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Abstracts of Oral and Poster Presentations

1. Construction of Neurexin Biosensor and Screening of Potential Ligands

Jeevan Baretto, Jingjing Li, David W. Wood

Neurexins are neuronal presynaptic proteins that bind to the postsynaptic protein neuroligin at the synaptic junction. Both neurexins and neuroligins are involved in transmitting signals across the neural synapse. Many neurodevelopmental disorders involve abnormal synaptic function. The Neurexin-neuroligin interaction appears to play a key role in autism and other mental disorders. We have constructed a protein-based biosensor that can detect chemical ligands that bind to a given receptor protein. Our engineered bacterial biosensor fusion protein is expressed from a bacterial plasmid DNA, and consists of multiple protein domains including a solubility/stability platform (Maltose Binding protein and an engineered intein domain) and a reporter gene (phage T4 thymidylate synthase - TS) fused to a ligand-binding domain (LBD). The TS assay involves expression of this fusion protein in thymine-knocked out *E. coli* cells (D1210ΔthyA) in a thymine-less media. Binding of the ligand in turn activates TS which is required for DNA synthesis in this *E. coli* strain. By measuring the growth phenotype of these cells at different ligand concentrations, we can calculate the EC50 for each of the ligands binding to Neurexin 2b. The biosensor system successfully developed in our lab has been previously used with estrogen receptors, thyroid receptors and Peroxisome Proliferator-Activated Receptor Gamma (PPARG), and has been published elsewhere. Here we describe the construction of a biosensor variant in which Neurexin 2b serves as an LBD within the intein domain, such that binding of ligands is transduced into a growth phenotype via TS. Using this neurexin-LBD biosensor strain, we found that Rosiglitazone, an anti-diabetic drug belonging to the thiazolidinedione class of drugs, causes a growth phenotype at low ligand concentrations, suggesting strong binding. This general approach could help identify ligands of Neurexin that interfere with the signaling across the synapse. Further, this might lead to a better understanding of the mechanism behind autism and other neural disorders.

2. Surface Morphology Variation and Solid-Phase Ionic Transfer Mechanisms in Chemical Looping Reactions

Zhenchao Sun, Siwei, Luo, Qiang Zhou and Liang-Shih Fan
Presented by Elena Chung

Chemical looping processes (CLP) have the potential to efficiently utilize the indigenously abundant carbonaceous fuels such as coal in an environment-friendly manner. CLP utilize an oxygen carrier particle to indirectly convert carbonaceous fuels while capturing the CO_2 byproduct for sequestration. The oxygen carrier particles loop between two reactors, namely the reducer and the combustor, to accomplish complete fuel conversion and oxygen carrier regeneration, respectively. Over the past two decades, this transformative process has resulted in the global development of the chemical looping technology.

Large quantities of oxygen carriers are required for commercial CLP. For this purpose, the use of synthetically-engineered iron oxide-based particles have been demonstrated to be effective oxygen carriers in terms of reactivity, recyclability and oxygen carrying capacity. However, the fundamental mechanisms behind these reactions are not well understood. Thus, recent developments in understanding the surface morphology and the ionic transfer mechanism of iron-based systems are discussed.

3. Screen Development for Directed Evolution of Controllable Inteins Using Yeast Surface Display

Michael Coolbaugh and David Wood

Inteins are naturally occurring-protein elements that splice themselves out of precursor proteins and have been engineered for use in self-cleaving purification tags. The major issue with the use of intein-based self-cleaving purification tag technology is controlling the cleaving reaction. One class of inteins can be induced with a pH shift. However, these inteins cleave rapidly under physiological conditions, precluding their use in mammalian cell culture. Here we aim to develop a screen that can be used to evolve an intein with an altered pH activity profile.

