic control.

Solubility study shows that a structurally related compound increases the solubility of a poorly soluble compound, MFA, as much as seven times in toluene and six times in cyclohexane. In addition, it is strongly suggested that there are specific interactions between FFA and MFA in toluene and in cyclohexane.

The results of this study show that the interactions between the additive and the host molecules in the solution state as well as in the solid state play a major role in determining the properties including morphology, polymorphic transformation, polymorph selection, and solubility,. However, the thermodynamics of the states also need to be considered to understand additive effects on the properties of host molecules. By understanding the relationships between the additive and host molecules in the solid state and in the solution state it may be possible to control the desired properties of solids.

IEC 60

The two-step mechanism of nucleation of crystals from solution

***Peter G. Vekilov**, Department of Chemical and Biomolecular Engineering, University of Houston, Department of Chemistry, Houston, TX 77204-4004, Fax: 713-743-4323, vekilov@uh.edu*

The nucleation of new phases is a crucial part of processes of interest to chemistry, physics, geology, pharmacy, meteorology, and materials science and engineering, yet nucleation is among the few areas where the discrepancy between theoretical predictions and experimental determinations reaches many orders of magnitude. This problem is even more severe for complex nucleating systems, such as nucleation of crystals from solution, where even the reproducibility of the determinations is often at issue. I will discuss recent findings, suggesting that the nucleation of crystals of many colloid and protein, and molecular and ionic small-molecule materials in solution occurs via a two-step mechanism: (1) the solute molecules assemble into disordered and fluid droplets of mesoscopic sizes, and (2) ordered crystalline nuclei form within these dense liquid droplets. I will summarize the experimental findings supporting this mechanism in various systems. I will then discuss a recent phenomenological theory which provides a rate law for the kinetics of nucleation via the two-step mechanism, and tests of the theory predictions using experimental data. I will present recent independent evidence of the existence of the fluid droplets which serve as precursors to the nuclei. I will discuss how this mechanism explains the role of foreign substrates in acceleration of the nucleation rate and the selection of the crystal polymorph emerging from the supersaturated solution. The low volume fraction of the dense liquid precursor explains the discrepancies between

nucleation theory and experiment, while its variability underlies inconsistencies of the experimental determinations of the nucleation rate.

Proc. Natl. Acad. Sci. USA 2000, 97, 6277; Crystal Growth and Design 2004, 4, 671-685; J. Chem. Phys. 2005, 122, 174905; J. Amer. Chem. Soc. 2005, J. Chem. Phys. 2005, 123, 014904; 127, 3433-3438; Biophys. J. 2007, 92, 267; J. Phys. Chem. B 2007, 111, 3106

IEC 61

Crystallization and polymorphism: Applied examples from the pharmaceutical industry

Surya Devarakonda, *Integrated Product Development, API R&D, Dr. Reddy's Laboratories Limited, Innovation Plaza, C-block, Bachupally, Hyderabad 500072, India, Fax: 040-4434-6285, suryad@drreddys.com*

Crystallization is an important unit operation in a pharmaceutical industry as it not only purifies the final drug substance but also controls many properties of the drug substance that are important to a formulator. These properties include but not limited to polymorph, crystal size distribution, bulk density etc. And often times in a generic API supplier setting, a situation arises that requires supplying the same drug substance to different customers with varying properties from the same process, with minimum or minor modifications to the process. This talk will focus on presenting some practical examples where fundamental principles of crystallization are applied to develop robust solutions, including some of the aforementioned type.

IEC 62

Elusive polymorphs: How to prevent them from "disappearing"

Alfred Y Lee, *Strategic Technologies, Chemical Development, GlaxoSmithKline PLC, 709 Swedeland Road, UW2830/PO BOX 1539, King of Prussia, PA 19406, Fax: 610-270-6570, alfred.y.lee@gsk.com*

Unexpected emergence of a different solid state form of a drug substance during processing, storage and shipping is a huge challenge for the pharmaceutical industry as an undesired form may give rise to different physical and chemical properties. The phenomenon of 'disappearing polymorphs' is becoming fairly common as a particular crystal form is suddenly elusive although in the past it could frequently be obtained over a long period of time. This talk will highlight recent examples of elusive polymorphs and discuss strategies to stabilize metastable solid forms.

IEC 63

Laser induced nucleation of protein crystals

James MB Evans¹, Allan S. Myerson², Deniz Erdemir², InSung Lee², Alfred Y Lee³, and Bruce A. Garetz⁴. (1) Chemical Development, Vertex Pharmaceuticals, 130 Waverly Street, Cambridge, MA 02139, james_evans@vrtx.com, (2) Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, (3) Strategic Technologies, Chemical Development, GlaxoSmithKline PLC, King of Prussia, PA 19406, (4) Department of Chemical & Biological Sciences, Polytechnic University, Brooklyn, NY 11201

Small droplets of supersaturated lysozyme solution were exposed to intense linearly polarized laser pulses with different wavelengths, intensities and pulse durations. Laser irradiation significantly increased the number of droplets in which crystals were observed in a given time period, compared with unirradiated samples. In addition, the results indicate that non-photochemical laser induced nucleation (NPLIN) for lysozyme solutions is strongly dependent on the aging time, wavelength, intensity and pulse duration. Bovine trypsin was also examined using NPLIN. However, the results indicate a much smaller effect when compared to lysozyme.

IEC 64

Development of a device for prion reduction based on affinity ligand

Patrick V. Gurgel¹, M. Omon Herigstad², Yong Zheng³, Luisa Gregori⁴, Julia Lathrop⁵, Robert Rohwer⁶, Peter Edwardson³, and Ruben G Carbonell². (1) Department of Chemical and Biomolecular Engineering, ProMetic Life Sciences and NC State University, 8168 chemin Montview, 911 Partners Way, Mont-Royal, QC H4P 2L7, Canada, (2) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, (3) ProMetic Life Sciences, Mont-Royal, QC H4P 2L7, Canada, (4) Medical Research Service 151, Veterans Affairs Medical Center, Baltimore, MD 21201, (5) Prolias, Laytonsville, (6) Department of Neurology, University of Maryland at Baltimore, Baltimore, MD, MD 21201

The potential presence of disease-associated prion proteins in blood and its derivatives poses a challenge for the blood transfusion industry. Prion inactivation has been suggested, but not reduced to practice while removal strategies focused on blood, such as leukodepletion reduce infectivity by less than one log. The use of affinity resins to capture specific targets from a complex medium is a viable complement for leukodepletion. In order to overcome the difficulties of passing a particulated material (red blood cell concentrate) through

a packed-bed column, a device containing multiple layers of particle-impregnated membranes was developed. Its performance was evaluated in regards to prion capture, blood quality, and removal of other proteins, among other parameters, with very good results. A comparison with resin in column format showed similar capacities and dissociation constants, indicating that the trapped resin particles are still accessible to the target material.

IEC 65

Integrated microfluidic devices for medical diagnostics and studying cell signaling

Anup K Singh, *Biosystems Research Department, Sandia National Laboratories, Mailstop 9951, PO Box 969, Livermore, CA 94551-0969, aksingh@sandia.gov*

Microfluidic devices have attracted a significant interest in the field of biochemical analysis because of a number of advantages they offer such as speed of analysis, portability, small sample and reagent consumption, and potential for multiplexing and automation. Application of microfluidic chips in two areas will be presented—in developing portable diagnostics devices and in studying cell signaling. We have developed a point-of-care device using chip-based immunoassays for detection of disease markers in saliva. The microfluidic chip performs rapid immunoassays (< 3-10 minutes) with low sample volume requirements (10 μ L) and appreciable sensitivity (nM-pM). The microfluidic device is being tested by detecting biomarkers in saliva samples from patients diagnosed with periodontal disease.

We are also developing integrated microfluidic systems for real-time interrogation of single cells to study cellular signaling involved in innate immunity. Our goal is to quantitatively measure components of TLR4 signaling pathway in macrophages challenged with lipopolysaccharide and pathogenic bacteria.

IEC 66

On bioseparations and gas antisolvent precipitation in the isolation of sclareol

Xenia Tombokan¹, **Remil Aguda**¹, **David Danehower**², **Ruben G Carbonell**¹, and **Peter K Kilpatrick**¹. (1) *Department of Chemical and Biomolecular Engineering, North Carolina State University, EB1, 911 Partners Way, Raleigh, NC 27695-7905, Fax: 919-515-3465, peter_kilpatrick@ncsu.edu*, (2) *Department of Crop Science, North Carolina State University, Raleigh, NC 27695*

Over the past 24 years, Ruben Carbonell and I have collaborated on 30 papers and 8 patents, mostly associated with protein purification and the interaction of proteins and macromolecules with surfaces. The theme throughout the majority of this work was creating new molecules and molecular assemblies with surface-active properties, affinity for binding proteins, and colloidal dimensions. In this retrospective, I will review some of the highlights of that research, with a particular emphasis on the collection of insights that came together with each innovation. I will conclude with a vignette focused on the latest research collaboration in which we have used the novel thermodynamic properties of carbon dioxide swollen organic solvents to separate nutraceuticals from plant materials.

IEC 67

On the consequences of being a colleague of Ruben G. Carbonell

Jan Genzer, Department of Chemical and Biomolecular Engineering, North Carolina State University, 911 Partners Way, EB1, Raleigh, NC 27695-7905, jan_genzer@ncsu.edu

A brief account of a few projects from the area of surface engineering using soft materials will be presented. These projects have one common theme: they all have been inspired by the work of my colleague, Ruben G. Carbonell. Specifically, in the first part of my presentation I will describe computer simulation work pertaining to the pattern recognition of synthetic polymers adsorbing onto physically flat but chemically heterogeneous substrates. The second part of my talk will deal with adsorption of proteins on engineered substrates. Here, I will demonstrate that substrate-bound assemblies of polymers with gradually-varying density and length provide a unique platform for systematic investigation of protein partitioning on man-made surfaces.

IEC 68

Polymer-inorganic hybrid materials: A platform to broaden the viability of large scale membrane applications

William J. Koros, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0100, Fax: 404-385-2683, wjk@che.gatech.edu

Energy and environmental challenges caused by global development are attractive targets for membranes as population expands and emerging economies compete for resources. Conventional solution-processable polymers and inorganic materials each have limitations that currently prevent their use

across the full spectrum of membrane-based separation applications. For polymers, penetrant size and shape-discriminating ability is often lower than desired. On the other hand, for pure inorganic membranes, brittleness and high manufacturing cost are drawbacks. Ideally, hybrid materials comprising blends of organic and inorganic materials can be formulated to combine the best characteristics of each of the components.

Besides offering technical advantages, hybrids are compatible with existing economical processes for membrane formation. This compatibility is valuable, since maintaining attractive economics is crucial to compete successfully with other separation technologies. Some examples of these types of materials that offer the greatest promised will be discussed to illustrate the above issues, challenges and opportunities.

IEC 69

Rate processes in dissolution and adsorption processes of polymer

Christine Grant and Yazan Hussain, Department of Chemical Engineering, NC State University, 911 Partners Way, Raleigh, NC 27695-7905, grant@unity.ncsu.edu

The dissolution kinetics of polymeric materials in CO₂ is crucial to the understanding, design and control of CO₂-based environmentally benign processes. This study utilizes a novel advanced microweighing process (high pressure quartz crystal microbalance (QCM)) to monitor and evaluate the dissolution of poly(1,1-dihydroperfluorooctyl methacrylate-r-2-tetrahydropyranyl methacrylate), poly(FOMA-r-THPMA), polymer films in supercritical CO₂ over a range of temperatures and pressures. Polymer dissolution rates at the range of pressures studied were evaluated to quantify the dissolution kinetics for the polymer. The experiments revealed that the polymer dissolution in supercritical CO₂ undergoes two apparent processes: a rapid absorption of CO₂ into the polymer film followed by a gradual dissolution of polymer film into the CO₂ at the polymer- CO₂ interface. The nature of these interfacial phenomena and their associated effect on the rate are discussed. Future work related to emerging issues in biomaterials applications of the films will also be presented.

IEC 70

Polymeric chelating-adsorbents and their application in the development of novel strategies to purify proteins and metal ions from aqueous solutions

Lian Wang¹, Omar Gonzalez¹, Brenda Verdugo¹, Javier Garcia¹, Jerker Porath², and **Roberto Guzman**¹. (1) Department of Chemical and Environmental

Engineering, University of Arizona, University Blv and Park, Tucson, AZ 85721, Fax: 520-621-6048, guzman@engr.arizona.edu, (2) Department of Biochemistry and Biochemical Separation Centre, Uppsala University, Uppsala S-75123, Sweden

Here we present an approach to obtain selective peptide separations by combining molecular size effects and specific affinities in adsorption procedures. This involves the incorporation of polymer- permeation control where specific ligands and a polymer are bound to an adsorbent. The polymer serves as barrier for large proteins. Thus only molecules of a certain size are able to penetrate the polymer and bind to the ligand on the surface. If these permeable molecules have affinity for the bound ligands, they are retained, other permeable solutes with no affinity will not. IMAC interactions with iminodiacetic acid (IDA) and polyethylene glycol (PEG) were used as a model system. IMAC technology was also used as arsenic adsorbents based on binding to chelating polymers. In this approach carboxymethylated-polyethyleimine-grafted-agar is used to bind metal ions with arsenic affinities, these in turn function as adsorption sites for arsenic. Arsenic can be removed from water by adsorption on the polymer-immobilized metal ions. Arsenic can be subsequently eluted as concentrated soluble alkali arsenate and subsequently precipitated. This method generates very small amounts of waste products in the form of non-bulky concentrated arsenicals. The adsorbents can, in principle, be regenerated indefinitely.

