William G. Lowrie Department of Chemical & Biomolecular Engineering

The Ohio State University

Abstract Book

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A.1 The Quaternary State of Polymerized Human Hemoglobins Regulates Oxygenation of Breast Cancer Solid Tumors

Donald A. Belcher and Andre F. Palmer

Inadequate oxygenation of solid breast cancer tumors can reduce chemotherapeutic efficacy. Polymerized human hemoglobin (PolyhHb) can be transfused into the systemic circulation to increase solid tumor oxygenation and potentially improve chemotherapeutic outcomes. PolyhHb in the relaxed (R) quaternary state, exhibits increased oxygen (O_2) offloading at low O_2 tensions. Furthermore, O_2 offloading at high O_2 tensions is facilitated with tense (T) state PolyhHb. Therefore, transfusion of R-state PolyhHb may be more effective than T-state PolyhHb for O_2 delivery at similar transfusion volumes. Reduction in the apparent viscosity resulting from PolyhHb transfusion may result in significant changes in blood flow distributions throughout the tumor microcirculatory network. Periodic top-load transfusions of PolyhHb into mice bearing breast tumors confirmed the oxygenation potential of both PolyhHbs via reduced hypoxic volume, vascular density, tumor growth, and increased expression of hypoxia inducible genes. Tissue section analysis demonstrated primary PolyhHb clearance occurred in the liver and spleen indicating a minimal risk for renal damage.

Anticipated Graduation: July 2019

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A.2 Technologies for the Isolation and Characterization of Extracellular Vesicles for Cancer Diagnostics

Jingjing Zhang, Eduardo Reategui and Andre F. Palmer

Extracellular vesicles (EVs) are lipid particles that contain proteins, mRNAs, microRNAs, and DNA fragments that resemble their cell of origin. Thus, EVs provide non-invasive molecular biomarkers for liquid biopsies. However, current methods for EV isolation have limited specificity towards tumor-EVs, and they have low throughput (0.1 to 1 mL). We enriched EVs at high-throughputs without sacrificing targeted EV specificity. We used tangential flow filtration (TFF) which has a large volumetric range for EV sample inputs (> 50 mL). We tested our TFF platform with cell culture supernatants for enrichment and characterization of EVs. We obtained up to 6 times more EVs (sized from 30 nm to 1500 nm) and protein contents compared with an ultracentrifugation method. Secondly, we have developed a sensitive analytical microfluidic platform (EV^{HB}-Chip) that enables tumor-specific EV-RNA isolation (94% specificity) that facilitates downstream clinical studies for cancer diagnosis and treatment.

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A.3 Neutrophil Swarming On-a-Chip for Characterization of Collective Cell Migration and Early Stages of Inflammation

Nicole Walters and Eduardo Reategui

Neutrophil swarms often form around sights of infection or injury in the body. Swarming is a tightly regulated process that accomplishes highly complicated tasks that an individual neutrophil could not accomplish. Understanding the early stages in neutrophil swarming at the molecular level has the potential to greatly improve the diagnosis and treatment of inflammation-based diseases. We generated 2-D chemoattractant patterns using microfabrication techniques. These arrays mimic neutrophil swarming in broad arrays that allow the collection and analysis of the chemical signals that control neutrophil swarming. We identified 45 lipid and protein mediators that have a variety of functions, including swarming initiation and resolution, intercellular communication, enzyme inhibition, and more. This suggests a high level of complexity in the innate immune response and the potential for improved intervention in patients with depressed or exaggerated immune responses.

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A.4 Developing a Bi-layered Capsule for Sustainable Delivery of Protein Therapeutics

Pengfei Jiang and Katelyn Swindle-Reilly

Age-related macular degeneration (AMD) is the fourth most common causes of blindness. The current treatment requires a monthly intravitreal injection of anti-vascular endothelial growth factor (VEGF) such as bevacizumab or ranibizumab to inhibit VEGF and to prevent the angiogenesis. However, frequent injection often leads to infection, elevated intraocular pressure and rhegmatogenous retinal detachment. Furthermore, it negatively affects the therapeutic compliance. To this end, we have developed the biodegradable drug delivery device that can control the drug release several months, which can potentially improve patient compliance and reduce the side effects associated with monthly injections.

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A.5 System metabolic engineering of Clostridium cellulovorans towards n-butanol production from cellulose

Teng Bao and Shang-Tian Yang

n-Butanol can be used as a significant industrial chemical and potential superior biofuel. In our previous research, consolidated bioprocessing (CBP), combined enzyme production, biomass hydrolysis, and sugar fermentation into one step, had been achieved in *Clostridium cellulovorans* for butanol production directly from lignocellulosic biomass. However, this mutant only produced 1.42 g/L n-butanol and 1.60 g/L ethanol from microcrystalline cellulose in 10 days. In this study, genome-scale metabolic model with omics analysis were firstly applied for guiding rational metabolic engineering in *C. cellulovorans*. Then, system-metabolic engineering strategies, including optimization of butanol biosynthesis pathway, increasing C4 carbon flux, weakening competitive synthesis pathway, and improving the intracellular NADH availability, carried out to redistribute the carbon flux towards butanol production in *C. cellulovorans*, leading to a high *n*-butanol titer of 5.2 g/L from cellulose. These results indicated that *C. cellulovorans* is a promising CBP platform host for bio-butanol production from cellulosic biomass.