We have developed a screen for the directed evolution of inteins based on the yeast surface display system developed by K. Dane Wittrup. The screen involves the expression of an intein between two fluorescently labeled epitope tags. The ratio of the fluorescence allows for the distinction between intein cleavage and non-cleavage events. This then provides the basis for screening mutant libraries with enhanced cleaving control using fluorescence activated cell sorting (FACS).

We report the optimization of the above mentioned screen, as well as its use in screening a mutant intein library. We also report progress toward the development of a pH inducible intein that can be used in mammalian cell culture.

4. Single-Step Process for Simultaneous Removal of CO_2, SO_x and NO_x from Coal Combustion Flue Gas

Niranjani Deshpande, Nihar Phalak and Liang-Shih Fan

Prior research has shown the effectiveness of carbon derived from inexpensive sources like coal char, in controlling post-combustion NO_x emissions. The reduction of NO using char is a widely researched phenomenon. Based on this concept, the CARBONOX Process was developed at OSU from lab-scale to pilot-scale demonstration. Studies conducted here have demonstrated ~98% reduction in NO levels using bituminous and lignite chars at moderate to high temperatures (500-800°C).

Our recent research has focused on the development of the Carbonation-Calcination Reaction (CCR) Process for post-combustion removal of CO_2 and SO_2 using a calcium-based sorbent. The CCR Process has also been demonstrated successfully at the sub-pilot scale, with >90% CO_2 capture and complete SO_2 removal achieved.

This work combines the two processes, resulting in a unique high-temperature (>500ºC) process for simultaneous removal of CO_2, SOx and NOx. The carbon-NO reaction is known to be catalyzed by alkali or alkaline earth metals, which favors the development of this process. Tests were conducted to demonstrate the simultaneous capture of NO and CO_2, using a mixture of coal char and calcium sorbent. The effect of variables such as temperature, Ca:char ratio, O_2 concentration, & char source, was quantified using a fixed-fluidized bed reactor. The results of these tests will be presented in the form of net NO and CO_2 capture, and selectivity of char toward NO. The merits and potential challenges of this novel process will be discussed.

5. High-yield and High-titer n-Butanol Production in *Clostridium tyrobutyricum* with External Driving Forces

Yinming Du and Shang-Tian Yang

The biosynthesis of n-butanol through aldehyde/alcohol dehydrogenase (*adhE2*) is usually limited by NADH availability and butanol titer. In order to alleviate these limitations and improve n-butanol production in solvent-producing *C. tyrobutyricum* mutant, external driving forces were created by introducing NADH driving force via the addition of methyl viologen to manipulate the electron flow and metabolic flux towards butanol synthesis pathway, and detoxification driving force through the integration of gas stripping to realize *in situ* butanol recovery and minimize butanol-induced inhibition. With these external driving forces, high-yield and high-titer butanol production from glucose in *C. tyrobutyricum* mutant was achieved for both batch and fed-batch fermentations. Metabolic flux analysis reveals that the improvement in butanol yield and titer was consistent with the increase in NADH availability. In addition, a continuous butanol production to a total titer of > 50 g/L and a final yield of ~ 0.33 g butanol per gram glucose with extremely low accumulation of ethanol, acetic and butyric acids was obtained in an integrated fed-batch fermentation and gas stripping process associated with cell immobilization in a fibrous-bed bioreactor (FBB). This study has demonstrated a stable and reliable process for high-yield and high-titer n-butanol production by non-native solventogenic clostridia.

6. Iron Looping Process Demonstration and Development

Mandar Kathe, Andrew Tong, Liang Zeng, Dawei Wang, Sam Bayham, Ray Kim, Elena Chung and Liang-Shih Fan