IEC 71

Diffusion prediction model of enzymes on IMAC chromatography

Ruth Gutiérrez, Eva M. Martín del Valle, and Miguel A. Galán, Department of Chemical Engineering, University of Salamanca, Plaza de Los Caidos, Salamanca 37008, Spain, emvalle@usal.es

A theoretical model to predict the effective diffusion coefficient of enzymes in adsorption processes as immobilized metal ion affinity chromatography (IMAC) has been proposed. The model is based on the generalized Stokes-Einstein equation, taking into account the contribution the surface diffusion has on the adsorption process. The hard-core two-Yukawa model with mean spherical approximation is introduced to evaluate the influence of thermodynamic interactions on the effective diffusion coefficient. From the comparison with the experimental effective diffusion coefficients, as determined in IMAC by dynamic methods, it can be concluded that the hard-core two- Yukawa model coupled with the sedimentation coefficient and with the surface diffusion contribution is a good theory to predict the behaviour of the effective diffusion coefficient of dilute enzyme solutions in electrolyte suspensions related to the pH of the medium.

IEC 72

Crystallization science and technology, past, present and future

Allan S. Myerson, Chemical and Biological Engineering, Illinois Institute of Technology, 10 W. 33rd St., Chicago, IL 60616, Fax: 312-567-7018, myerson@iit.edu

Crystallization from solution is an important separation and purification method used in pharmaceutical, chemical and food industries. The goals of crystallization processes include product purity, size, shape and correct crystal form (polymorph).

The current status of crystallization science and technology will be reviewed and discussed along with potential future research and technological advances.

IEC 73

Crystal engineering molecules

Leonard R. MacGillivray, Department of Chemistry, University of Iowa, 305 Chemistry Building, Iowa City, IA 52224, len-macgillivray@uiowa.edu

Molecular co-crystals provide an exciting opportunity to apply principles of organic and supramolecular chemistry to construct solids that exhibit tunable properties. The modular nature of the approach means that molecules can be readily replaced to determine affects of molecular size, shape, and functionality on the solid-state assembly process. This can be particularly appealing in a case where a robust structural unit, or supramolecular synthon, is known to affect a bulk physical property. In this presentation, we will demonstrate how molecular cocrystals can be constructed to affect chemical reactivity in the solid state. We will also discuss how molecular cocrystals can be developed to design organic semiconductors and pharmaceutical materials.

IEC 74

Polarization switching of crystal structure in the nonphotochemical laser-induced nucleation of supersaturated aqueous l-histidine

Bruce A. Garetz¹, Xiaoying Sun¹, and Allan S. Myerson². (1) Department of Chemical & Biological Sciences, Polytechnic University, 6 Metrotech Center, Brooklyn, NY 11201, bgaretz@duke.poly.edu, (2) Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616

Polarization switching of polymorphs has been observed in the non-photochemical laser-induced nucleation of aqueous L-histidine in the supersaturation range 1.40-1.60. Exposure of solutions to 0.24-GW/cm², 7-ns pulses of 532-nm light induced the nucleation of different polymorphs of L-histidine depending on polarization state of the light. Circularly polarized laser pulses tended to nucleate the orthorhombic A polymorph, whereas linearly polarized pulses tended to nucleate a mixture of the orthorhombic A and monoclinic B polymorphs. Higher supersaturation also favors the formation of mixed polymorphs. These observations support the hypothesis that the laser is organizing hydrogen-bonded groups of histidine molecules through an optical Kerr alignment.

IEC 75

Transforming pharmaceutical crystals to cocrystals by reaction crystallization methods

Nair Rodriguez-Hornedo, Adivaraha Jayasankar, Sarah J. Nehm, David J. Good, and L. Sreenivas Reddy, Department of Pharmaceutical Sciences, University of Michigan, 428 Church Street, Ann Arbor, MI 48109-1065, Fax: 734-615-6162, nrh@umich.edu

Active pharmaceutical ingredient (API) cocrystallization is an emerging research field of pharmaceutical relevance. Cocrystals are multicomponent solids with different physicochemical properties from the native API. Much of the focus in this field has been on the design and screening of cocrystals based on supramolecular concepts. Cocrystal synthesis is generally carried out by slow solvent-evaporation or cogrinding methods that are empirically based and not transferable to large scale processes. This talk will present cocrystal phase solubility diagrams, derived using mathematical models based on cocrystal and solution chemistry. These models explain the effects of ligand concentration, solution complexation, and ionization on cocrystal solubility and supersaturation. A Reaction Crystallization Method (RCM) for cocrystal screening and synthesis based on the above principles is applied to various systems including the generation of cocrystals by moisture sorption of crystals.

IEC 76

What do polymorphs teach us about nucleation and crystal growth?

Lian Yu¹, Jing Tao², Ye Sun³, Hanmi Xi², and Mark D. Ediger⁴. (1) School of Pharmacy and Department of Chemistry, University of Wisconsin - Madison, 777 Highland Avenue, Madison, WI 53705, lyu@pharmacy.wisc.edu, (2) School of Pharmacy, University of Wisconsin - Madison, Madison, WI 53705, (3)

*Department of Chemistry, University of Wisconsin - Madison, Madison, WI, (4)
Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*

The ability of a liquid to crystallize as multiple polymorphs is not only a phenomenon of industrial importance but also an opportunity to study nucleation and crystal growth. Precedents exist of using polymorphs to test principles of thermodynamics and structure-property relations. With the aid of polymorphs, we studied the heterogeneous nucleation of one crystalline phase on the advancing growth front of another. The fast-nucleating polymorph is not ensured to be the product of crystallization, but may nucleate another, faster-growing polymorph. We have also used polymorphs to study the diffusionless crystal growth that abruptly activates in certain fragile organic liquids near the glass transition temperature. For the ROY system, currently the top system for the number of coexisting polymorphs of solved structures, diffusionless growth exists for some polymorphs but not others, with those showing the growth mode being denser and more isotropically packed.

IEC 77

The influence of cadmium and temperature on crystallization of apoferritin

Ronald W. Rousseau, Karsten Bartling, and Athanassios Sambanis, School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0100, Fax: 404-385-0185, rwr@chbe.gatech.edu

Protein crystallization is used for purification, storage and x-ray structure analysis. But it also is of significance in the development and manifestation of certain human diseases. For example sickle-cell anemia belongs to the type of protein condensation diseases in which the underlying pathology involves a loss of protein solubility. Furthermore, cataracts are usually considered a protein condensation disease associated with protein precipitation or possibly protein crystallization. Clues in lens physiology and biochemistry in normal as well as cataractous lenses led us to investigate cataracts from the standpoint of protein crystallization. We have focused on Hereditary Hyperferritinemia Cataract Syndrome (HHCS) as a model system. HHCS is characterized by early onset of cataract formation, and the protein deposits that cause the lens to turn opaque were determined to be apoferritin crystals.

We have investigated the influence of temperature and divalent cations, as well as the effect of the tissue origin of apoferritin, on the onset of crystal formation. Additionally, different additives and their potential ability to delay the onset of crystallization have been tested. The initial evidence supports an hypothesis that the additives modify protein solubility and therefore expand the domain of conditions under which the protein remains in solution.

Protein crystallization experiments were performed in vitro to determine the short "range protein" protein interactions and the physicochemical factors influencing them, such as temperature and nature of the divalent cation precipitant. Dilute protein-protein interactions in the liquid phase were evaluated by measuring the osmotic second virial coefficient of solutions via static light scattering. Correlations between the osmotic second virial coefficient and the protein crystallization or precipitation outcome were determined and present the possibility of using this correlation to establish the potential of the disease to occur.

IEC 78

Utilization of hydrophilic ionic liquids in separations: Understanding and taming complexity

Robin D. Rogers¹, *Meghna Dilip*², *Nicholas J. Bridges*², *Marcin Smiglak*², *David B. Cordes*², *Katarzyna Materna*², and *Guillermo Moyna*³. (1) Department of Chemistry and Center for Green Manufacturing / School of Chemistry and Chemical Engineering, The University of Alabama, Tuscaloosa / The Queen's University of Belfast, Stranmillis Road, Belfast, Northern Ireland BT9 5AG, United Kingdom, Fax: 44 - (0)28 - 90974606, rdrogers@bama.ua.edu, (2) Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, AL 35487, (3) West Center for Computational Chemistry and Drug Design and Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia, Philadelphia, PA 19104

Hydrophilic ionic liquids can be used in aqueous phase separations via their salting-out and formation of aqueous biphasic systems, ABS, (e.g. aqueous [C4mim]Cl/K3PO4). For wider and more "intelligent" application, it is important to look below the surface and study these systems thoroughly at a fundamental level. Here we present our work to understand these salt/salt ABS, including phase diagrams (where for example it can be shown that these ionic liquid (IL) solutions generally exhibit upper critical solution type solution behavior) and DSC studies demonstrating the chaotropicity of the ILs studied. Clearly the role of water is critical to the behavior of these ABS, thus we have also studied IL solutions and inorganic salt solutions separately in order to isolate ion association and the interactions with water. The results of these studies will be presented.

IEC 79

Measurement and correlation of vapor-liquid equilibrium data for hexamethyl disilazane, hexane and hexamethyl disiloxane binary systems

Liucheng Wang¹, Hongqi Wu¹, Lei Li², Jianhong Zhao¹, and Chengying Song¹.
(1) College of Chemical Engineering, ZhengZhou University, No.100 of Science Road, ZhengZhou 450001, China, Fax: +86-371-67781027, wanglc@zzu.edu.cn,
(2) College of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China

HMDS-hexane, HMDS-hexamethyl disiloxane and hexamethyl disiloxane-hexane binary systems isobaric(101.30kPa) vapor-liquid equilibrium(VLE) data were measured with a modified Rose still. The experimental data were tested by area test method and showed that the VLE data conformed to the demand of thermodynamic consistency. Wilson, NRTL, Margules and Van Laar models were used to correlate the experimental data, the results showed the calculated data from Wilson and NRTL models accorded well with the experimental data, and could satisfy the request of industrialization. The VLE data provided essential theory for separation and purification of the HMDS.

IEC 80

Leachability and flame retardancy of wood treated with metaborates

Gao Ming and Yan Yuqing, Department of Environmental Engineering, North China Institute of Science & Technology, Box 206, Yanjiao Beijing 101601, China, gaoming@ncist.edu.cn

Wood specimens were first impregnated by a saturated borax solution and then diffuse-penetrated with Zn²⁺, Ca²⁺, or Pb²⁺ solution, which was called double-diffusion treatment to form the precipitates of metaborates in wood specimens. Their leachability in running water was evaluated. The precipitates of the three metaborates in the wood proved to be insoluble or hardly soluble in water by the leaching test, and the best leachability for that by double-diffusion treatment with Pb²⁺ solution. Their flame retardancy was evaluated by limiting oxygen index (LOI) and cone calorimeter. The resultant data showed that their flame retardancy and smoke suspension were increased by the double-diffusion treatment, and the best for that by the treatment with Zn²⁺ solution.

IEC 81

Studies on direct electrosynthesis conditions of 2-pyridinecarboxylic acid in the plate and frame electrolytic cell

Cheng-Ying Song, Shao-Hua Jin, Jian-Hong Zhao, and Liu-Cheng Wang, College of Chemical Engineering, Zhengzhou University, No.100 of Science Road, Zhengzhou 450001, China, Fax: +86-371-67781027, songcy@zzu.edu.cn

2-Pyridinecarboxylic acid (2-PCA) is prepared from 2-methylpyridine (2-MP) by direct electrooxidation method in sulfuric acid solution with Ti/PbO₂ as anode and Pb as cathode in the plate and frame electrolytic cell, which was separated by a cation-exchange membrane. Effects of mass fraction of 2-MP and the mass fraction of H₂SO₄ in anodic solution, charge amount, current density and reaction temperature on the yield and current efficiency were studied. Under the preferable reaction conditions of the mass fraction of 2-MP 6 %, the mass fraction of the H₂SO₄ in anodic solution 25 %, charge amount 0.5 times of theoretical value, current density 50 mA/cm² and temperature 50°C, parallel test results showed that mean yield of 2-PCA was 94.19 % and mean current efficiency was 57.29 %. With an improved operation method, the production cost of 2-PCA was decreased as wastage of H₂SO₄ was reduced in the process of producing unit mass of 2-PCA.

IEC 82

Analytical modeling of CO₂ separation through facilitated transport membranes containing amines as carrier

Aliakbar Heydari Gorji and Tahereh Kaghazchi, Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), No. 424 Hafez Avenue, Tehran 15875-4413, Iran, Tehran 15875-4413, Iran, a.heydari@sazeh.co.ir, kaghazch@aut.ac.ir

An analytical solution for the facilitated transport of carbon dioxide across a liquid membrane containing primary and secondary amine solutions as carrier has been developed where the reversible reaction $A(\text{CO}_2) + 2B(\text{amine}) \rightleftharpoons AB(\text{carbamate}) + BH(\text{protonated amine})$ occurs inside the liquid membranes. This mathematical model solves the dimensionless, nonlinear diffusion-reaction transport problem for CO₂ facilitated transport through facilitated transport membranes and predicts the facilitation factors for the range from the physical diffusion regime to the equilibrium chemical reaction regime, considering the unequal complexes and carrier diffusivities and cases of zero and nonzero permeate side solute concentrations. In the present mathematical model, constant free carrier concentration is assumed throughout the membrane phase. This theoretical model can provide a quick and reasonable prediction of facilitation factor in comparison with numerical results.