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Anticipated Graduation: June 2019

A.6 Numerical modelling of red blood cell separation using computational fluid dynamics

James Kim and Jeffrey Chalmers

Annually, average of 14 million units of human red blood cells are transfused in the U.S. To meet this demand, various studies focusing on minimizing the risk of contaminated transfusing units were done. Various microfluidic separation devices have been developed for this cause, but opportunities for improvement still exist. To optimize the design of these systems, the trajectory of those red blood cells has been numerically modeled using a combination of commercial computation fluid dynamics software, ANSYS Fluent, and user-defined function for force balance calculation on the red blood cells. Comparison with the experimental data suggests a close match between the two methods, yielding us a chance to further improve the separation system.

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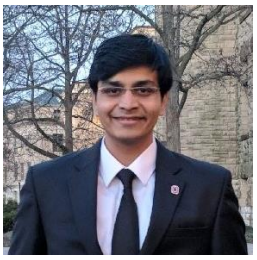
B.1 Selective glucose isomerization to fructose using immobilized tertiary amines

Nitish Deshpande and Nicholas A. Brunelli



Anticipated Graduation: December 2018

Developing catalysts for efficient biomass upgradation is essential for a sustainable chemical industry. Selective glucose isomerization to fructose is an important step in upgrading dry plant matter to high valued products. Fructose can either directly be used as high-fructose corn syrup or it can be upgraded to platform chemicals such as 5-hydroxymethylfurfural. While the industrial process for glucose isomerization is catalyzed using immobilized enzymes, recent reports demonstrate that simple homogeneous tertiary amines can selectively convert glucose to fructose. This presentation demonstrates synthesis, characterization, and catalytic performance of silica supported tertiary amine catalysts for the selective (~70%) isomerization of glucose to fructose. Systematic investigations reveal that various catalyst design parameters including the amine loading, amine structure, and support pore characteristics affect the catalytic performance significantly. Observations indicate an inverse relation between the catalytic performance and amine-surface silanol interactions. Through informed active site design, catalysis comparable to homogeneous tertiary amines is achieved.

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B.2 Synthesis and Catalytic Testing of Lewis Acidic Nano Zeolites for Epoxide Ring Opening Reaction with Alcohol

Aamena Parulkar and Nicholas A. Brunelli

Anticipated Graduation: December 2018

Well-defined pores in zeolites impart shape selectivity for a variety of reactions. However, these pores can also cause diffusion limitations reducing the catalytic performance. Several strategies have been investigated for overcoming diffusion limitation including synthesizing hierarchical structures and reducing particle size. Nonetheless, synthesizing Lewis acidic nano-zeolites still remains a challenge. In this work, five-fold reduction in particle size is achieved for Sn-MFI (nSnMFI) zeolite by modifying synthesis conditions, as compared to conventional synthesis (cSnMFI). For epoxide ring opening reaction, nSnMFI overcomes diffusion limitations associated with cSnMFI, resulting in increased catalytic performance. Higher conversion is achieved for the ring opening of bulky epoxide substrate such as epoxyhexane with methanol with nSnMFI as compared to cSnMFI. Precise engineering of zeolites with reduced crystal size provides an efficient route to overcome diffusion limitations of bulky reactants. To further expand the scope, nano-zeolites with other frameworks can be achieved by modification of synthesis strategies.

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B.3 Poly(ethylene sulfoxide) in presence of Bronstead acid for selective fructose to 5-hydroxymethylfurfural reaction in water

Mariah R. Whitaker and Nicholas A. Brunelli

Anticipated Graduation: August 2019

Biomass as a renewable carbon feedstock can be converted to 5-hydroxymethylfurfural (HMF), a useful platform chemical for production of valuable chemicals and fuels. Previous research has shown that high HMF selectivity can be achieved in dimethylsulfoxide (DMSO) due to its capability to stabilize HMF in solution. However, DMSO is not a preferred bulk solvent as product separation is difficult, Also, DMSO cannot be easily integrated into a continuous process, which uses water as the solvent for upstream biomass conversion steps. For this work, poly(ethylene sulfoxide) is synthesized and used in presence of HCl for fructose dehydration to HMF. The polymer is capable of providing beneficial stabilization interactions on its surface to obtain high HMF selectivity in pure water. Results show that the polymer increases HMF selectivity 2 fold in presence of HCl in water. High selectivity can be achieved with the polymer at a significantly lower sulfoxide concentration as compared to that obtained using liquid DMSO.

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B.4 High purity syngas and hydrogen coproduction using Cu-Fe based oxides in a chemical looping system

Sourabh Nadgouda and Liang-Shih Fan

Anticipated Graduation: May 2019

Chemical Looping technology is an attractive alternative to the conventional processes for chemicals and energy production from carbonaceous fuels with significant reduction in carbon emissions and high exergy efficiency. Syngas and hydrogen production is important because the former is a critical building block for valuable chemicals and later is a source of clean energy. Copper-Iron based oxides were demonstrated to produce high purity syngas and hydrogen while undergoing sequential reduction and steam oxidation reactions in a fixed bed reactor. Different compositions of Cu and Fe oxides were tested to find a balance between their high reactivity towards fuel and high selectivity towards syngas, respectively. Experimental results were used in ASPEN Plus simulation software to compare the overall energy efficiency of the chemical looping system against the conventional auto-thermal reforming process for producing syngas and hydrogen.