The Chemical Looping Process (CLP) has the potential to efficiently utilize the indigenously abundant coal in an environment friendly manner. The CLP utilizes oxygen carrier particles to indirectly convert carbonaceous fuels while capturing CO_2 for sequestration. At The Ohio State University, multiple chemical looping efforts ranging from pre-combustion to post-combustion of coal have been demonstrated on various scales. The Iron based CLP developed at The Ohio State University (OSU) presents a unique advantage compared to the other global chemical looping efforts. The combination of moving bed reactor system and the use of Iron based oxygen carrier particles results in the possibility of generating high purity H_2. This makes the Iron based CLP a fuel and product flexible technology. The Iron based CLP can be classified into Syngas Chemical Looping (SCL) process for processing gaseous fuels like syngas, natural gas and Coal-Direct Chemical Looping (CDCL) process for direct utilization of solid fuels like coal, biomass etc. The processes can be flexibly configured to generate exclusively or in a combination high purity H_2, electricity and liquid fuels. Currently, the SCL and the CDCL processes have been tested under a 25 kW_{th} operation for more than 300 hours and more than 230 hours respectively, with a consistently high fuel conversion and smooth operational demonstration with a 250 kWth pilot plant unit being constructed at the National Carbon Capture Center in Alabama.

7. Recent Computational Tools for the Analysis of Complex Biochemical Reaction Networks

Daniel Knight, Haixia Ji and Martin Feinberg

When studying biological systems, understanding of their dynamical properties is more readily inferred from knowledge of only the reaction network, as detailed kinetic information is generally not available with confidence. There are exemplary complex biochemical reaction networks with rich behavior (multiple steady states, oscillatory behavior, etc.), while others have relatively dull, stable dynamics. Recent theoretical developments allow for powerful statements to be made about the dynamics of even very complex networks, provided the kinetics falls within a very general and natural class. In particular, it is possible to distinguish in a precise way between networks that might provide the basis for a bistable switch, and networks – even very intricate ones – that cannot. These recent theoretical developments have been incorporated into a freely available computer program, Chemical Reaction Network Toolbox (CRNT). The theory will be discussed, and examples of its implementation via the Toolbox will be given.

8. Expansion of human amniotic fluid stem cells in 3 dimensional fibrous scaffolds in bioreactors

Meimei Liu and Shang-Tian Yang

Due to their easy accessibility and broad multipotnetility, amniotic fluid stem cells (AFSCs) have emerging as an important cell source for tissue engineering and regenerative medicine applications. In clinical applications, a large amount of stem cells are required and conventional cell culture systems cannot meet this demand. In this study, the proliferations of human bone marrow derived mesenchymal stem cells (hBM-MSCs) and hAFSCs were compared, and hAFSCs exhibited extensive self-renewal capacity. The proliferation of hAFSCs was then investigated on 2-D surfaces and 3-D polyethylene terephthalate (PET) scaffolds in static cultures. Our results indicated that 3-D PET scaffold provided a large specific surface area for cell adhesion and growth, and its in vivo-like environment significantly facilitated cell expansion. Furthermore, hAFSCs were expanded in a PET based 3-D dynamic fibrous bed bioreactor. It is demonstrated that clinical does hAFSCs were generated in this bioreactor and the expanded cells maintained their characteristic phenotype, multipotent differentiation capacity and clonogenic ability. Overall, hAFSCs combined with the PET based 3-D fibrous bed bioreactor provide an excellent platform for the efficient clinical-scale expansion of stem cells for regenerative medicine applications.

9. Magnetic quantum dots coupled with magnetic microarrays for molecular detection and separation

Kalpesh Mahajan, Greg Vieira, Gang Ruan, Jeffrey J. Chalmers, R. Sooryakumar and Jessica O. Winter

Biomarkers are indicators of biological processes. Their analysis is important not only in diagnostics, but also in monitoring disease progression and response to therapy. Because of their size nanomaterials interact with biomarkers at molecular level. A number of nanotechnology based diagnostic assays have been developed in recent years. However most these schemes have detection capability only, a chemical assay capable of detection and isolation would help in further analysis and manipulation of biomarkers.