IEC 83

Auger parameters applied to radiation detection materials

Dale L. Perry¹, Andrew Olson², Erik Topp³, Zhixun Ma¹, and Samuel S. Mao¹. (1) Lawrence Berkeley National Laboratory, # 1 Cyclotron Road, Berkeley, CA

94720, (2) Carleton College, Northfield, MN 55057, (3) College of Chemistry & Chemical Engineering, University of California, Berkeley, CA 94720

The present research discusses the use of X-ray photoelectron and Auger spectroscopy to study the bonding of solid-state radiation detection materials that are useful for detecting various types of nuclear radiation. The two types of spectroscopies, when used in tandem with one another, allow one to derive what are known as Auger parameters. The core levels of the X-ray photoelectron spectrum of an element and the Auger kinetic energy lines are used to define these parameters, whose values are dependent on the chemical state for a particular element in a compound or material. This approach is useful for looking at chemical heterogeneities that form in materials during the fabrication process and films that form on these materials due to interaction with air and other fluids in the processing phase. This work was supported by the U. S. DOE under Contract No. DE-AC0205CH11231 and NA-22 of the NNSA.

IEC 84

X-ray photoelectron and Auger studies of rare earth-doped telluride semiconductors

*Dale L. Perry¹, **Andrew Olson²**, Erik Topp³, Zhixun Ma¹, and Samuel S. Mao¹. (1) Lawrence Berkeley National Laboratory, # 1 Cyclotron Road, Berkeley, CA 94720, (2) Carleton College, 300 N College Street, Northfield, MN 55057, (3) College of Chemistry & Chemical Engineering, University of California, Berkeley, CA 94720*

Zinc telluride is a well-characterized semiconductor used in a variety of electronic devices. As cadmium zinc telluride (CZT), it is valuable for X-ray and gamma-ray detections materials and solar cells. In the case of zinc telluride doped with gadolinium (ZnTe:Gd), there is high expectation that the material will be suitable for use as a semiconductor and radiation detector making use of gadolinium's large neutron capture cross-section. Here, (ZnTe:Gd) has been extensively characterized by X-ray photoelectron (XPS) and Auger electron spectroscopy (AES) in order to determine the chemical states and shifts in electronic energy levels of the elements present in the material. Chemical shifts of gadolinium, zinc, and tellurium photoelectron and Auger lines are compared to analogous lines in various other similar compounds that have been studied. This work was supported by the U. S. DOE under Contract No. DE-AC0205CH11231 and NA-22 of the NNSA.

IEC 85

Biocidal polyurethane coating

Lei Kou¹, Akin Akdag¹, Xuehong Ren¹, J. Liang², Changyun Zhu¹, S. D. Worley¹, and T. S. Huang³. (1) Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, koulei1@auburn.edu, (2) Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, (3) Department of Nutrition and Food Science, Auburn University, Auburn, AL 36849

Several precursor N-halamine monomers were synthesized and reacted with commercial polyol and diisocyanate to produce polyurethane coatings on plastic surfaces. Exposure to household bleach solution rendered the cured coatings biocidal. Upon loss of the biocidal property due to long-term use, the coated surfaces could be recharged by further exposure to household bleach solution to regain biocidal activity. The biocidal coatings were used to inactivate both Gram-positive and Gram-negative pathogenic bacteria, which could cause infectious disease.

IEC 86

Synthesis and application of a novel biocidal polymer

Changyun Zhu¹, Akin Akdag¹, Xuehong Ren¹, Lei Kou¹, S. D. Worley¹, and T. S. Huang². (1) Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, zhuchan@auburn.edu, (2) Department of Nutrition and Food Science, Auburn University, Auburn, AL 36849

The new N-halamine monomer, 3-(3'-allyl-5'-methylhydantoinyl)acetanilide (AMHA), was synthesized and copolymerized with commercial vinyl acetate (VAC) to form copolymer VAC-co- AMHA film coatings. The films were characterized by NMR, FTIR, and DSC. The films gained biocidal character after treatment with household bleach; they inactivated E.coli in 10 min contact time and killed S. aureus in 5 min contact time, and thus were effective in inactivating both Gram-positive and Gram-negative bacteria. This copolymer has many potential applications for medical devices, hygienic materials, and the food-processing industries.

IEC 87

Nanosized antimicrobial polyarylonitrile fiber

Xuehong Ren¹, S. D. Worley¹, Lei Kou¹, Akin Akdag¹, Changyun Zhu¹, and T. S. Huang². (1) Chemistry and Biochemistry, Auburn University, Auburn, AL 36849, renxueh@auburn.edu, (2) Department of Nutrition and Food Science, Auburn University, Auburn, AL 36849

An N-halamine precursor material was synthesized in our laboratory and loaded onto electro-spun polyarylonitrile fiber which could be rendered antimicrobial by exposure to household bleach. The ultra-fine fibers with diameter from 200 to 600 nm were formed and then characterized by SEM. The chlorinated nanofibrous mats were challenged with *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* 0157:H7 (ATCC 43895) and provided promising efficacies against the two bacterial species. Potential uses of the antimicrobial fibers include water and air filters and protective clothing.

IEC 88

Correlation of polymeric molecular structure with ablation energy

Christopher T. Lloyd and Robert F. Cozzens, Chemistry Division, Naval Research Laboratory, 4555 Overlook AVE, SW, Washington, DC 20375, christopher.lloyd@nrl.navy.mil

Ablative processes involving polymers are commonly used in the manufacturing of several types of commercial goods. It is necessary to understand the relationship of materials with respect to laser interaction before any such process is attempted. The damage mechanisms that polymers undergo during laser irradiation and their corresponding ablation energies can provide valuable insight as to polymeric molecular structure. At sufficiently high irradiation thresholds, some polymers can depolymerize (unzip), leading to clean ablation, while others undergo random scissioning resulting in char formation, clean ablation or some degree of both. The molecular make-up of the polymer is responsible for how it reacts upon irradiation. Determining polymeric structure in terms of aromaticity, degree and type of crosslink and molecular weight can be used to estimate relative ablation energy and predict the degree of char formation before experimental testing is performed. Unknown polymeric structures can also be identified from laser ablation characteristics such as magnitude of the ablation energy, degree of char formation, etc. This research focuses on high intensity laser ablation (at 1 micron) of common polymers with varying polymeric structure with the goal of correlating polymer structure with the mechanism of laser ablation.

IEC 89

Designing amine-based solid sorbents for carbon dioxide capture in simulated flue gas conditions

Jeffrey H. Drese¹, Jason C. Hicks¹, Daniel J. Fauth², McMahan L. Gray³, and Christopher W. Jones⁴. (1) School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, NW, Atlanta, GA 30332-0100,

Fax: 404-894-2866, jeffrey.drese@chbe.gatech.edu, (2) U.S. Department of Energy, National Energy Technology Laboratory (NETL), Pittsburgh, PA 15236-0940, (3) Separations and Fuels Processing Division, U.S. Department of Energy, Pittsburgh, PA 15235, (4) School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0400

Solid regenerable sorbents for use in carbon dioxide capture from flue gas streams have been designed to combat global climate change. Sorbents that chemically bind CO₂ and can be fully regenerated by temperature swing are promising alternatives to energy intensive absorption using aqueous amines. In this work, mesoporous silicas were functionalized with primary amines, diamines, and hyper-branched poly(ethylenimine)s using silane or related chemistries. Physisorbed aminosilicas were also synthesized for comparison. Capture capacities were measured in a flow system consisting of a fixed bed reactor and mass spectrometer. Dilution effects, which result from switching inlet gases, can be negated by subtracting backgrounds run on unmodified silica from subsequent measurements. Due to these corrections, capacities for typical aminosilica materials are lower than suggested literature values. In contrast, our new hybrid aminosilica-polymer material has high capacity (8 times higher) at moderate temperatures (25-75 °C) and is fully regenerable over 10+ cycles.

IEC 90

Dielectric properties of surface treated barium strontium titanate powder-polybenzoxazine composite

Nidchakarn Krueson, Department of Polymer Science, The Petroleum and Petrochemical College, Chulalongkorn University, Phayathai Road, Soi Chula 12, Pathumwan, Bangkok 10330, Thailand, pretty_nidchy@hotmail.com, Hathaikarn Manuspiya, Department of Polymer Science, Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand, and Hatsuo Ishida, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202

This research was purposed a novel BST powder-polybenzoxazine composite as a new dielectric material. In this work, the dielectric properties of surface treated BST powder- polybenzoxazine composite were studied. The surface of BST powder was modified by using two different chemicals: 3-aminopropyl-trimethoxysilane and benzoxazine monomer. The distribution of BST powder in polybenzoxazine matrix was observed by SEM. The dielectric properties (dielectric constant and dielectric loss) of the composites with a function of frequency (1 kHz-10 MHz) at room temperature were investigated by LCR meter. It was found that the composites with modified BST powders showed good distribution in polybenzoxazine matrix and the dielectric properties could also be enhanced than those with untreated BST powder. Comparing between silane

and benzoxazine modification, the composite with silane modified BST powder showed higher dielectric constant and lower dielectric loss than the composite with benzoxazine monomer modification.

IEC 91

Efficient synthesis of 5'-O- propionyl 5-fluorouridine via highly regioselective acylation catalyzed by Novozym 435 in cosolvent mixtures

Huai Wang¹, Jian Wu², and Min Hua Zong². (1) School of Chemistry and Engineering, Hefei University of Technology, Tunxi Road 193#, Baohe District, Hefei 230009, China, whuai76@gmail.com, (2) Laboratory of Applied Biocatalysis, South China University of Technology, Guangzhou 510640, China

For the first time, a comparative study was made of Novozym 435-catalyzed acylation of 5-fluorouridine with vinyl propionate for the preparation of its 5'-O-monoester in various co-solvent mixtures and pure organic solvents. Novozym 435 exhibited a high regioselectivity (98%) towards the 5'-hydroxyl of 5-fluorouridine, giving 5'-O-monoester exclusively. The reaction proceeded with much higher rate and substrate conversion in the co-solvent mixture of tetrahydrofuran and acetone than in other co-solvent mixtures and pure solvents tested. The polarity of the co-solvent mixture had strong link with the reaction rate. Additionally, the acylation was dependent on the tetrahydrofuran content and the water activity of the co-solvent mixture and reaction temperature as well, with 20 % (v/v), 0.07 and 55 °C being the optimal reaction parameters, respectively, under which the maximum substrate conversion was 98.4%. The high efficient, facile and mild nature of the procedure makes it promising for industrial application.

IEC 92

Evaluation of ionic liquids as green separation agents for the capture of carbon dioxide and sulfur dioxide

Samuel A Morton III, Department of Chemical Engineering, Lafayette College, 266 Acopian Engineering Center, Easton, PA 18042, Fax: 610-330-5059, mortons@lafayette.edu

One concern for the sustainable recovery of carbon dioxide from fossil fuel combustion waste gas streams using aqueous-based biological approaches is the potential negative impacts of secondary gases such as sulfur dioxide. This study experimentally determined the ability of a range of room-temperature ionic liquids and ionic liquid-based mixtures to absorb the combustion-related acid gases, carbon dioxide and sulfur dioxide, from gas streams. Ionic liquids are

novel organic salts that are liquids at or near room temperature. These solvents have a negligible vapor pressure and a wide range of physical property tunability due to the vast number of potential anion-cation combinations. This study employs an inexpensive and rapid quartz-crystal microbalance (QCM) method to determine the efficacy of ionic liquids for use in gas purification applications. Additionally, attention will be paid to the variation of results with respect to ionic liquid structural composition.

IEC 93

Fe-containing ionic liquids for deep desulfurization

Nan Hee Ko¹, Eunsoo Huh², Hyunjoo Lee³, Hoon Sik Kim¹, and Minserk Cheong¹. (1) Department of Chemistry, Kyung Hee University, 1 Hoegi-dong, Dongdaemooon-gu, Seoul, South Korea, ophelia015@hotmail.com, (2) Kyung Hee University, Seoul, South Korea, (3) Division of Environment & Process Technology, Korea Institute of Science & Technology, Seoul 130-650, South Korea

Recently, deep desulfurization of gasoline and diesel oil has attracted much attention, due to the increasing demand of lower S-content diesel oil and gasoline, because sulfur-containing compounds is a source of SO_x. Current hydrodesulfurization (HDS) process, however, has a limitation in removing S-compounds such as DBT and 4,6-Dimethyl-dibenzothiophene. In this regard, extraction of S-compounds from oil by ionic liquids (ILs) could be a promising alternative to conventional HDS. Sulfur-containing compounds which are hard to remove by HDS have been successfully removed under mild condition using various Fe-containing imidazolium-based ionic liquids.

IEC 94

High performance organic thin film transistor using 6, 13-bis(4-pentylphenylethynyl) pentacene by ink-jet printing

Sun Hee Lee¹, Seung Hoon Han¹, Min Hee Choi¹, Yong Hee Kim¹, Ji Young Jeon², Jae Yeol Lee², Jin Jang¹, and Dong Joon Choo². (1) Advanced Display Research Center & Dept. of Information Display, Kyung Hee University, 1 Hoegi-dong, Dongdaemooon-gu, Seoul 130-701, South Korea, Fax: 82-961-9154, shlee@tftlcd.khu.ac.kr, (2) Department of Chemistry, Kyung Hee University, Seoul 130-701, South Korea

We have prepared the ink-jet printed organic thin-film transistor (OTFT) employing 6, 13-bis(4-pentylphenylethynyl) pentacene as an active material which had been synthesized by a 1-step reaction starting from 6, 13-

pentaquinone. The material was easily dissolved in the aromatic organic solvents of high boiling points and provided the 2 wt% solution having a suitable viscosity for ink-jet printing. Substitution with an appropriate solubilizing ethynyl group, which is expected to extend the π -electron delocalization of the pentacene core at the 6- and 13-positions, leads to an enhancement in both solubility and photooxidative stability of the organic semiconductor. To improve the OTFT characteristics, the solution of 6, 13-bis(4-pentylphenylethynyl) pentacene was printed at the substrate temperature of 60 °C by an overlapping method. Treatment of the gate dielectric surface with various self-assembled monolayer materials such as octadecyltrichlorosilane resulted in the much improved device characteristics. Analyses of the semiconductor layer by XRD, AFM and optical microscopy image revealed that the surface properties differ depending on the experimental conditions. The initial OTFT exhibited an on/off current ratio of $\sim 10^6$, a threshold voltage of 5 V, a gate voltage swing of 0.8 V/decade and a field-effect mobility of 0.0063 cm²/Vs in the saturation region.