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B.5 Heteroatom-Doped Carbon Nanostructures as Oxygen Depolarized Cathodes for Chlorine Production

Deeksha Jain and Umit S. Ozkan

Anticipated Graduation: May 2019

Electrolysis of hydrochloric acid is a widely used process for manufacture of chlorine gas, which is an essential chemical in the production of many indispensable products including polymers like polyvinyl chloride. Traditional HCl electrolysis suffers from its high energy requirements, however, significant amount of energy can be conserved by replacing the traditional H_2-evolving electrode by an oxygen depolarized cathode (ODC) where oxygen is reduced instead of protons. Successful operation of this technology depends on the oxygen reduction reaction (ORR) activity and stability of ODC catalysts, along with high resistance to poisoning in the presence of chloride anions. In this work, we have evaluated the use of nitrogen-doped carbon nanostructures (CN_x) and iron-nitrogen coordinated carbon-supported (FeNC) materials as ODC catalysts in chlorine manufacturing process. These catalysts demonstrate good ORR performance in acidic media. Their resistance to chloride poisoning is compared by systematically understanding the effect of chloride-ion exposure on these materials under both in-situ and ex-situ conditions using techniques like cyclic voltammetry, X-ray photoelectron spectroscopy, Raman and infrared spectroscopy, temperature programmed desorption and X-ray absorption spectroscopy.

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B.6 Mechanistic Studies to Improve Product Yields for Oxidative Coupling of Methane in a Chemical Looping System

Deven Baser and Liang-Shih Fan

Oxidative coupling of methane (OCM) is one of the promising pathways for direct conversion of methane to higher hydrocarbons. Under the chemical looping mode, methane is oxidized by a metal oxide, instead of molecular oxygen as done in the traditional co-feed OCM, to produce higher hydrocarbons as the desired product. Thus, the chemical looping mode avoids molecular oxygen, minimizing over-oxidation of methane. The focus of this study will be to gain mechanistic insights for chemical looping OCM and to design a composite metal oxide which gives a high hydrocarbon yield. Density functional theory (DFT) calculations along with fixed bed experiments will aid in understanding the mechanism of OCM over a base metal oxide, Mg_6MnO_8. Several dopants and configurations will be screened using DFT and verified experimentally to achieve optimum yield. Additionally, solid characterization will help in tracking the redox reactions over the metal oxide. Results from this study would provide key understanding into the development of such metal oxides for chemical looping application.

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B.7 Preferential oxidation of Carbon Monoxide over Swellable Organically Modified Silica (SOMS) supported Cobalt Oxide Catalyst

Dishari Basu and Umit S. Ozkan

The global interest in eco-friendly processes has increased the demand for proton exchange membrane fuel cells (PEMFCs). PEMFCs require an ultra pure hydrogen (H_2) stream as the feed gas. However, this feed may contain traces of carbon monoxide (CO) and water vapor (H_2O). As little as 10ppm of CO can poison the platinum anode catalyst present in PEMFCs. Thus, this hydrogen feed stream must be purified. The preferential oxidation (PROX) of CO to CO_2 is a simple and low cost method to reduce the CO concentration in the H_2 feed. Among the relatively inexpensive transition metals, cobalt (Co) based catalysts are highly active for this reaction. However, H_2O present in the H_2 feed considerably decreases PROX performance over supported Co catalysts. Therefore, the aim of this project is to synthesize an inexpensive, hydrothermally stable Co based catalyst by supporting it on a novel hydrophobic material known as swellable organically-modified silica (SOMS).

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B.8 Aqueous phase hydrodechlorination of trichloroethylene using Pd supported on swellable organically modified silica (SOMS)

Saurabh Ailawar and Umit S. Ozkan

Trichloroethylene (TCE) is a major groundwater contaminant with the maximum allowable concentration limit of 5 ppb in drinking water. Catalytic hydrodechlorination (HDC) of TCE is an economic, environmentally friendly and efficient remediation technology. Challenges faced by HDC of TCE include slow kinetics, inhibition by side-product and poisoning by anions present in groundwater such as chlorides. A novel material, swellable organically modified silica (SOMS) is being investigated as a catalyst support due to its hydrophobicity, swelling in presence of organics and high absorptivity. Pd is the active metal for HDC of TCE. Herein, properties of Pd/SOMS have been compared to those of the commercial catalyst, Pd/Al_2O_3. In several cases, Pd/SOMS has been found to exhibit more resistance to deactivation than Pd/Al_2O_3. Along with kinetic experiments, techniques such as infrared spectroscopy, x-ray absorption spectroscopy, inductively coupled plasma-optical emission spectrometry etc. have been employed to study the catalytic properties of Pd/SOMS.

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B.9 CO_2 Utilization Mechanism Over an Iron Based Metal Oxide in a Chemical Looping System for Conversion of Methane to Syngas

Deven Baser and Liang-Shih Fan

Carbon management strategies such as CO_2 utilization to value added products such as syngas is proving to be a key technology. High purity syngas can be produced by employing a novel co-current moving bed configuration in the chemical looping system which has been well understood on iron-titanium composite metal oxide (ITCMO). Due to ITCMO's inherent thermodynamic capabilities, it can process CO_2 as a feedstock for methane reforming, thus converting it to an easily disposable product, syngas. This study aims to explore the reaction mechanism for CO_2 utilization over ITCMO. The study focuses on $FeTiO_3$ as the target phase which is thermodynamically calculated to be in equilibrium with high purity syngas in the co-current moving bed system. Experiments for gauging CH_4 reactivity and CO_2 utilization rate were carried out on thermogravimetric analyzer and differential fixed bed. These experimental results will help guide the computational analysis to give the oxygen vacancy interaction mechanism. This will give a better understanding of the CO_2 utilization mechanism in this process and help provide a pathway to improve the utility of this technology.