Here, we describe a lab-on-chip detection and separation assay to detect and separate biomarkers. the assay consists of magnetic quantum dot nanoparticles (Magdots), with magnetic discs or nanowires array, and electromagnets that apply external magnetic field. This assay can isolate Magdot labeled cells with *in situ* surface protein quantification. With a small variation this assay can also be used to detect and isolate biomolecules (Proteins, DNA, and RNA) in very small concentration solutions. We have successfully shown isolation of human leukocytes with *in situ* CD45 surface protein quantification. We have also detected and separated avidin and p53 single strand DNA from 10^{-10} M solution separately or multiplexed in combination. This technology can be combined in a lab-on-chip platform incorporating mixing, detection, separation and quantification. This assay has a potential to impact diagnostics, small scale synthesis, and molecular chromatography.

10. Life Cycle Assessment of Multimegawatt Wind Turbines with Carbon Nanofiber-Reinforced Polymer Composite Rotor Blades

Laura A. Merugula and Bhavik R. Bakshi

Previously developed life cycle inventories for carbon nanofibers (CNFs) and 2 MW offshore wind turbines were integrated to assess a conceptual blade design employing CNFs as reinforcement of polymer composite materials. CNF manufacture is an energy-intensive operation requiring about 10.9 GJ/kg nanofibers, mostly due to energy requirements in pyrolysis of methane. Life cycle impacts of wind turbines are associated primarily with materials manufacturing and construction. Energy and midpoint impact analyses were applied to determine how the new material would affect overall environmental performance. If research and development of the conceptual design leads to increased deployment and improvements in kinetic energy conversion, loadings of CNFs up to about 2% lead to overall improvements in energy return on investment (EROI) and midpoint indicator performance. Higher loadings would result in less absolute improvements, though the system remains competitive to coal-powered generation in EROI and outperforms in midpoint indicators. High solvent use (499 g acetone per g CNF) for dispersing the CNFs prior to composite molding is infeasible at the development stage. If solvent use can be reduced through more efficient application and solvent recycling, the respective reductions in relative life cycle performance would be offset if enabling improvements in power generation.

11. Evidence for surface freezing in supercooled n-alkane nanodroplets

Viraj P. Modak, Harshad Pathak, Mitchell Thayer, Sherwin Singer, Barbara E. Wyslouzil

Crystallization from the melt is a fundamental process that plays a central role in semiconductor processing, chemical separations, pharmaceutical production and purification and material science and metallurgy. In many cases, the transition to the most stable solid phase can proceed via an intermediate metastable phase. For example, n-alkanes (C_nH_{n+2}) of intermediate chain length (n>15) can form a series of rotator phases. Moreover, in contrast to most other molecules that pre-melt at temperatures below the bulk melting point T_m, intermediate chain length n-alkanes ($16 \leq n \leq 50$) form an ordered surface monolayer up to 3 K above T_m. Our experiments strongly suggest that even the short chain alkanes, n-octane and n-nonane appear to freeze at the surface of supercooled liquid droplets prior to the initiation of bulk freezing. In our experiments we create liquid nanodroplets in highly non-equilibrium states in a continuous flow supersonic nozzle. We characterize the flow using axially resolved static pressure measurements, and study the droplets using spatially resolved Small Angle X-ray Scattering (SAXS) and Fourier Transformed Infrared Spectroscopy. In addition we complement our experiments with molecular simulation studies at the united atom level to develop molecular level insight into homogeneous liquid-solid nucleation and strengthen our interpretation of the experimental results.

12. CO_2 Assisted Development of PCL-Gelatin Based Scaffolds for Biomedical Applications

Hrishikesh Munj, Tyler Nelson, John Lannutti and David Tomasko

Polymer based biomedical systems need biocompatible and biodegradable polymer based structured scaffold/drug release systems with incorporation of multiple biomolecules and controlled release. Polycaprolactone (PCL)-gelatin blend shows improved chemical and mechanical properties along with better cell adhesion. High pressure CO_2 assisted plasticization of polymers has been used for development of biodegradable foams and incorporation of additives in polymers. Infusion of biomolecules in the PCL has been explored only for subcritical CO_2 since supercritical CO_2 causes structural deformation of pure PCL. We have recently demonstrated that different compositions of PCL-gelatin bend can be swelled reversibly by subcritical as well as supercritical CO_2 without loss of structural integrity.