IEC 95

Mechanical properties of polyimide composites reinforced by multiwalled carbon nanotubes

Xinfei Gu and Qinghua Zhang, Department of Polymer Science and Engineering, Donghua University, 2999 Renmin Rd. (N), Songjiang District, Shanghai 201620, China, qhzhang@dhu.edu.cn

Polyimide nanocomposites containing multiwalled carbon nanotubes (MWNTs) were prepared by incorporating the nanotubes into poly(amic acid) (PAA) in DMAc, followed by mixture casting, evaporation and thermal imidization. To increase the interfacial adhesion between polyimide matrix and MWNTs, MWNTs were purified with mixed strong acid. The measurement of mechanical properties showed that the loadings of 3 wt% MWNTs resulted in the increase of tensile strength and initial modulus by 30% and 100%, respectively; whereas, the elongation at break decreased as increasing MWNTs loadings. Dynamic mechanical analysis (DMA) indicated that the addition of MWNTs in polyimides increased the storage modulus of the composites, but did not affect glass transition temperatures. X-ray spectra of the nanocomposites exhibited that the MWNTs did not change the fact of amorphous polyimides.

IEC 96

Mechanism of phosphate removal from Hanford tank sludges by caustic leaching

Gregg J. Lumetta, Radiochemical Processing Group, Pacific Northwest National Laboratory, P.O. Box 999, MSIN P7-22, Richland, WA 99352, gregg.lumetta@pnl.gov

The Hanford Waste Treatment Plant (WTP) is being designed and constructed to process radioactive waste stored in underground tanks into stable waste forms for permanent disposal. One function of the WTP is to reduce the high-level waste volume to the extent economically practicable through application of leaching and ion exchange processes. Due to the relatively low tolerance for phosphorus in the borosilicate glass waste form, it is necessary to remove much of this element from the high-level waste. Caustic leaching is the primary means by which phosphorus will be removed from the Hanford HLW solids. No detailed mechanistic studies have been performed on the removal of phosphorus in the caustic leaching process. We report here the results of experiments performed with pure phosphate phases that have been identified to be present in the Hanford sludges: AlPO_4 , BiPO_4 , $\text{Ca}_3(\text{PO}_4)_2$, and $\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$. Each of these phosphate were treated with 3 M NaOH at 90°C and the solid phases were characterized by FTIR and Raman spectroscopies, and by XRD, both before and after treatment.

IEC 97

Microreactor technology for biodiesel production

P Zhang, United Environment & Energy, LLC, 111 Ridge Road, Horseheads, NY 14845, p-zhang@unitedee.com, and **Ben Wen**, United Environment & Energy LLC, Horseheads, NY 14845

Although interest in biodiesel is rapidly increasing, the process by which biodiesel is synthesized has not changed much in the last two decades. Currently, biodiesel is made commercially by a homogeneous catalyst based transesterification process wherein soybean oil is reacted with methanol in the presence of sodium methoxide. This process is far from being efficient, and the cost of biodiesel production is still high.

United Environment & Energy LLC has developed a structured catalytic micro-reactor for highly efficient, high throughput, and low cost biodiesel production. The successful application of this reactor in commercial biodiesel production will significantly increase biodiesel productivity, simplify product separation and purification, improve glycerin quality, and eliminate the washing step and associated waste stream, making it a revolutionary change to the current homogeneous catalyst process.

IEC 98

High efficiency nitrogen fertilizer production from coal power plant fly ash

P Zhang, United Environment & Energy, LLC, 111 Ridge Road, Horseheads, NY 14845, p-zhang@unitedee.com, and Ben Wen, United Environment & Energy LLC, Horseheads, NY 14845

This research concerns an innovative manufacturing technology for high efficiency nitrogen fertilizer from fly ash, which is a recycled material from coal power plants that may contain high concentrations of mercury and carbon. The traditional nitrogen fertilizers are water-soluble compounds, resulting in significant loss of fertilizer and pollution of streams and ground water. America's coal power plants produce more than 76.5 million tons of fly ash per year, and most of it is disposed of in landfills. The high mercury content in the fly ash makes the disposal more difficult and costly. In this study, the technical and commercial feasibility of converting the fly ash to high efficiency water-insoluble nitrogen fertilizer is verified. The optimal operating conditions for synthesizing the fertilizer and the rate of nitrogen release in the form of ammonia are determined. Additionally, the mercury in the fly ash is recovered.

IEC 99

Process improvement on the synthesis of menadione sodium bisulfite

Chengying Song, Hongzhi Shen, Liucheng Wang, and Jianhong Zhao, Chemical engineering, Zhengzhou University, No.100 of Science Road, Zhengzhou 450001, China, Fax: +86-371-67781027, songcy@zzu.edu.cn

In the synthesis of menadione sodium bisulfite (MSB), the traditional raw material 2-methyl- 1, 4-naphthoquinone (2-MNQ) contains 6-Methyl- 1, 4-naphthoquinone (6-MNQ), resulting in lower product. To improve product quality, 6-MNQ was separated and removed from the mixture of 2-MNQ, then 2-MNQ and sodium bisulfite react to obtain MSB in n-hexane solution. The ratio of raw materials, reaction temperature and reaction time to the effects of yield and mass fraction on synthesis of MSB were investigated, and the optimum process conditions were mole ratio of 2-MNQ to sodium bisulfite 1:1.45, reaction temperature 40°C and reaction time 4h. The results showed that after process improvement, yield of MSB was over 81 %, mass fraction of MSB was more than 98 %, and the improved synthetic procedure is practical and fit to popularize in industry, and the production cost is reduced.

IEC 100

Preparation and properties of carbon nanotubes and polyurethane nanocomposites

Qinghua Zhang, Zhenjun Chang, and Dajun Chen, Department of Polymer Science and Engineering, Donghua University, 2999 Renmin Rd. (N), Songjiang District, Shanghai 201620, China, qhzhang@dhu.edu.cn

Multiwalled carbon nanotubes (MWNTs) were purified by a mixed strong acid and then functionalized using epoxy. The resulting functionalized nanotubes (MWNT-Epoxy) exhibited a good solubility in organic solvents. Nanocomposites were prepared by casting a solution of MWNT-Epoxy and polyurethane (PU) in DMF. The incorporation of MWNT-Epoxy into the PU resulted in both the tensile strength and elongation at break of the elastic polymer. The tensile strength of the nanocomposite containing 5wt% MWNT-Epoxy was up to 39.7 MPa, while that pure of PU film was merely 22.5 MPa. The elastic recovery rates of the nanocomposites containing MWNT-Epoxy had a little increase. Rheological behaviors exhibited that the addition of MWNT-Epoxy increased the viscosity, storage modulus and loss modulus. These changes were maybe attributed to the fact that the nanotubes played a role of the physical crosslinking points.

IEC 101

Study on synthesis of diphenyl phosphorazidate using tetraethylammonium bromide as phase transfer catalyst

Jian-hong Zhao, Lei Li, Hong-qi Wu, Liu-cheng Wang, and Cheng-ying Song, College of Chemical Engineering, ZhengZhou University, No.100 of Science Road, ZhengZhou 450001, China, zhaojh@zzu.edu.cn

Diphenyl phosphorazidate (DPPA) is a useful and versatile reagent in organic synthesis. Using tetraethylammonium bromide as phase transfer catalyst, DPPA was synthesized via phase transfer catalysis method from diphenyl phosphorochloridate and sodium azide. The effects of reaction conditions were examined. The optimum conditions of the reaction were determined as following: molar ratio of diphenyl phosphorochloridate to sodium azide is 1:1.5, the mass fraction of catalyst to total is 4.3%, reaction time is 12 h, and reaction temperature is 30°C. Under the optimum conditions the yield of DPPA is 85.8%.

IEC 102

On the analytical solution to damped wave conduction and relaxation by hybridized methods of relativistic transformation and separation of variables

Kal Renganathan Sharma, Adjunct Professor, Department of Chemical Engineering, Prairie View A & M University, PO Box 519 MS 2505, A. E. Greaux

*Building, Room 206C, Prairie View, TX 77446, Fax: (936) 261 9419,
jyoti_kalpika@yahoo.com*

Eight reasons are provided to seek a generalized Fourier's law of heat conduction and relaxation. Sharma (2006) presented analytical solutions to the damped wave conduction and relaxation equation by four different methods for three different conditions. By use of the final condition in time for the wave temperature it was shown that bounded solution to the problem of finite slab subject to constant wall temperature on either sides can be found by the method of separation of variables. The governing equation was decomposed into a decaying component and wave component. The solution exhibited no discontinuities. In this study, a hybridized method of relativistic transformation and separation of variables is used to obtain the analytical solution to the problem of finite cylinder subject to constant wall temperature boundary condition. The relativistic transformation of coordinated $\eta = X^2 - \tau^2$ transforms the governing equation in cylindrical coordinates in the radial direction, into a equation in time and the transformed variable. This is solved by the method of separation of variables. The solution is presented as infinite series of Bessel function of the first kind and 1/2th order of the composite variable. The cn can be solved for by using the principle of orthogonality. This is a direct solution without any decomposition.

IEC 103

Three methods to solve the constant wall flux problem during damped wave conduction and relaxation

***Kal Renganathan Sharma**, Adjunct Professor, Department of Chemical Engineering, Prairie View A & M University, PO Box 519 MS 2505, A. E. Greaux Building, Room 206C, Prairie View, TX 77446, Fax: (936) 261 9419,
jyoti_kalpika@yahoo.com*

Eight reasons are given to seek a generalized Fourier's law of heat conduction and relaxation. Bounded solutions are obtained for the damped wave conduction and relaxation equation in one dimension in Cartesian coordinates for a semi-infinite medium subject to the constant wall flux boundary condition. Three different methods were employed. In the first approach the method of Laplace transforms was used. The solutions are domain restricted. Three regimes can be identified a) zero transferring regime; b) rising regime and c) falling regime. In the second approach a generalized substitution is used to transform the hyperbolic PDE into a parabolic PDE. The transform selected is one with spatiotemporal symmetry. The resulting parabolic PDE can be solved for using the Boltzmann transformation. In the third approach the damping term was first removed from the governing equation. The resulting equation was transformed into a Bessel differential equation using a spatiotemporal symmetric

transformation variable. An approximate solution for the flux was obtained. The inertial regime, rising and falling regimes were identified in the solution. Thus care must go into the selection of boundary and time conditions. It is not sufficient to solve the hyperbolic PDE mathematically correctly. It is intended for use to depict the transient heat conduction. The physical realities of heat conduction have to be borne in mind and consistent space and time conditions need be utilized. Only then the solutions are within the constraints of the second law of thermodynamics as well as depict transient heat conduction events better.

IEC 104

Preparation and pervaporation performances of PEA-based polyurethaneimide (PUI) membranes to benzene/cyclohexane mixture

Hong Ye, chemical engineering, Tsinghua University, Gong Wu Guan, Tsinghua University, 100084, Beijing 100084, China, Fax: 86-10-62770304, yehcn@163.com, and Jiding Li, Tsinghua University, China

Pervaporation is a promising technology in separation of benzene/cyclohexane mixture for petrochemical industry. It offers many advantages, such as high separation efficiency, low energy consumption and simple operation. Two kinds of poly(ethylene adipate)diol (PEA)-based polyurethaneimide (PUI) membranes were successfully synthesized from the same soft segment of PEA, and different hard segments via a two-step method. The hard segments of PEA-MDI-PMDA membranes were from 4,4'-methylene-bis(phenylisocyanate) (MDI) and pyromellitic dianhydride (PMDA), while those of PEA-TDI-PMDA were from toluene diisocyanate (TDI) and PMDA. The structures and properties of two kinds of PUI membranes were characterized by means of FT-IR, DSC and TGA. Besides, their pervaporation performances to benzene/cyclohexane mixture were also investigated. The results appeared that the two kinds of the membranes showed permeability and selectivity towards benzene. During the pervaporation experiment, the PEA-MDI-PMDA membranes had a flux of $12.13 \text{ kg } \mu\text{m m}^{-2} \text{ h}^{-1}$ and separation factor of 8.25, while the PEA-TDI-PMDA membranes had a flux of $3.68 \text{ kg } \mu\text{m m}^{-2} \text{ h}^{-1}$ and separation factor of 6.06 for 50 wt% benzene in the benzene/cyclohexane mixture at 40°C. The structures of hard segments and feed temperature had great effects on pervaporation performances. The investigation of relationship in molecular structure and PV performances will be helpful for the choice and design of membrane materials in the separation of benzene/cyclohexane mixture.

IEC 105

Modeling of non-isothermal crystallization kinetics of poly (vinylidene fluoride-co-hexafluoropropylene)

Jianhua Cao, Department of Chemical Engineering, Membrane Technology and Engineering Research Center, Tsinghua University, Beijing 100084, China, caojh@mem.tsinghua.edu.cn, **Jiding Li**, Department of Chemical Engineering, Tsinghua University, Beijing, China, **Baoku Zhu**, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China, and **Youyi Xu**, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Non-isothermal melt crystallization kinetics of Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was investigated via differential scanning calorimetry (DSC) measurement. The effect of cooling rate on the crystallinity and crystal rate was studied. Non-isothermal crystallization kinetics data obtained from DSC in conjunction with a non-linear regression method were employed to estimate the kinetic parameters of mathematical models describing the non-isothermal crystallization of PVDF-HFP. Avrami and Ozawa plots were used to describe the non-isothermal crystallizations. However, the Avrami treatment cannot predict the mechanisms of non-isothermal crystallizations for the PVDF-HFP, while the Ozawa explanation can be taken to reveal that the non-isothermal crystallization is dominated by heterogeneous nucleation. The activation energies of crystallization were calculated from the Kissinger equation. The non-isothermal crystallization kinetics presented here are the first for PVDF-HFP.