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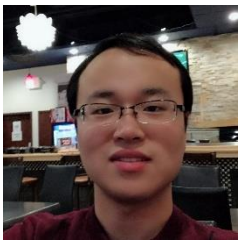
B.10 Hydrogen Production from Natural Gas using Chemical Looping Technology: Heat Integration and Exergy Analysis

Fanhe Kong and Liang-Shih Fan



The production of H_2 under a carbon constrained scenario has attracted increasing research focus. OSU has been investigating a three-reactor chemical looping system for H_2 production from natural gas. In this system, an iron-based oxygen carrier circulates through three reactors, namely a reducer, an oxidizer and a combustor, which perform the natural gas oxidation, water splitting and oxygen carrier regeneration, respectively. This design eliminates downstream CO_2 separation and H_2 purification units, thus achieving significant energy savings. This study focuses on systematic heat integration and exergy analysis of the chemical looping natural gas to H_2 process using ASPEN Plus and ASPEN Energy Analyzer. Compared to the SMR process with 90% CO_2 capture, the chemical looping process shows 10% increase in cold gas efficiency and 7% increase in exergy efficiency and achieves an equivalent H_2 purity (99.9%) and higher CO_2 capture (100%), showing considerable advantages of the chemical looping process.

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B.11 Boron Heteroatom Modification of Carbon-nanostructure Catalysts for the Oxygen Reduction Reaction

Vance Gustin and Umit S. Ozkan

Fuel cell technologies, such as the proton-exchange membrane (PEM) fuel cell, are a promising renewable power source for automotive applications. One of the key barriers to the widespread commercialization of PEM fuel cells is the cost of the platinum catalysts used to facilitate the cathodic oxygen reduction reaction (ORR). Nitrogen doped carbon nanostructures (CNX) are an inexpensive alternative to platinum catalysts but further improvement to their electrochemical activity is required to overcome the commercialization barrier. This work seeks to improve the electrochemical performance of CNX by inclusion of boron heteroatoms via gas and liquid phase doping methodologies. The electrochemical performance of these boron-nitrogen-carbon nanostructures (B-CNX) was determined using rotating ring disk electrode experiments to measure ORR activity and selectivity.

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B.12 : Crystallization of Lewis Acidic Nano Zeolite Beta

Alex Spanos and Nicholas A. Brunelli

Silica based frameworks are effective building blocks for heterogeneous catalysts. The size of the catalyst particles, however, can greatly limit their efficient use caused by diffusion limitations. These limitations can be overcome through the use of nanoparticles, which because of their smaller size, allow for an increased mobility of reactants and a higher amount of available catalyst, leading to faster reaction rates. In this work, pure silica and tin incorporated nano zeolite beta are synthesized at a low temperature through the use of a specialized dipiperidine structure directing agent. The particle size and loading of the materials are characterized. The zeolite is catalytically tested through an epoxide ring opening reaction. Nano Sn-Beta shows to be a highly active Lewis acidic catalyst which size allows it to overcome diffusion limitations. Overall this represents an important modification that can benefit future work in the designing of heterogeneous catalysts.

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B.13 Production of synthesis gas with tunable H_2/CO ratio by high temperature co-electrolysis of CO_2 and H_2O using doped lanthanum ferrite cathode

Dhruba Jyoti Deka and Umit S. Ozkan

Conversion of CO_2 into valuable chemicals is an attractive way of mitigating CO_2 emission. In this study, a solid oxide electrolysis cell is employed to co-electrolyze CO_2 and H_2O into a mixture of CO and H_2 (synthesis gas). The cell is operated at 800°C and consists of yttria-stabilized zirconia (YSZ) electrolyte, Ni and Co doped lanthanum strontium ferrite cathode and lanthanum strontium manganite anode. CO_2 and H_2O get reduced at the cathode to form CO, H_2 and oxide ions. These oxide ions then travel through the YSZ electrolyte and combine to form molecular oxygen at the anode. Faradaic efficiencies of near 100% are obtained during the co-electrolysis process which yields synthesis gas with tunable H_2/CO ratios. Surface and bulk properties of the ferrite cathode materials are investigated using high temperature *in-situ* XRD, XPS, conductivity measurements and temperature-programmed experiments. *Operando* XAS studies under voltage applications have also been done to elucidate the role of the metal ions during the electrolysis process.

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B.14 Silver nanoparticle synthesis in a jet-mixing reactor

Pinaki Ranadive and Nicholas A. Brunelli

Silver nanoparticles (Ag NPs) are used as catalysts for organic reactions and antimicrobial and bio-imaging agents. Conventional production via batch processes results in a wide variability in properties such as the particle size distribution (PSD), because of poor mixing. Further, batch processes in literature use excessive reactants and capping agent. Expensive capping agents like surfactants make up a major part of the overall synthesis cost and have other process disadvantages. Microreactors offer high reaction rates and hence are an attractive alternative to batch processes. We use a simple, inexpensive continuous jet-mixing reactor for room temperature Ag NP synthesis. Ag NPs were synthesized by silver nitrate reduction by sodium borohydride, using trisodium citrate as the capping agent. The effects of the capping and reducing agent concentration on the PSD were investigated. Stable long-term operation of the reactor was also tested. Future work involves bimetallic NP synthesis and reactor mixing time characterization.

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B.15 Production of hydrogen and sulfur from hydrogen sulfide containing stream using chemical looping approach

Kalyani Vijay Jangam and Liang-Shih Fan

Hydrogen sulfide (H_2S) naturally occurs in crude petroleum, natural gas streams as well as produced in the industrial activities such as fuel refining, coal gasification and wastewater treatments. Its removal becomes essential because of its toxic nature and negative effects on the process. Commercially, Claus process allows only sulfur recovery from H_2S containing acid gases. However, process of H_2S splitting makes hydrogen (H_2) recovery possible along with sulfur. H_2S splitting can be conducted in a two-step cyclic process using sulfide/s of Fe, Ni, Co, Cr, Mn and W. The cyclic approach involving appropriate sulfide/s allows production of separate streams of hydrogen and sulfur from acid gases. In this process, H_2 is produced during sulfidation of metal sulfide/s with H_2S while sulfur is recovered by thermally decomposing the sulfur-rich metal sulfide/s produced in 1st step. Thus, this process provides a way to make H_2S an unconventional source of hydrogen and sulfur.