Pure PCL is swelled in the presence of CO_2. However pure gelatin is compressed by high pressure CO_2. Differential scanning calorimetry and weight loss study on pure gelatin confirmed water extraction from gelatin by CO_2 phase. In the PCL-gelatin blend, this simultaneous mass transfer of CO_2 and water in the blend stabilizes the structure in the presence of supercritical CO_2. As the degree of swelling of PCL is higher than extent of compression of gelatin, the blend shows overall increase in the volume in the presence of CO_2. This characteristic behavior of the blend allows supercritical CO_2 assisted processing of PCL-gelatin without compensating structural integrity. Impregnation and release study of dye has been studied for PCL-gelatin (50/50 by vol.) which shows linear release profile avoiding huge initial burst.

If water is externally added to the system, mechanical stability of the blend is affected due to swelling of gelatin. In the presence of humidified CO_2, both PCL and gelatin phases of the blend swell. Due to loss of mechanical strength from gelatin phase, depressurization of humidified CO_2 results in foaming of the blend. Foamed scaffolds can be then infused with drugs/proteins using ‘dry’ high pressure CO_2 without compromising porosity and structure of scaffold.

13. Nano-pore confinement of volatile C-H-O species

Sumant Patankar, Liu Tingting, David Cole and David Tomasko

Fluids play an important role in the evolution and localization of our planets mineral and energy resources. Geological fluids consist mainly of methane and associated volatile organics as well carbon dioxide. Not much is known about the behavior of geological fluids under nanopore confinement at temperatures and pressures encountered below the earth`s surface. This knowledge is integral to two major areas- abiogenic origins of hydrocarbons and carbon dioxide sequestration. This study will focus on the adsorption-desorption dynamics and transport behavior of carbon dioxide and volatile hydrocarbons as well as their mixtures on naturally occurring porous solid matrices under sub-crustal conditions. Sorption studies will be carried out using a high-temperature high-pressure Rubotherm magnetic suspension balance. Measurement of pore-confined fluid density will be undertaken using the novel technique of Vibrating-tube densimetry developed at Oak Ridge National Lab. Neutron scattering and NMR will also be employed to interrogate fluid behavior at mineral surfaces and under pore-confinement. Since it is impossible to study the fluid behavior at all mineral substrates under all possible temperature-pressure conditions, predictive models will be developed using MD simulations to expand our work beyond the limit of current experimental capability.

14. D_2O and nonane non-equilbrium droplet growth in the free molecular regime

Harshad Pathak, Kelley Mullick, Shinobu Tanimura and Barbara Wyslouzil

Nanodroplet growth of water and n-alkanes is observed in industrial processes including, for example, the removal of condensibles from natural gas or during the expansion of steam in low pressure turbines. The process commences with homogenous nucleation of the supersaturated vapor to form droplets. Droplet growth then quenches nucleation by depleting the vapor and releasing heat to the flow. The competition between nucleation and the initial stages of droplet growth determines the number of droplets formed and, thus, strongly influences the aerosol size distribution. We study the growth of D_2O or nonane droplets in the free molecular regime under the highly non-equilibrium conditions found in supersonic nozzles and compare the measured growth rates to the predictions of the isothermal Hertz-Knudsen (HK) and non-isothermal Hertz-Knudsen-Smolders (HKS) growth laws. Pressure trace measurements (PTM) combined with small angle X-ray scattering (SAXS) characterize the droplet size and number densities as a function of the flow time in a supersonic nozzles with 5-10 microsecond time resolution. For the D_2O aerosols coagulation clearly plays a role, while for the nonane aerosols number densities are low enough that coagulation is not important. Fourier transform infrared spectroscopy experiments also detect freezing in the coldest D_2O droplets. For the nonane droplets, there is essentially no difference between the predictions of the isothermal and non-isothermal growth laws since the equilibrium vapor pressures are so low that the ratio of the evaporation to condensation rates is effectively zero. The experimental D_2O growth rates are more closely predicted by the non-isothermal growth law rather than isothermal growth law, but there are still significant differences that cannot be explained by coagulation.