IEC 106

Prediction of activities of small molecules in polymer membrane materials with the UNIQUAC model

Junqi Huang, **Jiding Li**, **Xia Zhan**, **Yangzheng Lin**, and **Cuixian Chen**, Membrane Science and Technology, Tsinghua University, Beijing, China, huangjq06@mails.tsinghua.edu.cn

Estimation of the activities or solubilities of small molecules in polymers is of great significance in a number of process applications such as the mixture separation by polymeric membrane, polymeric membrane preparation, polymer preparation, especially, the selection of membrane material for a predefined separation process. In this paper, the original UNIQUAC model, with the new interaction parameters, has been used to predict the activities of various small molecules in various polymers. The influence of temperature and the molar mass of polymer on the activities of small molecules in the polymeric membrane are discussed. The results predicted by the UNIQUAC model are in good agreement with the experimental ones and the total average relative deviation between the experimental and the calculated is no more than 2%.

IEC 107

Preparation of PDMS-PVDF composite flat-sheet membranes: Application in recovery of propane from propane-nitrogen mixture

Jianhua Cao, Yangzheng Lin, Jiding Li, and Cuixian Chen, Membrane Technology and Engineering Research Center, Tsinghua University, Beijing 100084, China, caojh@mem.tsinghua.edu.cn

Microporous polyvinylidene fluoride (PVDF) flat-sheet membrane prepared using the dry-wet phase inversion was coated with cross-linkable polydimethylsiloxane (PDMS). Cross-section and surface structure of the composite membranes formed was examined using scan electron microscopy (SEM). Recovery of propane from propane/nitrogen mixtures was tested at a temperature of 16°C and pressure difference of 0.3MPa using the composite membranes obtained. Effects of the ratio of prepolymer and cross-linking agent, the cross-linking temperature on the permeability of propane and nitrogen and perm-selectivity of propane over nitrogen were investigated. From the SEM images, a much smoother membrane surface was observed on the coated PVDF membrane as compared to the coarse surface of the non-coated membrane and a uniform coating thickness of approximately 7-10µm was measured. Propane/nitrogen selectivity over 18.9 was obtained. The PDMS/PVDF composite membrane prepared in this work can be successfully used to separate propane/nitrogen mixtures.

IEC 108

Improvement on polydimethylsiloxane/polyvinylidene fluoride composite membranes for ethanol concentration from aqueous solution by pervaporation

Xia Zhan¹, Jiding Li², and Cuixian Chen². (1) Department of Chemical Engineering, Tsinghua University, Beijing 100084, China, zhan-x06@mails.tsinghua.edu.cn, (2) Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

The PDMS/PVDF composite membrane was prepared for ethanol concentration from aqueous solution by pervaporation. The improvement of combination for PDMS top layer and PVDF porous substrate was accomplished by adding three different reagents (γ-aminopropyltriethoxysilane (APTEOS), fluoro-containing polysiloxane, and hydrogen-containing polysiloxane respectively) into PDMS homogeneous solution. It was found that the influence of the three additives on the pervaporation performance were much different. APTEOS containing PDMS showed better combination with PVDF substrate, and much lower separation

factor compared with the others due to the increase of hydrophilicity of the membrane surface. And separation factor of PDMS with fluoro-containing polysiloxane and hydrogen-containing polysiloxane didn't change appreciably, and the total flux was much higher than that of common PDMS membranes.

IEC 109

Joe Breen: The heart and soul of green chemistry

Mary M. Kirchhoff, American Chemical Society, 1155 Sixteenth Street, NW, Washington, DC 20036, Fax: 202-872-8068, m_kirchhoff@acs.org

Joe Breen was a leading advocate for green chemistry and education. He spent 20 years working at the U.S. Environmental Protection Agency on such issues as lead poisoning, dioxins, and pollution prevention. Following retirement, Dr. Breen became executive director of the Green Chemistry Institute, a not-for-profit organization that promotes and fosters green chemistry. His untimely death on July 19, 1999, left a void within the green chemistry community that can only be filled by continuing his work in this field. Joe's twin passions, the environment and education, serve as the inspiration for this poster session, one that highlights the work being carried out by students in the area of green chemistry.

IEC 110

Preparation of ionic liquids and their use in the synthesis of polyamine analog reactions

Francis Charles Mayville Jr., Natural Science Department, DeSales University, Center Valley, PA 18034-9568, Fax: 610-282-0525, francis.mayville@desales.edu, and Kara Merancy, Natural Science Department, DeSales University, Center Valley, PA 18034, Fax: 610-282-0525, fcm0@desales.edu

This investigation will involve the preparation of several ionic liquids containing the 1-hexyl-3-methyl-imidazolium cation coupled to various anion systems. These ionic liquids can be substituted for typical organic solvents and used in the substitution reactions of spermidine to produce several spermidine analogs. There are many advantages for using these ionic liquids over organic solvents in synthesis reactions. Ionic liquids are recyclable, they can stabilize intermediates better than traditional solvents and the product yield is much higher. The ionic liquids can also be used for synthesis at lower temperatures and are a less toxic alternative to typical organic solvents.

IEC 111

A study of ionic liquids for applications in the continuous separation of butanol from fermentation media

Ashley A Jermusyk and Samuel A. Morton III, Department of Chemical Engineering, Lafayette College, 223A Acopian Engineering Center, Easton, PA 18042, Fax: 610-330-5059, jermusya@lafayette.edu

Alternatives to fossil fuels are being explored to meet the increasing demand for energy and the decreasing supply of natural resources. As an alternative, butanol has many advantages over ethanol: a higher energy value, lower vapor pressure, and decreased susceptibility to separation in the presence of water. The main obstacle to the economic viability of this process is the separation of the butanol from the fermentation broth. Ionic liquids could be used as solvents for the continuous removal of butanol by liquid-liquid extraction. To test the ability of this separation mechanism, the liquid-liquid equilibrium of butanol-water-ionic liquid using a range of hydrophobic ionic liquids will be studied. A similar study will also be conducted using fermentation media-butanol-ionic liquid, conducted at temperature relevant to fermentation. These studies will provide data that can be used to determine an appropriate ionic liquid for use with liquid-liquid extraction. New developments will also be studied.

IEC 112

Development of ionic liquid-supported catalysis by iminium activation

Amy L. Grote, Joseph M. Cosco, Nina R. Collins, and Richard J. Mullins, Department of Chemistry, Xavier University, 3800 Victory Parkway, Cincinnati, OH 45207-4221

An emerging topic in the area of organic synthesis involves the use of ionic liquid (IL) supported reagents, substrates and catalysts for greener synthetic processes. While several inorganic catalysts have been bound to ionic liquids, the binding of organic catalysts has not received as much attention. Although a few IL-supported proline derivatives have been explored, to date, no examples of IL-bound catalysis via iminium activation have been put forth. Thus, in our group, several novel ionic liquid-supported organocatalysts will be designed and synthesized for their application in green organic synthesis. These catalysts will be examined for their efficiency and selectivity in effecting a number of asymmetric transformations in ionic liquids. The enhanced ability to separate the organic products from the ionic liquid phase without extracting the catalyst will result in efficient and reusable catalyst/solvent systems. Our progress toward the development and application of these systems will be presented.

IEC 113

Cyclopropanation reactions using metal conjugates

Samit A. Patrawala, *Department of Chemistry, University of South Alabama, Chemistry Building (CHEM) , Room 223, Mobile, AL 36688-0002, Fax: 251-460-7359, dforbes@jaguar1.usouthal.edu*

Although total point source and fugitive emissions have been on a steady decline within the chemical industry, unacceptable levels of pollutants have still been released nationally and locally. Therefore, in order to reduce total air emissions, both point source and fugitive, the development and implementation of alternative technologies in chemical reactions has been one active area of research. A common alternative pathway includes the use of ionic liquid technologies. A transition metal complex covalently bound to an organic salt offers a unique opportunity to explore issues of catalysis in an ionic liquid medium. Ligand exchange of acetate with imidazolium functionality tethered to a carboxylic acid afforded the desired metal-conjugate. The modified dirhodium(II) dimer was found to be an effective catalyst in the intermolecular cyclopropanation reaction of styrene using ethyl diazoacetate.

IEC 114

Extraction of water soluble contaminants using water in carbon dioxide microemulsions with newly prepared CO₂-soluble amino acid-based surfactant

Woonha Kim, *Younja Kwon, and Hakwon Kim, Department of Chemistry and The Institute of Natural Science, Kyung Hee University, Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, South Korea, Fax: 82-31-202-7337, unha1323@nate.com*

We have designed and synthesized CO₂-soluble amino acid-based surfactants and evaluated their CO₂-solubility, microemulsion formation ability and extracting ability for removal of water-soluble contaminants, such as metal ions and some dyes. Proline, aspartic acid, valine and serine have been converted to the corresponding CO₂-soluble derivatives through the simple chemical modification of amino group to amide group. These derivatives showed high solubilities and formed microemulsions in carbon dioxide under the mild conditions. With our newly synthesized amino acid surfactants, metal extraction (Co, Cu, Cd) by water-in-CO₂ microemulsion methods were tested. It was observed also that removal of water-soluble dye, for example methyl orange and Congo Red, using this method with our surfactants is efficient. This method may suggest a green

process for the remediation of solid materials contaminated with heavy metals or radioactive waste and removal of waste dye.

IEC 115

Investigation into the use of oxidized and cross-linked poly(methylhydro)siloxane as a support for a heterogeneous catalyst

Corey A. Mocka and Denyce K. Wicht, Department of Chemistry and Biochemistry, Suffolk University, 41 Temple Street, Boston, MA 02114, Fax: 617-573-8668, corey.mocka@suffolk.edu

Cross-linked poly(dimethyl)siloxane (PDMS) and oxidized cross-linked poly(methylhydro)siloxane (PMHS) have been used as solid matrices for heterogeneous catalysts. The active catalytic species, however, is either occluded or trapped within the cross-linked network, rather than covalently bonded to it. We were interested in the synthesis of a cross-linked siloxane in which a model catalyst was covalently bonded to the material, as this would presumably prevent catalyst leaching. To this end, trimethyl-[3(triethoxysilyl)propyl] ammonium chloride was added to PMHS and the polymer was then oxidized and cross-linked. The triethoxysilyl groups condensed with silanol functional groups and the quaternary ammonium salt served as a model for a covalently bonded catalytic species. The final siloxane material was treated with anionic dyes in order to probe electrostatic interactions between the dyes and the quaternary ammonium salt.

IEC 116

Metal-loaded AC catalysts to promote 4-chlorophenol degradation in pulsed high-voltage electrical discharge plasma process

Xiaolong Hao¹, Lecheng Le², Guocheng Du¹, and Jian Chen³. (1) Laboratory of Environmental Pollution Prevention, Jiangnan University, School of Biotechnology, Wuxi 214122, China, Jiangsu Province, Wuxi City 214122, China, Fax: +86-510-85913881, xlhao@jiangnan.edu.cn, (2) Department of Environmental Engineering, Institute of Environmental Engineering, Zhejiang University, Hangzhou 310027, China, (3) Key Laboratory of Industrial Biotechnology, Ministry of Education, Jiangnan University, School of Biotechnology, Jiangsu Province, Wuxi City 214122, China

To enhance degradation rate and removal efficiency of organic contaminations, avoid the drawback of homogeneous catalyst separation, and utilize catalytic activity of metal, three activated carbon (AC) supported metal catalysts, i.e. AC/Fe, AC/Cu and AC/Mn (50-110 μm) made by impregnated method were first

examined for removal of toxic organic pollutant *para*-chlorophenol (4-CP) in aqueous solution using pulsed high-voltage electrical discharge plasma (PDP) process. Experimental results showed that through SEM, TEM and XRD analysis, each of three metal oxides were found at the presence of CuO, MnO and Fe₃O₄ on AC surface, respectively. The optimal load amount of metal oxide for AC-supported metal catalyst was approximately 1.48~2.24% (Wt.). On the other hand, AC/Fe was superior to AC/Cu or AC/Mn in terms of 4-CP removal and removal efficiency. The pseudo-first rate constant of 4-CP degradation (k_{cp}) for 0.2 g/L AC/Fe catalyst present in pulsed high-voltage electrical discharge process was greatly promoted, from $1.56 \times 10^{-3} \text{ s}^{-1}$ without AC, $1.86 \times 10^{-3} \text{ s}^{-1}$ with AC to $2.10 \times 10^{-3} \text{ s}^{-1}$ with AC/Fe catalyst. Moreover, energy efficiency of 4-CP removal with AC/Fe catalyst was enhanced by 116.8% compared with no AC, and by 82.3% compared with AC. In addition, little 4-CP after treatment remained on each AC/metal catalyst (<2.5% compared with initial 4-CP load amount), indicating AC-supported metal catalysts could be renewed and reused in PDP process, so this was a novel combined process in which AC/metal catalysts were introduced into PDP process.