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B.16 Enhancing Activity of Heterogeneous Catalytic Materials by Designing Accessible Catalytic Sites for Fine Chemical Production

Ashwin Kane and Nicholas A. Brunelli

SBA-15 is a tuneable heterogeneous support for immobilizing homogeneous catalytic species for fine chemical applications. Despite widespread use, such heterogeneous systems are less active/selective than homogeneous counterparts due to complicated catalyst-surface interactions. In this presentation, the impact of microporosity on catalytic activity is demonstrated for SBA-15 supported tertiary amines by grafting dimethylpropylamine onto regular and low micropore SBA-15 through two approaches: (i) "grafting to" and (ii) "grafting from" where iodopropyl analogues are grafted and then replaced with dimethylamine. Using Knoevenagel condensation as test reaction, it is shown that high activity of regular micropore catalysts from “grafting from” approach occurs not just because of homogeneous distribution of iodopropyl groups on silica surface, but also due to micropore blockage by iodopropyl groups which increases effective amine loading. Moreover, low micropore SBA-15 supported amines give comparable activity irrespective of grafting technique employed. Overall, this demonstrates importance of microporosity for mesoporous silica supported catalysts.

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B.17 Exergy Analysis on a Chemical Looping System for Sulfur Recovery

Sharath Reddy and Liang-Shih Fan

Combustion products from energy production facilities often produce sulfur compounds such as hydrogen sulfide that must be removed. To achieve this, facilities utilize sulfur capture and recovery techniques to convert hydrogen sulfide to elemental sulfur. The Claus process remains the most popular method for sulfur recovery. However, the Claus process is iterative, requiring multiple converting and condensing steps. Alternative strategies to the Claus process using iron-sulfide as a reaction intermediate in chemical looping systems are analyzed in this study using exergy analysis. The aim of exergy analysis is to assess the irreversibility of process and chemical value of products. The exergy analysis on the chemical looping processes developed in this study indicates increased exergy efficiency over the Claus process. Thus, there is potential in applying chemical looping techniques to sulfur recovery due to less irreversibility and higher value products.

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B.18 Aqueous phase hydrogenation of toluene over Swellable organically-modified silica

Anagha Hunoor and Umit S. Ozkan

Hazardous organic pollutants such as benzene, toluene, ethylbenzene and xylene (BTEX) enter groundwater through industrial effluents and spills from underground storage tanks. In the past, methods such as adsorption, oxidation and bioremediation have been employed to remove/treat these pollutants. The current study aims to explore hydrogenation of these compounds in aqueous phase. In this study, toluene is considered as a representative molecule. A new class of catalyst support known as Swellable organically-modified silica (SOMS) is being investigated. SOMS exhibits properties such as hydrophobicity, swellability and absorptivity towards polar and non-polar organic compounds. The catalysts were synthesized with Ru as the active metal. Batch experiments were conducted to study the activity of the catalysts. The textural properties of the catalysts were determined by Brunauer–Emmett–Teller (BET) method using N_2 physisorption. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with CO and pyridine was performed to understand the nature of active sites.

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B.19 Non-Intrusive Measurement and Imaging of Fluidized Beds Using Electrical Capacitance Volume Tomography

Yaswanth Pottimurthy and Liang-Shih Fan

Real time flow rate measurements and characterization of gas-solid flows is desirable in process applications utilizing solids transport. Electrical Capacitance Volume Tomography (ECVT) is a noninvasive 3-D imaging technology which provides real time images of multi-phase flows. The ECVT sensor consists of multiple capacitance sensor plates designed to externally fit around sensing domain. The capacitance measurements from all possible plate pairings are recorded and processed using various image reconstruction techniques to generate 3-D images of sensing domain.
In this study, ECVT technology was used to study flow characteristics of gas-solid systems such as packed moving bed and fluidized bed regimes. Algorithms were developed to extract solid circulation rate, linear velocity of solids, and 3-D imaging of flow patterns. Flow rate and velocity measurements were calculated using cross correlation and peak matching techniques. Data measurement and analysis techniques of both the raw sensor data and reconstructed 3-D images will be discussed.

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B.20 Active Sites in Nitrogen-Doped Carbon Nanostructures for Oxygen Reduction Reaction

Deeksha Jain and Umit S. Ozkan

Nitrogen-doped carbon nanostructures (CN_x) have been shown to be promising materials to replace state-of-the-art Pt-based catalysts for oxygen reduction reaction (ORR) in hydrogen fuel cells. Identifying the active sites in these materials will help in a rational design of electrocatalysts for ORR applications. We have used several approaches to investigate the nature of active sites in CN_x catalysts including the use of phosphate anions as poisoning probes, modification of synthesis parameters to vary the distribution of nitrogen species and post reaction characterization using X-ray photoelectron spectroscopy. Lack of poisoning of CN_x by CO, cyanide, chloride and sulfur indicates the absence of metal centered active sites. Conventional CN_x catalysts that utilize Fe during the synthesis process are systematically compared to “truly” metal-free CN_x catalysts obtained from graphene oxide precursors using electrochemical and spectroscopic measurements to understand the role of Fe and identify characteristics that could contribute to improved ORR characteristics in these materials.