15. Calcium Looping Process (CLP) for Clean H_2 and Electricity Production from Coal

Nihar Phalak, Niranjani Deshpande, Shwetha Ramkumar, Yao Wang, William Wang and Liang-Shih Fan

The Calcium Looping Process (CLP), which is being developed at The Ohio State University (OSU), is a clean coal technology for the production of hydrogen (H_2) and electricity from coal-derived syngas. It integrates the water gas shift (WGS) reaction with in-situ removal of carbon dioxide (CO_2) and other contaminants like sulfides and halides, thus resulting in the production of high purity H_2. The in-situ removal of CO_2 drives the equilibrium limited WGS reaction forward. The CLP has the potential to reduce the overall footprint of a coal-to-H_2 process due to the integration of several unit operations in a single stage reactor. The high temperature operation and the different exothermic reactions involved provide various sources of heat which when integrated appropriately, result in a process with low energy penalty. Prior work conducted in a fixed bed reactor has shown that high carbon monoxide (CO) conversions and high H_2 purities can be obtained, depending on the operating pressures. Based on the encouraging results obtained from the fixed bed reactor, a sub-pilot scale fluidized bed reactor (carbonator) has been designed and constructed at OSU. The design of this reactor and some operational results will be presented. Laboratory-scale experimental results of sorbent reactivation study using hydration will also be discussed.

16. Scale-up of an Amine-based Polymer Membrane for Fuel Cell Hydrogen Purification

Kartik Ramasubramanian, Lin Zhao, Varun Vakharia and W.S. Winston Ho

Hydrogen is usually produced by steam or autothermal reforming of a carbonaceous fuel. Along with H_2, the syngas produced by these processes contains CO_2 as the major diluent while CO and H_2S as the major impurities. Industrially, absorption is typically employed to remove CO_2 and H_2S, while CO is converted by water gas shift reaction (CO + Steam $\rightarrow$ CO_2 + H_2). This reaction is equilibrium limited due to which the outlet CO concentration cannot be reduced to <0.5 – 1%. For use of H_2 in platinum-based proton-exchange membrane fuel cells, the CO needs to be reduced to <10 – 100 ppm depending upon the operating temperature of the fuel cell. H_2S should go down to 10 ppb to protect both the fuel cell and the water gas shift catalyst. Our approach is to use a CO_2- and H_2S-selective membrane process to tackle this separation issue. The CO_2 removal can shift the equilibrium towards the product side and help in almost complete removal of CO via the water gas shift reaction.

Previous lab-scale work in our group has successfully shown that a hydrophilic blend of crosslinked polyvinylalcohol, polyamines and amino acid salt is a promising membrane material for the above separation [1]. The current work focuses on both modeling as well as fabrication aspects of scaling up this membrane to pilot-scale operation. Through a detailed transport model for a spiral-wound membrane, we have shown the feasibility of reducing CO and H_2S down to low levels. The modeling has taken into account both material and energy balances. Different processes with and without a membrane reactor were considered for this feasibility study. For the actual fabrication of a spiral-wound module, the first step is to make a flat-sheet membrane of the required area. For this purpose, we designed and installed a pilot-scale continuous membrane fabrication machine. Preliminary results have shown that the membranes fabricated using this machine yield comparable performances to those of lab-scale membranes. Along with these results, the presentation will highlight the ongoing efforts to produce a thinner and more uniform membrane.