IEC 117

Solvent-free hydrogenation of solid olefins and nitroaromatics by palladium nanoparticles embedded in alumina hydroxide

Fei Chang, *Department of Chemistry and Advanced Materials, College of Environment and Applied Chemistry, Kyunghee university, yongin city , Gyeonggi-do 446-701, South Korea, Fax: 82-31-202-7337, changshaofei@hotmail.com, Hakwon Kim, Department of Chemistry and Advanced Materials, College of Environment and Applied Chemistry, Kyung Hee University, Yongin city, Gyeonggi-do 449-701, South Korea, and Jaiwook Park, Dept. of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 790-784, South Korea*

Solvent-free hydrogenation of various solid olefins and nitroaromatics was investigated using palladium nanoparticles entrapped in alumina hydroxide [Pd/AlO(OH)] as a catalyst in the presence of molecular hydrogen. It was observed that quantitative yields in these reactions were achieved within several minutes at room temperature under one atmospheric hydrogen pressure. On the contrary, the same hydrogenation reaction in organic solvents did not provide desired products. As observed in this reaction, simple reaction procedure, mild reaction condition (room temperature and atmospheric H₂ gas) and easy separation of products from robust, highly effective and recyclable Pd catalyst make these transformations more prominent than the normal reaction in organic solvent. In addition, most important advantage of this reaction is no requirement of an organic solvent for reaction and removal of a solvent, which can meet the requirement for "Green" chemical process.

IEC 118

Au/TS-1 catalysts for propylene epoxidation

W. Nicholas Delgass, Ajay M. Joshi, Bradley Taylor, and Kendall T. Thomson, School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100, delgass@ecn.purdue.edu

Among the many interesting uses for TS-1 is as a support for Au nanoparticles. Au/TS-1 catalysts for propylene epoxidation using H₂/O₂ (Direct PO) have high selectivity and stability. Both DFT computations and experiments suggest that a significant portion of the activity is due to < 1 nm Au clusters which can catalyze H₂O₂ formation from H₂/O₂. Alloying of the Au can affect that activity. The Ti-defect sites are catalytically active and may prevent the Au-cluster sintering. Kinetic analysis shows that a “simultaneous” mechanism operates on our 0.02-0.06 wt% Au/TS-1 catalysts containing invisible < 1 nm Au particles, but a “sequential” mechanism may dominate on other supported Au materials.

IEC 119

Regioselective mononitration of toluene over MFI zeolite catalysts

Seong-Su Kim and Thomas J Pinnavaia, Department of Chemistry, Michigan State University, East Lansing, MI 48824, Fax: 517-432-1225, Pinnavaia@cem.msu.edu

We show for the first time that the NH₄⁺ exchanged form of ZSM-5 zeolite is just as effective as the H⁺ form of the catalyst for the regioselective conversion of toluene to mononitrotoluene (MNT) using 90% nitric acid as the sole nitrating agent. The auto-ionization of the acid in the absence of protons on the zeolite surface is sufficient for the formation of reactive nitronium ions. More importantly, the regioselectivity for the formation of the para isomer is substantially increased over both forms of the zeolite by first intercalating the acid in the zeolite micropores prior to the introduction of toluene. For instance, the p/o isomer ratio is increased from values in the range 1.3 - 2.3 under conventional batch reaction conditions to values of 1.8 - 8.9 when the acid is sequestered in the zeolite micropores. However, the NH₄⁺-exchanged form of the zeolite is preferred as a catalyst over the H⁺ form, in part, because the ammonium ion form substantially suppresses the formation of benzaldehyde and other undesired oxidation products, whereas the proton form does not. Possible mechanisms for the improved regioselectivity will be discussed.

IEC 120

Catalytic CO oxidation by Au: Elucidation of the active sites

Harold H. Kung, *Mayfair C Kung, Sean M Oxford, and Juan Henao, Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, E136, Evanston, IL 60208-3120, Fax: 847-4671018, hkung@northwestern.edu*

The unusual activity of supported Au catalysts for low-temperature CO oxidation has generated world-wide effort to understand its origin. Although the data point to the importance of Au particle size, there is still controversy as to whether the activity is due to size-electronic effect, the presence of low-coordination surface atoms or atoms at the perimeter, or whether it is due to the presence of Au ions. We have attempted to address these questions by following the development of catalytic activity starting from the catalyst precursors and the effect of halide poisoning. Starting from Au oxyhydroxy complexes deposited on a support, catalytic activity is developed in conjunction with reduction of the complex to metallic Au particles. On the contrary, much reduced activity observed on a halide-containing sample is accompanied by the presence of unreduced Au complexes. On a fully reduced, highly active sample, the activity can be effectively suppressed when Br ions are bonded to Au atoms without oxidizing Au. The Br ions preferentially poison the active sites instead of CO adsorption sites. The data supports the model that either perimeter sites or low coordination sites accounts for the high activity of Au catalysts for CO oxidation.

IEC 121

Effects of pretreatment conditions on the adsorption and reactive properties of titanium dioxide

Ronald J. Willey, *Edward Viveiros, and Bruno Notari, Department of Chemical Engineering, Northeastern University, 360 Huntington Avenue, 342 SN, Boston, MA 02215, r.willey@neu.edu*

Much interest exists in the application of titanium dioxide (titania) and related mixed oxides for catalytic applications. As covered in other papers devoted to this session, many exciting examples will be presented. What is still not well understood is a description of why titania has such a range of activity. In our work, we investigated the adsorption of 2-Chloroethyl Ethyl Sulfide (2-CEES) to determine whether differing annealing conditions altered surface behavior. Oxidized and reduced samples of several commercial samples of titania were prepared by thermal annealing at 400 °C and 200 torr oxygen and hydrogen, respectively, and desiccated overnight prior to observation. FTIR spectroscopy was utilized to monitor adsorption and catalytic behavior of these annealed samples. The presentation will concentration of the results found in this study.

IEC 122

Oxidation reactions in the synthesis of intermediate and fine chemicals using environmentally benign oxidants

Wolfgang F. Hoelderich, *Department of Chemical Technology and Heterogeneous Catalysis, University of Technology, RWTH - Aachen, Worringer Weg 1, Aachen 52074, Germany, Fax: 49 241 8888291, Hoelderich@RWTH-Aachen.DE*

Environmental concerns and regulations have been increased in the public, political and economical world over the last 20 years because quality of life is strongly connected to a clean environment. In recent years increasingly severe environmental constraints have led to a great interest in the application of new catalytic oxidation methods for synthesizing fine and intermediate chemicals. Still up to date, organic chemists are used to employ traditional stoichiometric inorganic and organic oxidants such as dichromate/sulfuric acid, permanganates as well as relatively expensive hydroperoxides, alkylperoxides and peroxy-carbonic acids. In the bulk chemical industry for manufacturing e.g. ethylene oxide, phthalic anhydride environmentally unacceptable processes have been already replaced by cleaner catalytic procedures a long time ago, thereby using molecular oxygen in gas phase reactions and applying fixed bed or fluidized bed technology. On the other hand, in the field of fine and intermediate chemicals has been less pressure in the past to replace the traditional stoichiometric oxidants. But it is getting more and more difficult to carry out industrial scale oxidations in this manner. Therefore, the use of solid catalysts for oxidations in the liquid phase as well as heterogeneously catalyzed gas phase processes in the presence of various cheaply available and environmentally benign oxidants such as hydrogen peroxide and molecular oxygen have to be developed.

The direct oxidations of beta-picoline and benzene, as well as epoxidation of olefins such as propylene, pinene and oleochemicals are chosen as examples to demonstrate such environmentally benign technology.

IEC 123

Metal zeolites selective Lewis acid catalysts

Avelino Corma, *Instituto de Tecnologia Quimica (UPV-CSIC), Universidad Politecnica de Valencia, Camino Naranjos s.n, 46022 Valencia, Spain, Fax: 963877809, acorma@itq.upv.es*

The discovery of TS-1 was a breakthrough in the field of zeolite catalysis. This opened the work for the synthesis of new metal-zeolite synthesis. Will present how it was possible through a rational catalyst design to produce new large pore zeolites containing different metals, as for instance Ti, Sn, Zr with controlled adsorption properties. Their catalytic properties for the production of chemicals and fine chemicals will be presented. When combining more than one type of sites it has been possible to carry out cascade reactions that have lead into the intensification of different catalytic processes.

IEC 124

The impact of zeolite catalysis on the development of new technologies and industrial processes

Ugo Romano, Vice President Strategies and Technologies Development, Eni S.p.A, Via Felice Maritano 26, San Donato Milanese 20097, Italy, Fax: +39 0252036338, ugo.romano@eni.it

To be provided

IEC 125

An overview of Titanium crystalline silicate catalysts after 25 years

Bruno Notari, Department of Chemical Engineering, Northeastern University, 360 Huntington Avenue, Boston, MA 02115, Fax: 508-540-8653, Brunotari@aol.com

The discovery of TS-1 in 1983 marks the beginning of a new era in selective oxidation processes. The industrial use of H₂O₂ was limited by its high cost and high decomposition rate. This situation changed when it was found that with TS-1 as catalyst yields of 90% could be achieved. Plants have been built for the production of catechol, hydroquinone and cyclohexanoneoxime. Recent technological improvements have now made the production of basic chemicals economically attractive. The key factor has been the dedicated feedstock supply of H₂O₂ and improvements in the manufacture of TS-1. New Ti catalysts have also been discovered. Major chemical companies have started construction of Propylene Oxide plants based on H₂O₂. The origin of the unique selectivity of TS-1 has been attributed to the fact that Ti active sites are isolated in the silica matrix. Recent results on the properties of Ti-Si oxides, particularly their acidity, will be presented.

IEC 126

Science and policy perspectives on sustainability

John C. Warner, *President and Chief Technology Officer, The Warner-Babcock Institute for Green Chemistry, 66 Cummings Park, Woburn, MA 01801, John.Warner@WarnerBabcock.Com*

Abstract not available

IEC 127

Energy perspectives of sustainability

Robert C. Armstrong, *Department of Chemical Engineering, Massachusetts Institute of Technology, Room 66-544, 77 Massachusetts Ave, Cambridge, MA 02139, rca@mit.edu*

Abstract not available

IEC 128

Business perspectives of sustainability

Andrea Larson, *Darden Graduate School of Business Administration, University of Virginia, P.O. Box 6550, Charlottesville, VA 22906-6550, Fax: 434-243-7677, larsona@arden.virginia.edu*

Abstract not available

IEC 129

Common obstacles and strategic opportunities in implementing a sustainability program

Mark Curran, *Sustainability National Practice Leader, Shaw Environmental & Infrastructure Inc, 2916 Blue Teal Lane, Signal Mountain, TN 37377, mark.curran@shawgrp.com*

Abstract not available

IEC 130

Sustainable chemistries at Rohm and Haas: Environmentally friendly and economically viable innovations

Catherine T. Hunt, *Immediate Past President of the ACS and Leader, Technology Partnerships, Emerging Technologies, Rohm and Haas Company, P.O. Box 0904, 727 Norristown Road, Spring House, PA 19477, Fax: 215-619-1667, catherinehunt@rohmmaas.com*

Environmental and economic goals are not mutually exclusive and more to the point can be fully aligned through the application of green chemistry and green engineering principles. Moving forward, successful companies, universities and governments will understand that scientific collaboration and innovation are essential to making breakthroughs in the development of environmental and economic sustainability. Rohm and Haas is a two-time winner of the Presidential Green Chemistry Challenge Award. I will discuss how we reviewed our research and development portfolio within the context of the principles of green chemistry and green engineering and identified specific opportunities where being environmentally friendly could, and has, increased our competitiveness. Special attention will be given to the role of collaboration and innovation in green chemistry research and development.

IEC 131

Sustainability at Interface America

David Gustashaw, *Vice President of Engineering, Interface Americas, Inc, 1603 Executive Drive, LaGrange, GA 30240, Dave.Gustashaw@interfaceglobal.com*

No abstract available

IEC 132

Rilsan® Polyamide-11: A success story for sustainable resource based engineering thermoplastic

Jim Mason, *Technical Services and Applications Development Manager – Polyamides, ARKEMA Inc, 900 First Ave., King of Prussia, PA 19508, jim.mason@arkemagroup.com*

Rilsan® polyamide-11 (poly omega-amino undecanoic acid) is an engineering thermoplastic developed in 1942, and sold commercially for nearly 60 years. The monomer is a long chain amino acid that is synthesized through a complex process. All of the carbons comprising the polymer are from a renewable resource - the oil of the castor plant. This thermoplastic has been the preferred

material for a variety of engineering applications from truck air brake hoses and automotive fuel lines to flexible pipes that transport crude oil from subsea wellheads to floating production platforms. Other technical applications include cell phone cases and corrosion resistant coatings for potable water system components such as valves and pump cases. This paper will describe some of the applications of polyamide-11, the eco-profile of the material as defined by ISO 14040 and 14043, and compare it to those of other engineering plastics.

IEC 133

A green fire fighting technology: Hope for the future or the kiss of death

Robert E. Tinsley, President & CEO, PYROCOOL Technologies, Inc, 3540 South Amherst Highway, Monroe, VA 24574, pyrocool@earthlink.net

Abstract not available

IEC 134

Sustainable chemistry: Moving from theory to practice

Roger McFadden, Vice President of Science and Technology, Corporate Express US Inc, 1 Environmental Way, Broomfield, CO 80021, roger.mcfadden@cexp.com

More companies and organizations are specifying products designed using Green Chemistry. Major barriers still exist. U.S. government continues to work towards a viable approach. However, some companies are not waiting. These companies are overcoming barriers by pioneering innovative feedstock, process, creative and informed substitutions, product redesign around sustainability protocols and implementing programs to educate consumers about the value of buying preferring products designed using green chemistry. The incentive for these companies is the opportunity to develop capabilities that position them to add a sustainable competitive advantage and economic sustainability. Leaders in their perspective fields recognize that they must work in partnership to create sustainable supply chains and differentiate their products as being truly sustainable. The goal of these leaders is to move their organizations beyond compliance with regulatory requirements to innovative product design and stewardship. The impact of implementing green chemistry, DfE and creative substitution in these companies can be impressive.