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Anticipated Graduation: May 2019

B.21 Optimized Chemical Looping Methane Partial Oxidation Using Hybrid Perovskite-Hematite Oxygen Carriers

Yan Liu and Liang-Shih Fan

Developing efficient oxygen carriers is significant for the commercialize Chemical looping partial oxidation (CLPO) processes. Iron-based oxygen carriers, have been widely applied in the CLPO technology for its low cost, and good regeneration ability. However, the moderate reactivity and selectivity of iron oxide impedes the commercialization of CLPO. $LaFeO_3$, on the other hand, can dramatically decrease the methane activation energy and improve the yield of syngas. However, limited oxygen carrying capacity and vulnerability for carbon deposition hindered its development. In our recent work, we found hybrid low concentration of $LaFeO_3$ can dramatically increase the reactivity of iron oxides in CLPO without carbon deposition or losing oxygen carrying capacity. Experiment shows that $LaFeO_3$-$LaxFe_2$-xO_3 can universally enhance the reactivity and selectivity of iron based oxygen carriers where the optimal concentration of $LaFeO_3$ is 0.5%. This work provides a promising way to develop oxygen carriers with high reactivity and selectivity for CLPO.

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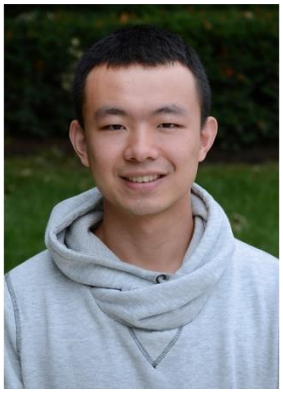
C.1 Inverse Emulsion Polymerization of Polyvinylamine for CO_2 Capture from Flue Gas

Kai Chen and W. S. Winston Ho



Post-combustion capture of CO_2 from the flue gas, generated by coal-fired power plants, is one of the potential methods to reduce carbon emissions. In this work, a composite polymeric membrane was employed to separate CO_2 from N_2. The selective layer of the membrane was made from polyvinylamine (PVAm) blended with an amine-based mobile carrier. The synthesis of PVAm was improved using the method of inverse emulsion polymerization so that the polymer can have a significantly higher molecular weight (MW) and viscosity. The synthesis conditions, including the concentrations of monomer, initiator and emulsifier, were varied and their effects on the weight average MW of the polymer were studied. With a higher MW, the PVAm provided a stronger matrix such that a higher percentage of the mobile carrier to be incorporated. As a result, the separation performance of the composite membrane was improved.

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C.2 Mechanisms to control dynamics in novel plasmonic nanoparticle - DNA origami composites

Abhilasha Dehankar and Jessica Winter

Anticipated Graduation: August 2019

Nanomaterials offer tremendous potential for energy harvesting, electronics, and modern medicine applications. State-of-the-art, top-down/bottom-up fabrication techniques are thus facing insurmountable challenges for complex, 3D, stimuli responsiveness nanoparticle assembly. Recent, bio-inspired, molecular recognition self-assembly method, Deoxyribonucleic acid (DNA) origami, is a great platform to overcome these challenges. Unfortunately, strand invasion, the standard DNA origami actuation method have slow time response (minutes-hours) from DNA diffusion limitations. We are exploring bulk and nanoparticle derived local thermal actuations as alternative routes to improve DNA origami kinetics. Specifically, we investigated kinetics of gold nanoparticle (AuNP) restrained DNA origami hinges using bulk and localized, optical input induced AuNP thermoplasmonic heating. Hinge vertex was modified with Förster Resonance Energy Transfer (FRET) reporters to indicate hinge opening/closing. Kinetics was evaluated using fluorescence spectroscopy with simultaneous actuation. We are currently evaluating plasmonic heating. A strategy for improved DNA origami kinetics could pave way for its application in cutting-edge technologies.

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C.3 Molecular model development with accurate charge distributions for gaseous adsorption in porous materials

Eun Hyun Cho and Li-Chiang Lin

Porous adsorbent materials possess significant potential in gas separation. For an effective materials search, molecular simulations can play an important role. For its successful employment, an accurate description of the gas molecule is critically important. To this end, we present herein a systematic and robust scheme for the molecular model development. In this method, all the model parameters are extensively and efficiently optimized. To ensure a reliable representation of the electrostatic potential (ESP) surrounding the molecule of interest, the number and location of pseudo-sites and the corresponding charge distribution are fitted to the ESP determined by *ab initio* density functional theory calculations. Subsequently, van der Waals interaction parameters are fitted to reproduce experimental vapor-liquid equilibrium. As a proof of concept, hydrogen sulfide model is developed herein and our results indicate that these models can accurately predict adsorptive properties in nanoporous materials. We anticipate this method can largely facilitate the development of accurate molecular models.

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C.4 Study of drug encapsulation and release in Polymeric micelles

Atefeh Alizadehbirjandi and Jessica Winter

Delivery of hydrophobic chemotherapeutic drugs to cancer cells is a known challenge. This challenge arises from their low water solubility which results in considerably low efficiency in treating cancer cells. Delivering hydrophobic drugs by encapsulation in polymeric nanoparticles (NPs) is one potential solution to resolve this problem. Not only does the NP delivery of drugs lower the side-effects of chemotherapeutics [2], but also Polymeric NPs show higher efficiency in drug delivery to cancer cells and more rapid uptake of the encapsulated model drug compared to when the model drug is administered by itself. In addition, the exposure of healthy cells to the toxic drug is limited, which will help reduce the side effects compared to treatment with an un-encapsulated drug [3]. Considering a large number of hydrophobic anticancer drugs, developing an efficient delivery method using NPs could improve cancer therapy, and potentially have large clinical relevance.