References

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17. Hemoglobin Regulates the Migration of Glioma Cells Along Poly(ε-caprolactone)-Aligned Nanofibers.

Alexander Roth, Ruipeng Xue, Tyler Nelson, Jed Johnson, Jacob Elmer, Joseph Huntley, John Lannutti, Mariano Viapiano and Andre Palmer

U251 aggregate migration on poly(ε-caprolactone) (PCL) aligned fibers was studied in cell culture media supplemented with the O_2 storage and transport protein hemoglobin (Hb) obtained from bovine, earthworm and human sources at concentrations ranging from 0-5 g/L within a cell culture incubator exposed to O_2 tensions ranging from 1-19% O_2. The presence of bovine or earthworm Hb improved cell viability at 1% O_2, while human Hb adversely affected cell viability. Hb auto-oxidation rate constants increased with decreasing O_2 levels, increasing Hb concentrations, and was greatest for bovine Hb and the least for earthworm Hb under identical culture conditions. The wound healing assay showed no differences in individual cell migration under most conditions. Decreasing the O_2 tension in the incubator from 5% O_2 to 1% O_2 decreased aggregate dispersion on PCL aligned fibers. However, the addition of bovine Hb at 5% O_2 significantly improved aggregate dispersion. At 19% O_2, Hb did not impact aggregate dispersion, and at 1% O_2, aggregate dispersion appeared to increase in the presence of earthworm Hb, but only at the latter time points. Taken together, these results show that Hb-based O_2 carriers can be utilized to improve O_2 availability and the migration of glioma spheroids *in vitro*.

18. Photo-responsive Micellar Solutions as Smart Drag-Reducing Fluids for Use in District Heating/Cooling Systems

Haifeng Shi and Jacques Zakin

A light-responsive micellar solution is developed to be used as a promising working fluid for district heating/cooling systems (DHCs). It can be reversibly switched between a drag reduction (DR) mode and an efficient heat transfer (EHT) mode by light irradiation. The DR mode is advantageous during fluid transport while the EHT mode is favored when the fluid passes through heat exchangers. This smart fluid is an aqueous solution of 5 mM of the cationic surfactant oleyl bis(2-hydroxyethyl)methyl ammonium chloride (EO12) and 2 mM of the sodium salt of 4-phenylazo-benzoic acid (PABA). Initially, PABA is in a *trans* configuration and the EO12/PABA solution is viscoelastic and exhibits DR (up to 80% relative to pure water). At the same time, this solution is not effective at heat transfer and its heat transfer properties are reduced by up to 85% relative to water. Upon UV irradiation, *trans*-PABA is converted to *cis*-PABA and in turn the solution is converted to its EHT mode, i.e., it loses its viscoelasticity and DR; however, it now shows a heat transfer capability comparable to that of water. Subsequent irradiation with visible light reverts the fluid to its viscoelastic DR mode. The above property changes are connected to light-induced changes in the microstructure in the fluid. In the DR mode, the OHAC/*trans*-PABA molecules assemble into long threadlike micelles, which impart viscoelasticity and DR capability to the fluid. On the other hand, in the EHT mode, the mixture of EO12 and *cis*-PABA forms much shorter cylindrical micelles that contribute negligible viscoelasticity – this structure is conducive to effective heat transfer. These changes in fluid microstructure are confirmed by cryo-transmission electron microscopy (cryo-TEM).

19. Role of Biogeochemical cycles in Supply Chains: Improved C & N Footprints for Sustainability Assessment

Shweta Singh and Bhavik R. Bakshi

Bio-geochemical cycles play a crucial role in sustaining production activities by providing various ecosystem services. Several of these cycles are degraded due to lack of accounting methods that can include role of these services in economic activities. In, this work we develop a framework to include the role of these cycles in supply chains and life cycle assessment (LCA). Specifically, we focus on Carbon and Nitrogen, as these are the two most important and degraded cycles. Based on the framework, we developed a Ecologically Based Life Cycle Assessment (Eco-LCA) inventory on economy scale using Economic Input-Output (EIO) model for C and N. This inventory can be used to study the dependence of supply chains on these cycles. In this work, we use the developed inventory to study the differences in supply chain of bio-fuels and gasoline. We also propose improved C & N footprints based on our framework and data which will be used to enumerate the differences between the supply chains of two fuels. The study will highlight critical opportunities to improve the functioning of these supply chains in order to reduce impact on C & N cycles, thereby ensuring long term sustainability of ecosystems and economic systems together.