IEC 135

Green chemistry and sustainable innovation

William Greggs, *Product Safety, Procter & Gamble, Chemicals Division, Miami Valley Laboratories, P.O. Box 538707, Ross, OH 45061*

Abstract not available.

IEC 136

Internal challenges in adopting sustainable chemistry within a firm

Georjean L. Adams, *EHS Strategies, Inc, 1350 Belmont Dr, St. Paul, MN 55125-2345, gla@ehsstrategies.com*

Several internal policies and practices within firms can interfere with adoption of sustainable chemistry. Lack of knowledge and technical expertise in green chemistry and engineering, internal Return on Investment (ROI) requirements, lack of clear corporate and management expectations and metrics at all levels within the organization, insufficient internal cultural support, uncertainty about market advantages, among other disconnects can exist for individuals within companies who wish to incorporate sustainability principles in their work. The poster will present suggestions to meet these challenges.

IEC 137

From red light to green light: Policies to advance green chemistry

Kira JM Matus, *Science, Environment, Development Group; Kennedy School of Government, Harvard University, 79 JFK St., Cambridge, MA 02138, kira_matus@ksgphd.harvard.edu, Kai Itameri-Kinter, Harvard College, Harvard University, Cambridge, MA, Paul T. Anastas, Center for Green Chemistry and Green Engineering, Yale University, New Haven, CT 06511, and William C Clark, Belfer Center for Science and International Affairs, Kennedy School of Government, Cambridge, MA 02138*

Green Chemistry provides an ideal platform for the analysis of innovation for sustainable development. Currently, the chemical enterprise presents challenges to the environment, economy, and society, but also offers unique opportunities to advance the goal of sustainability through innovations in chemical product and process design. Green chemistry has managed to make significant progress in the relatively short time-frame of its existence, despite the fact that its implementation often requires major changes to ways of framing and solving problems, in the design process for compounds and for manufacturing processes, and in the implementation of these practices. This poster will present

research on the unique impediments to Green Chemistry innovations and a framework for analyzing what strategic and tactical actions and policies can be used to overcome these impediments by the communities that confront them.

IEC 138

Unintended consequences: Potential pitfalls for the future

Frankie Wood-Black, *Trihydro Corporation, 6855 Lake Road, Ponca City, OK 74604, fwblack@cableone.net*

When looking at new technology or change, only the positive aspects are general focused upon. Yet, each technology, adaptation or change comes with its own negatives. Recent examples include the inclusion of MTBE as an oxygenate in fuels and the impact on food prices as corn has been redirected into ethanol production. Unintended consequences have significant implications for the implementation of sustainable products and technologies. Several examples will be explored.

IEC 139

Greening of chromatography and separation chemistry

Sut Ahuja, *Ahuja Consulting, Inc, 106 Rutledge Ct, Calabash, NC 28467*

Chromatography offers an illustration of how the acceptance of new methods can advance the goals of sustainability. The main objective of green chemistry is to promote research, development, and implementation of innovative chemical technologies that accomplish pollution prevention in a scientifically sound and cost-effective manner. In industrial settings, a significant amount of solvents and other chemicals are used in the purification processes based on separations to assure that requisite quantity and quality have been achieved. Besides quality control and analytical R&D, testing is also done in various areas such as manufacturing, in-process testing, pilot-scale production, and formulation. In the not-too-distant past, solvent-solvent extractions were commonly used to extract the desired materials to purify them. One of the solvent was generally at various pHs and the other was a nonpolar solvent. The nonpolar solvents of choice were generally chloroform, carbon tetrachloride, etc. This meant that at times a large volume of potentially carcinogenic solvent(s) had to be vaporized to obtain the desired material. The evolution of chromatographic methods in the beginning of the twentieth century have ushered in methods that require a minimal amount of solvents. These methods in order of development and/or acceptance by separation chemists are column chromatography (CC), paper chromatography (PC), thin-layer chromatography (TLC), gas chromatography (GC), high pressure

liquid chromatography (HPLC), capillary electrophoresis (CE), and supercritical fluid chromatography (SFC). The utilization of more modern chromatographic techniques (viz. GC, HPLC, CE, and SFC) has helped solve complex problems that have added greatly to the well-being of humanity. Discussion will focus on how these methods use miniscule amount of solvents and avoid utilization of carcinogenic solvents thereby effectively meeting or exceeding the goals of green chemistry in that besides pollution prevention there is a real cost savings in terms of utilization of solvents and disposal of solvent waste.

IEC 140

Using total business cost assessment to link sustainability to the bottom line

Dickson de la Haye, Sustainability Resource Center, The Dow Chemical Company, Wilmington, DE 15478, Fax: 979-238-9293, dchelahaye@dow.com, and Lise Laurin, EHS Strategies, Wilmington, DE 15748

For many, protecting the environment, employees, and communities has been considered an expense, requiring equivalent return on investment to any other expense taken on by a company. In the last few years, this approach has been recognized to be unsustainable. While shareholders have begun demanding sustainable actions from corporations, they have not reduced the pressure on profitability. So how does a company justify expenditures toward more sustainable management practices when traditional cost accounting shows a negative return on investment? Total Business Cost Assessment (TBCA) successfully shows return on investment in areas not considered in traditional cost accounting: areas such as potential legal liabilities, employee morale, community and regulator relations, and brand value--areas that affect profitability, even if the effects are difficult to measure.

The Dow Chemical Company has been using TBCA to evaluate its EH&S goals and to enable better decision making Utilizing the TBCA methodology, Dow estimated a total value of \$950 million generated from the EH&S 2005 incident reduction goals. Furthermore, Dow estimated spending close to \$1 billion on the resource productivity goals and achieved an overall value of over \$5 billion. The TBCA process and the results of the analyses are opening the eyes of participants and reviewers to new ways of approaching decisions, business, and the marketplace.

IEC 141

Common obstacles and strategic opportunities in implementing a sustainability program

Mark Curran, Sustainability National Practice Leader, Shaw Environmental & Infrastructure Inc, 2916 Blue Teal Lane, Signal Mountain, TN 37377, mark.curran@shawgrp.com

This presentation will focus on some of the common obstacles and strategic opportunities in implementing a Sustainability Programs. Particular emphasis will be on how to overcome senior management's varying perceptions and definitions of "what sustainability is" and what a comprehensive program can mean to their organization. The presentation will include case studies from a variety of organizations both public and private and will highlight the following: How to establish an organization wide sustainability Vision and Mission; Enabling senior management to define sustainability within the context of their organization and its culture; From vision to implementation - how to get it done!; Meaningful metrics and measures; Internal and External Reporting.

IEC 142

Challenges in life cycle management of chemical products at 3M

Mike J. Falco, 3M Center, 3M, St. Paul, MN 55144, mjfalco1@mmm.com

The poster will describe some of the challenges and successes in developing new chemical products that meet goals for both sustainable environmental, health and environmental performance and business needs at 3M.

IEC 143

Sustainability at Cytec

Carol English, SHE Services, Cytec Industries, Inc, 5 Garret Mountain Plaza, West Paterson, NJ 07424, carol.english@cytec.com

Abstract not available

IEC 144

Tools and strategies for greening chemical inventories

Lauren G. Heine, Green Blue Institute, 515 Whitecap Road, Bellingham, WA 98229, lauren@lheinegroup.com

Abstract not available

IEC 145

Is there a big future for green nanotechnology?

Barbara Karn, *Center for Science in the Public Interest, Georgetown University, Washington, DC 20057, karn.barbara@green-nanotech.com*

Green nanotechnology has two goals: 1. Producing nanomaterials and products without harming the environment or human health; 2. Producing nanoproducts that provide solutions to environmental challenges. The first incorporates the source reduction principles of green chemistry and engineering and focuses on the processes of making nanomaterials without emitting harmful pollutants. The second goal involves practical use of nanoproducts in either direct or indirect applications to environmental problems.

This paper will focus on the opportunities for nanotechnology to "grow up greenly" and be part of the solution that leads to sustainability. The present symposium will be discussed in the context of these green nano goals. Examples of green nanotechnologies that lead to both goals will be given. Whether a product or process is truly green will be discussed in a life cycle/systems context.

IEC 146

Green nanotechnologies: Potentials and prospects

A. Vaseashta, *Graduate Program in Physical Sciences, Department of Physics & Physical Sciences, Nanomaterials Processing and Characterization Laboratories, Marshall University, One John Marshall Drive, Huntington, WV 25755-2570, prof.vaseashta@marshall.edu, M. Vaclavikova, Slovak Academy of Sciences, Institute of Geotechnics, Kosice 043 53, Slovak Republic, G. Gallios, Aristotle University of Thessaloniki, Department of Industrial Chemistry and Chemical Technology, Thessaloniki GR-541 24, Greece, J. Schoonman, Faculty of Applied Sciences, DelftChemTech, Delft 2628 BL, Netherlands, and I. Stamatina, 3NANO-SAE, Res. Center, Polymer science Dept, Faculty of Physics, Bucharest-Magurele Mg-38, Romania*

Materials at nanoscale exhibit remarkable properties with numerous unique applications such as in chem.-bio sensors, nanophotonics, nanobiotechnology, and in-vivo analysis of cellular processes. Use of nanomaterials to produce energy and to remediate environmental pollution is in its preliminary stages and requires urgent and detailed investigation as environmental pollution is a leading contributor to chronic and deadly health disorders and diseases affecting millions of people each year. A perpetual increase in population and thus consumption of fossil fuels has led to increased pollution worldwide. Although correlation

between environmental pollution and global warming is debatable, the effects of pollution and its impact on human health are irrefutable and highly observable. Long-term exposure to air pollution provokes inflammation, accelerates atherosclerosis, and alters cardiac function. This presentation describes responsible manufacturing of nanomaterials to drastically reduce and isolate emission by-products with its use as catalysts for enhanced efficiency; materials in underground CO₂ sequestration; remediation of toxic metals in water streams; efficient thin film photovoltaic devices; fuel cells; and biodegradable consumable products. The presentation will cover an exhaustive overview of the scope of our investigation and some specific applications relating to the use of nanomaterials in environmental friendly investigations. Nanotechnologies are expected to make a major contribution to improving the quality of the life of citizens worldwide, in particular in sectors such as material sciences, health care, and information technology. The convergence of nano-bio-info-cogno-physico-chemical technologies offers tremendous opportunities for the improvement of human life, individual productivity, and our overall quality of life. Furthermore, it also offers a new direction in research and development.

IEC 147

Environmental applications of nanocrystalline zeolites

Sarah C. Larsen and Vicki H. Grassian, Department of Chemistry, The University of Iowa, 305 CB, Iowa City, IA 52242, sarah-larsen@uiowa.edu

Nanocrystalline zeolites were synthesized with crystal sizes of 100 nm or less. These porous nanomaterials were extensively characterized to determine the structural and surface properties using techniques such as FTIR, solid state NMR, nitrogen adsorption isotherms, and powder x-ray diffraction. The surface properties were varied by functionalization with aminopropyltriethoxysilane and other organosilanes containing different functional groups in order to tailor the nanozeolites for specific applications. Nanocrystalline zeolites were evaluated for environmental applications including the adsorption of volatile organic compounds and toxic metals, deNO_x catalysis, and decontamination.

IEC 148

A combinatorial approach to solving the problem of splitting water with sunlight

Bruce A. Parkinson and Michael Woodhouse, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, Fax: 970-491-1801, Bruce.Parkinson@colostate.edu

A simple, low cost and high-throughput method for screening oxide materials for photoelectrolysis activity has been developed. The method involves ink jet printing of oxide precursors onto conductive glass substrates and, after pyrolysis, screening them in electrolytes for photoelectrolysis activity using a scanned laser. A ternary oxide, containing cobalt, aluminum and iron and not previously known to be active for the photoelectrolysis of water, was identified using this high throughput combinatorial technique. The composition and optimum thickness for photoelectrochemical response of the newly identified material was further refined using quantitative ink jet printing. Chemical analysis of bulk and thin film samples revealed that the material contains cobalt, aluminum and iron in a Co_3O_4 spinel structure with Fe and Al substituted into Co sites with a nominal stoichiometry of $\text{Co}_{3-x-y}\text{Al}_x\text{Fe}_y\text{O}_4$ where x and y are about 0.18 and 0.30 respectively. The material is a p-type semiconductor with an indirect band gap of around 1.5 eV, a value that is nearly ideal for an efficient single photoelectrode for water photoelectrolysis. The need for optimized nanomorphologies for efficient water splitting devices will also be discussed,

IEC 149

Surface characterization and electrocatalytic activity of ordered intermetallic PtBi(001) surfaces by ultrahigh vacuum-electrochemistry (UHV-EC)

*Jean Sanabria-Chinchilla*¹, *Hiedki Abe*², *F. J. DiSalvo*¹, and *Hector D. Abruña*¹.
(1) Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, js589@cornell.edu, (2) NIMS, Ibaraki, Japan

Surface characterization of an ordered intermetallic PtBi(001) single crystal have been performed by a combination of surface-sensitive electron spectroscopic techniques under ultra-high vacuum conditions and conventional electrochemistry. The clean surface was characterized by a chemical composition of 54 % Pt and 46 % Bi (Auger analysis). LEED patterns indicated that the surface was smooth and well-ordered with a hexagonal array of atoms. The electrochemical studies indicated that the electrode surface is Pt-terminated with a behavior similar to that of a pure Pt electrode. The intermetallic phase was more prone to chemisorption by oxygenated species over the studied potential window. The nature of this species was potential dependent. The crystal exhibited enhanced electrocatalytic activity for the oxidation of small organic molecules such as formic acid. A competition between the oxidation of the organics and surface oxide formation was observed. The presence of fuel retarded the electrochemically-induced changes on the electrode surface.