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C.5 Effect of structure and entanglement network on the mechanical reinforcement of adsorbed polymer-grafted nanoparticles

Jeffrey Ethier and Lisa Hall

Anticipated Graduation: May 2019

Neat polymer-grafted nanoparticles (PGNs) have been of recent interest for designing next generation printed electronics and energy storage devices. In the absence of solvent or free matrix polymer, mechanical behavior stems from the formation of entanglements between neighboring PGN brushes. We perform coarse-grained molecular dynamics (MD) simulations of neat PGNs adsorbed on a flat, attractive surface with various graft densities and graft lengths to show how these synthetically controllable parameters affect the interdigitation of PGNs and entanglement network. We simulate adsorbed hexagonally packed PGN monolayers with both unentangled and entangled grafts. By analyzing the entanglement network in detail, we show that average entanglement properties do not fully explain the toughness of PGN materials. We analyze entanglements using a geometrical method and find that interparticle entanglements (a subset of overall entanglements, occurring between grafts on different nanoparticles) relate to the degree of interpenetration and stress-strain behavior of the monolayer systems.

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C.6 Surface Area Determination of Porous Materials

Archit Datar and Li-Chiang Lin

Metal-organic frameworks are an emerging class of crystalline porous materials. They have been shown to be promising for several applications such as gas storage and separation processes. One of the key properties of these materials is their surface area. The most widely used method to determine surface area is the BET method. However, it has been shown that the BET method may lead to surface area predictions which differ significantly from those made by geometric methods based on the atomic structures of the materials. In this work, we employed molecular simulations to carry out a systematic study of a large number of MOF structures with diverse geometry features to gain a comprehensive understanding of the predictive capabilities of the BET method. We also investigated the use of the excess sorption work function (ESW) to determine the surface area of these MOFs and incorporated it into the BET method in order to make the predictions more reliable.

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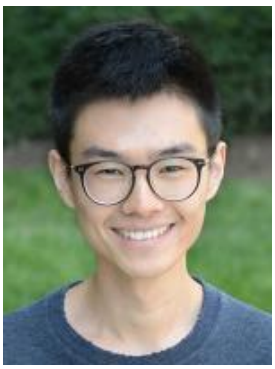
C.7 Nanotube-reinforced facilitated transport membrane for CO_2/N_2 separation with vacuum operation

Yang Han and W.S. Winston Ho



A novel facilitated transport membrane was synthesized in a composite membrane configuration with a 170-nm selective layer coated on a polyethersulfone nanoporous substrate. In the selective layer, poly(*N*-vinylformamide-*co*-vinylamine) with amino groups covalently bound to the polymer backbone was used as the fixed-site carrier, and an aminoacid salt, synthesized by deprotonating sarcosine with 2-(1-piperazinyl)ethylamine, was blended as the mobile carrier. The membrane demonstrated an exceptionally attractive performance with a CO_2 permeance of 975 GPU (1 GPU = 10-6 cm^3 (STP)·cm^2·s^{-1}·$cmHg^{-1}$) and a CO_2/N_2 selectivity >140 at 57°C with 1 atm feed and permeate pressures. The membrane performance was also characterized with a vacuum pulled on the permeate side to simulate actual separation process conditions. However, the elastic selective layer of the synthesized membrane sunk into the nanoporous substrate, resulting in a drastically reduced CO_2 permeance. To address this issue, multi-walled carbon nanotubes (MWNTs) wrapped by a copolymer poly(1-vinylpyrrolidone-*co*-vinyl acetate) were dispersed in the selective layer as reinforcement nanofillers. The gas permeation measurements showed that the incorporation of MWNTs strengthened the polymer matrix and the selective layer penetration was refrained by a 3 wt.% MWNT loading**.**

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C.8 Computational Studies of Zeolite Nanosheets as Pervaporation Membranes for Ethanol Extraction

Changlong Zou and Li-Chiang Lin

Pervaporation is a promising approach for anhydrous ethanol extraction from dilute biomass fermentation broth. Using siliceous zeolite membranes can offer outstanding separation factors but relatively low fluxes. Zeolite nanosheets, synthesized with a thickness of a few nanometers, may overcome this limitation because of their intrinsically short diffusion paths. However, the potential of zeolite nanosheets as pervaporation membranes for ethanol extraction remains unknown. In this study, by employing molecular dynamics techniques, we demonstrated the outstanding performance of zeolite nanosheets for ethanol extraction. The ethanol flux of zeolite nanosheets was found to be orders of magnitude higher than currently available membranes reported in the literature, while a high separation factor can be still achieved. We have also discovered the critical role of nanosheet surfaces in the separation performance. The outcomes of this work are anticipated to be instrumental to the future development of zeolite nanosheet membranes.

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C.9 The Steric Hindrance Effect in Poly(N-methyl-N-vinylamine) Membranes for CO_2 Capture from Flue Gas

Ting Yu Chen and W.S. Winston Ho

Aqueous solutions of sterically hindered amines and sterically hindered amine-based polymers have been demonstrated to have superior advantages for carbon dioxide capture over unhindered amines and unhindered amine-based polymers in commercial gas treating process and recent research papers for removing CO_2. In this work, poly(N-methyl-N-vinylamine) was synthesized by mono-methylation and blended with an amine-containing mobile carrier to make the selective layer of the composite polymeric membrane. Compared to the unmodified polyvinylamine, poly(N-methyl-N-vinylamine) demonstrated a higher loading capacity of CO_2 while maintained sufficient viscosity for membrane casting. As a result, the performance of the composite polymeric membrane was improved by steric hindered poly(N-methyl-N-vinylamine).