20. Non-noble metal catalysts for the Oxygen Reduction Reaction (ORR) in Proton Exchange Membrane (PEM) fuel cells

Deepika Singh, Juan Tian and Umit S. Ozkan

One of the major roadblocks in the commercialization of Proton Exchange Membrane (PEM) fuel cells is the cost associated with platinum electrodes. While the hydrogen oxidation reaction on the anode is relatively fast, requiring low platinum loadings, the oxygen reduction reaction (ORR) on the cathode exhibits slow kinetics, necessitating higher platinum loadings (up to 0.5 mg/cm^2).

Transition metal containing nitrogen and carbon catalysts have been found to be a viable replacement of platinum for ORR. Previous work in our research group led to the development of non-noble metal ORR catalysts which consisted of carbon nanostructures containing nitrogen (CN_x) which were grown on an Fe or Co-impregnated oxide support by pyrolysis at 900^oC in the presence of an organic nitrogen precursor: acetonitrile. The catalyst thus obtained was then acid washed to leach out any exposed surface metal and non-conductive species. More recently, our efforts have been directed towards resolving the active site debate of these non-noble metal catalysts. We have shown that CN_x is not sensitive to poisoning by known metal poisons such as H_2S, CO and cyanide[1, 2], which would not have been possible if there existed a single active site comprising of a metal center.

Our more recent efforts focused on synthesizing ORR catalysts, which consist of iron impregnated on a high surface area carbon support along with an organic porefiller. These catalysts have been thought to have a metal-N_2 or metal-N_4 type active site and are commonly known as Fe/N/C catalysts. Our current studies involve synthesizing and tailoring both metal-free CN_x as well as Fe/N/C catalysts while optimizing their stability under half cell and fuel cell conditions. Comparisons between CN_x and Fe/N/C catalysts based on spectroscopic techniques such as extended X-ray absorption fine structure (EXAFS), transmission electron microscopy (TEM) and X-ray photon spectroscopy (XPS) are aimed at providing additional insight for differences pertaining to their active sites.

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21. Catalytic Steam Reforming of Bio-derived Liquids

Ibrahim Ilgaz Soykal and Umit Ozkan

Hydrogen is a major candidate for future energy carriers. However, the difficulties associated with its transportation with the current energy infrastructure poses problems. An intermediate substance with high molecular hydrogen to carbon ratio may be reformed on-site or on-board to provide hydrogen. Bio-derived liquids such as ethanol from renewable sources would be easily transportable with the existing infrastructure and would provide clean energy with minimal carbon footprint. Cobalt based catalysts show promising activity and are significantly less expensive than the traditional noble metal based steam reforming catalysts (Ru, Rh). A detailed study of the behavior of the surface species under actual steam reforming conditions would enable tailoring of the catalyst to maximize hydrogen production at a relatively lower temperature range of 350-500 °C. Previously, promising activities and selectivities for cobalt-based catalyst formulations were reported [1]. Oxygen mobility and the change of the Co oxidation state during the reaction are found to play a significant role in achieving high activity with the catalysts [2]. Co-based ethanol steam reforming catalysts were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and temperature programmed techniques. A wide array of *in-situ* and operando spectroscopy techniques including diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and X-ray absorption fine structure spectroscopy (XAFS) was utilized to investigate the active sites for ethanol steam reforming over Co-based catalysts under reaction conditions.

References

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