IEC 150

Aqueous-phase hydrogenation of ketones using colloidal platinum nanocatalysts

Anderson L. Marsh, Jason K. Navin, Carrie A. Kauffman, Kimberly A. Manbeck, and Michael W. Porambo, Department of Chemistry, Lebanon Valley College, 101 N. College Ave., Annville, PA 17003, marsh@lvc.edu

In recent years, the focus of catalysis research has shifted from increasing activity to achieving 100% selectivity, as well as to performing reactions using “greener” processes. One area of particular interest is the chemoselective hydrogenation of carbonyl (C=O) bonds in unsaturated ketones, a reaction lying at the heart of various chemical industries. Our efforts in this research area take advantage of colloidal platinum nanoparticles synthesized in the 1-10 nm size range using solution-based methods that allow for fine control over particle sizes. These platinum nanocatalysts are then used in the hydrogenation of selected ketones in the “green” solvent water, which reduces the use of harmful organic solvents for the reaction. Through measurement of turnover rates we are connecting reaction selectivity with catalyst properties (particle size) and reaction conditions (temperature, pressure, and reactant concentrations). By combining this knowledge together, we hope to enhance environmentally-friendly and efficient routes for manufacturing desired chemical commodities.

IEC 151

Microfluidic synthesis/functional Patter-fabrication for advanced nanotechnology

Kyung Choi, Chemistry, University of California, Irvine, CA 92697, Fax: 949-824-1174

The ability to fabricate small patterns on flexible substrates has received considerable attentions due to potential applications to develop low cost plastic/organic/molecular electronics. We demonstrate here both of microfluidic synthesis and microfabrications of functional polymers to bring innovations in nanotechnology. For example, we employed a microfluidic approach to synthesize molecularly imprinted polymer (MIP) particles, which is a highly cross-linked macroporous thermoset with both high internal surface areas and specific molecular recognition sites for fabricating bio-chemical sensors. In order to achieve high sensitive, we provide micro-sized MIPs' particles, which have only high affinity receptor sites since particle sizes of MIP polymers are directly related to their affinity functions of specific molecular recognition. We also carried out the microfabrications of MIP through MIMIC process using photomasks. This study presents fluorescence microscopic images of MIPs' system by rebinding synthesized fluorescent templates. We also present designs of new materials for functional fabrications.

IEC 152

Green synthesis, separation and analysis of water-soluble, monolayer-protected quantum dots

*Corwin A. Miller, Stephanie A. Owens, Margaret C. Carpenter, James W. H. Sonne, and **Deon T. Miles**, Department of Chemistry, Sewanee: The University of the South, 735 University Avenue, Sewanee, TN 37383, Fax: 931-598-1145, dmiles@sewanee.edu*

Monolayer-protected CdSe and ZnSe quantum dots (QDs) were synthesized in a green solvent (water). Several water-soluble thiols were used to protect the semiconducting core from surface oxidation and to improve the water solubility of the QDs for possible biological applications. Differences in the spectral properties of the QDs were observed as a function of reaction time and protecting thiol ligand, as well as metal:thiol ratio. The stability of the QDs in different pH environments was studied, with the QDs decomposing in acidic conditions. The diameter of the QDs was calculated from UV-vis spectra and investigated by high-resolution transmission electron microscopy. Separation of the QDs by size was performed using reversed-phase HPLC with green solvents (e.g., methanol, isopropanol). From fluorescence spectra of separated QDs, full-width at half-maximum values of 15 nm and less were observed.

IEC 153

Green nanostructure synthesis

***Stanislaus S. Wong**, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-3400, Fax: 631-632-7960, sswong@notes.cc.sunysb.edu*

Environmentally friendly synthetic methodologies have gradually been implemented as viable techniques in the synthesis of a range of nanostructures. In this work, we focus on the application of green chemistry principles to the synthesis of complex metal oxide and fluoride nanostructures. In particular, we describe advances in the use of the molten salt synthetic methods and template-directed techniques as environmentally sound, socially responsible, and cost-effective methodologies that allow us to generate nanomaterials without the need to sacrifice on sample quality, purity, crystallinity, in addition to control over size and shape.

IEC 154

Toward greener nanotechnology: Lessons from functionalized nanoparticle synthesis

James E. Hutchison, Department of Chemistry, the Materials Science Institute, and the Oregon Nanoscience and Microtechnologies Institute, University of Oregon, 1253 University of Oregon, Eugene, OR 97403, Fax: 541 346-0487, hutch@uoregon.edu, and Lallie C. McKenzie, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR 97403

Nanotechnology promises considerable benefit to society and the environment. However, the products of nanotechnology and the manufacturing processes used to produce these products may pose threats to human health and the environment. As we move from the discovery phase to full implementation of nanotechnology, the challenge will be to develop nanotechnology to provide maximum benefit, while minimizing the hazards. Green chemistry and engineering principles can be adopted to guide the early stages of product and process development to meet this challenge. In this presentation, I will discuss how green chemistry principles guide the responsible development of nanotechnology and how nanoscience can enable the discovery of greener products and processes. Recent advances in nanoparticle synthesis, functionalization, and purification will be presented that illustrate how the principles of green chemistry can guide the development of high performance processes that are more economical and reduce hazard and waste.

IEC 155

Creating environmentally friendly reactive nanoparticles through surface modification

Gregory V. Lowry¹, Tanapon Phenrat¹, Sufia K Kazy², Pedro J. J. Alvarez², and Bellina Veronesi³. (1) Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, Fax: 412-268-7813, glowry@cmu.edu, (2) Department of Civil and Environmental Engineering, Rice University, Houston, TX 77251-1892, (3) Neurotoxicology Division-Cellular and Molecular Branch, National Health and Environmental Effects Research Laboratory U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Reactive nanomaterials used for environmental remediation require surface modification to make them mobile in the subsurface. Nanomaterials released into the environment inadvertently without an engineered surface coating will acquire one (e.g. adsorption of natural organic matter). Thus, the chemistry of the surface coating controls a nanoparticle's interactions with mineral surfaces, organic matter, and living organisms, and hence controls its overall fate and potential for exposure and toxicity. This study investigates the effects of polyelectrolyte

surface coatings on the mobility of nano-sized Fe₀ (NZVI) particles in porous media, and its potential toxicity to microorganisms and neurotoxicity in vitro. NZVI is surface modified with polyaspartate (MW=2000 to 3000 g/mol), characterized in terms of size, adsorbed layer mass and conformation, surface charge, and aggregation. The transport of bare and modified particles is determined in saturated sand columns, the cytotoxicity of bare and surface-modified NZVI to *B. subtilis* and *E. coli* is measured in batch systems, and the potential neurotoxicity is assayed in vitro using a number of toxicity end points. In all cases, the presence of a surface coating significantly increased the mobility of the nanomaterials in sand columns, thereby increasing the potential for exposure. However, the surface coatings significantly decreased the toxicity of the NZVI compared to unmodified NZVI, suggesting that surface modification can be used to enhance functionality AND MICROBIAL PARTICIPATION IN THE REMEDIATION PROCESS while decreasing the potential for human or ecotoxicity.

IEC 156

Expanding nanoscience by thinking green: New capabilities for the synthesis of high-temperature solids using low-temperature solution chemistry

Raymond E Schaak, Department of Chemistry, Pennsylvania State University, 104 Chemistry Building, University Park, PA 16802

Metallurgical solids, including alloys and intermetallic compounds of the late transition metals, represent a large class of technologically important materials that have widespread use in variety of applications. Most of these solids are synthesized using high temperature reactions (> 1000 deg. C) because solid-solid diffusion is the rate limiting step in their formation. In many cases, low-temperature strategies can (< 300 deg. C) be used to form metallurgical solids under conditions where the diffusion problem can be avoided or minimized. These mild synthetic strategies sometimes offer advantages over traditional high-temperature techniques, including the ability to (a) access new or elusive structures, (b) control important morphological features such as nanoscale shape and size, and (c) use inexpensive benchtop processes to form materials into films, coatings, and micropatterned structures. This talk will discuss our ongoing attempts to expand capabilities in nanoscience by thinking "green", particularly in terms of energy efficiency. The focus will be on elaborating new capabilities and nanomaterials that emerge as a result of environmentally-conscious thinking, rather than the formation of existing materials by alternative means. New results on the formation of metallurgical solids using safe, renewable, and edible "solvents" will also be described.

IEC 157

Greener synthesis of noble metal nanostructures and nanocomposites

Rajender S. Varma and Mallikarjuna. N. Nadagouda, Sustainable Technology Division, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, 26 West Martin Luther King Drive, MS 443, Cincinnati, OH 45268, Fax: 513-569-7677, Varma.Rajender@epa.gov

A brief account of a greener preparation of nanoparticles which reduces or eliminates the use and generation of hazardous substances is presented. The utility of vitamins B₁ and B₂, which can function both as reducing and capping agents, provides an extremely simple, one-pot, greener method to synthesize bulk quantities of nanospheres, nanorods, nanowires, and nanoballs of aligned nanobelts and nanoplates of the metals in water without the need for large amounts of insoluble templates. A bulk and shape-controlled synthesis of noble nanostructures with various shapes occurs via microwave (MW)-assisted spontaneous reduction of noble metal salts using an aqueous solution of α -D-glucose, sucrose, and maltose. A general MW method has been developed that accomplishes the cross-linking reaction of poly (vinyl alcohol) (PVA) with metallic systems such as Pt, Cu, and In; bimetallic systems, namely Pt-In, Ag-Pt, Pt-Fe, Cu-Pd, Pt-Pd and Pd-Fe; and single-wall carbon nanotubes (SWNT), multi-wall carbon nanotubes (MWNT), and Buckminsterfullerene (C-60) in various shape forms such as spheres, dendrites, and cubes. The strategy is extended to the formation of biodegradable carboxymethyl cellulose (CMC) composite films with noble nanometals; such metal decoration and alignment of carbon nanotubes in carboxymethyl cellulose is possible using MW approach which also enables the shape-controlled bulk synthesis of Ag and Fe nanorods in poly (ethylene glycol). A clean synthesis of core (Fe, Cu)-shell (Au, Pt, Pd and Ag) nanocrystals has been achieved using aqueous vitamin C. Newer form of carbon-doped titania has also been prepared using a benign natural polymer dextrose that helps generate a spongy porous structure and the general method is applicable to other transition metal oxides such as ZrO₂, Al₂O₃, and SiO₂.

IEC 158

Microwave-induced controlled purification of single-walled carbon nanotubes without sidewall functionalization

Yuhong Chen, Department of Chemistry, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, Fax: 973-596-3586, yc58@njit.edu, and **Somenath Mitra**, New Jersey Institute of Technology, Department of Chemistry and Environmental Science, Newark, NJ 07102, mitra@njit.edu

A microwave-induced controlled method for the purification of single-walled carbon nanotubes (SWCNTs) by removing residual metal catalysts and carbonaceous impurities is reported. Compared to conventional strong acid treatment, this one-step method uses dilute acids and complexing agents and reduces the reaction times to the order of minutes. Furthermore, the SWCNTs retain their chemical and physical properties and are not functionalized. Electron microscopy, Raman spectroscopy, Fourier Transform Infrared Spectroscopy, Thermogravimetric Analyses and Atomic Absorption spectrometry studies were used to characterize the purified SWCNTs.

IEC 159

High quality nanocrystals produced in edible oils: Toward green, accessible nanomanufacturing

Vicki Colvin, Department of Chemistry, Rice University, Houston, TX 77251, colvin@rice.edu

Nanomaterials may enable technological solutions to critical problems now faced by the developing world in the areas of water treatment, energy production and healthcare. To see these technologies applied successfully, however, requires innovative manufacturing strategies that not only make these materials using 'green' techniques, but also in ways that are transferable to the low infrastructure settings found in the developing world. In this paper, we present a new scheme for generating nanocrystals that relies on everyday items and simple tools of the type found in restaurants. The method takes advantage of the particle growth mechanism found when metal salts are decomposed in fatty acid mixtures; surprisingly high quality magnetic nanocrystals can be generated even using starting materials such as edible oils (olive) and rust collected from refuse. Quantum dot materials formed in a similar fashion are not as uniform in size, but the products still display the striking optical features essential for their applications. The optical and magnetic properties of these systems can be verified using relatively simple tools, and this information can provide feedback on a given sample's utility. Potential users of nanotechnology in the developing world could use these methods as a starting point to develop nanomanufacturing for micro-businesses or possibly even household settings.³ Ultimately, we envision that the methods described here will be adapted and refined by the global community using open source techniques pioneered by hackers and software engineers.

IEC 160

Green chemistry synthesis of polyaniline nanofibers

Sanjeev K. Manohar¹, Sumedh Surwade², Vineet Dua², Robinson Anandakathir², and Xinyu Zhang¹. (1) Chemical Engineering, University of Massachusetts Lowell, One University Ave, Lowell, MA 01854, Fax: 978-934-3047, sanjeev_manohar@uml.edu, (2) Chemistry, University of Massachusetts Lowell, Lowell, MA 01854

Ammonium peroxydisulfate is commonly used as the oxidant in the classical chemical oxidative polymerization of aniline in dilute aqueous acids. Attempts to make the synthesis greener using hydrogen peroxide, typically involve the use of enzymes or transition metal as catalysts. This study describes the synthesis of an electrically conductive polymer of aniline using hydrogen peroxide without any added catalysts, and the use of the nanofiber seeding method to synthesize rapidly, and in one step, bulk quantities of electrically conducting nanofibers.