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C.10 Molecular simulations of polymer membranes: effects of water

Xuepeng Deng, W. S. Winston Ho and Li-Chiang Lin

Facilitated transport membranes (FTMs) have been proven to be a promising candidate for CO_2 removal from flue gas in coal- and natural gas-fired power plants. Water vapor has been identified as a key component in FTM systems as its presence can substantially improve the transport properties. However, the function of water vapor has not been thoroughly investigated and quantified. We intend to explore the swelling and activation mechanisms of water vapor at a molecular level using the methods of Monte Carlo (MC) and molecular dynamics (MD) simulations. We have simulated the swelling of the membranes at different relative humidities (RHs). Future work will further demonstrate the quantified improvement of transport properties in the presence of water vapor. Such findings will help us better understand the vital role of water vapor in FTM systems in particular and in polymer membranes in general.

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C.11 Magnetic nanoparticle induced proximity effects in Graphene

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The monolayer honeycomb carbon lattice of graphene is responsible for its exceptional properties (high electron mobility, flexibility, thermal conductivity) causing its exploration for electronic, energy, and biosensing applications. However, graphene lacks intrinsic magnetic order desirable for potential magneto-electronic/spintronic applications. Unlike most investigations, a recent study successfully induced long range magnetism in graphene while preserving its pristine attributes [1]. This research examines the superparamagnetic iron oxide nanoparticles (SPIONs) for proximity induced magnetism with potential additional advantage of locally control. Composites assembly involved transferring graphene to a silicon dioxide substrate with SPIONs depositions. Spin coating and Langmuir Blodgett methods were utilized for controlled, scalable self-assembly of SPIONs with different ordering/surface densities levels. Atomic and Magnetic Force Microscopy, Raman spectroscopy and Hall/Quantum Hall measurements were used to evaluate the topography, structural integrity and electronic/magnetic properties of the composite graphene. Ultimately, this research will elucidate localized and global coupling potential of graphene to proximal nanomaterials.

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D.1 Framework for Evaluating TES: Air Quality Regulation Service

Utkarsh Shah and Bhavik R. Bakshi

The engineering desire to out pace and outsmart ecological systems has led to the unsustainable Anthropocene era. Customarily, engineering has focused on designing and operating large-scale continuous system at steady state irrespective of intermittent seasonal availability of ecological goods and services required to sustain these activities. In this work, we propose to design a traditional chemical engineering production process that operates in synergy with ecosystem services of air quality regulation. Using a biodiesel production facility as case study, we demonstrate that the novel synergistic approach is economically superior sustainable manufacturing approach compared to traditional systems approach that ignore nature's ability to provide goods and services. These results demonstrate the need to shift from traditional engineering paradigm of out pacing nature to adopting the dynamics of nature to get maximum sustainable profitability.

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D.2 Quantification of fracture roughness and its insight into mechanical property assessment

Yiwen Gong and Ilham El-Monier

During the hydraulic fracturing process, fractures rough surface and viscous suspension flow bring great challenges to the proppants distribution in the fracture. Thus, detailed understanding of the effect of surface roughness on proppant sedimentation seems essentially indispensable. A newfangled developed algorithm using image analysis software (ImageJ) is applied to characterize the morphological features of the damaged fracture system. Statistical analysis in addition to mechanical moduli are investigated. We found that the fluid delivery to the main fracture essentially depends on the level of the damage in FPZ. Additionally, mechanical moduli were interpreted by image analysis, where a novel approach was developed to calculate the rock mechanical properties. The result from image analysis is compared to other methods. The better understanding of the fracture network serves as a valuable guide to the fracturing job design and managing the damaged FPZ. The novel approach will commit to supporting the lab measurements and field preliminary field assessment.

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D.3 Locality-Dependent Data Sets for QSAR Modeling

Bryan Hobocienski and James Rathman

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Quantitative structure-activity relationships (QSARs) are computationally-based statistical models which attempt to relate the molecular structure of chemical compounds to their observed biological activities. Traditional QSAR modeling approaches are largely “global” in character; a model is constructed using all available training observations and a single set of relevant descriptors. In contrast, the work presented herein adopts a “local” strategy wherein training observations in proximity to each test compound are selected for learning multiple, query-specific models. Additionally, the variability of descriptor data within these local training sets is analyzed to yield a descriptor set tailored to each test query. Local modeling approaches can provide accuracy and interpretability by describing complex, non-linear systems in terms of locally-linear components. Improvements to QSAR modeling are beneficial in many areas, including the development of new pharmaceuticals, cosmetics, and food ingredients, where screening candidate molecules with unacceptable toxicity or therapeutic properties early in the development pipeline is of paramount importance.

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D.4 Evolutionary-based algorithm for descriptor refinement in quantitative structure-activity models

Vinnie Ribeiro and James Rathman

Anticipated Graduation: May 2019

Computational modeling of complex endpoints such as chemical toxicity or protein activity is becoming increasingly more important in many industries, including cosmetics, foods, and pharmaceuticals. These models help prioritize compounds and reduce the number of necessary experiments, making the process more cost and time effective. Quantitative structure-activity relationship (QSAR) models built using available experimental data to predict the behavior of compounds for which there are no empirical results. One of the main challenges in this type of modeling is determining a good way to represent the structural information in molecules of interest. Improving the quality of the structural variables used in QSAR modeling is crucial to the development of high performing models and can be labor-intensive. Given an initial set of chemical structure descriptors, our work uses an evolutionary algorithm to generate new descriptors. QSAR models developed using these new descriptors can in some cases outperform models based only on the original descriptors.

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D.5 Calculating Experimental Rates of Homogeneous Carbon Dioxide Nucleation in a Supersonic Nozzle

Kayane Dingilian and Barbara Wyslouzil

Characterizing the homogeneous nucleation of carbon dioxide (CO_2) is critical to understanding and modeling its behavior in the atmosphere. Previously, we calculated the characteristic nucleation times for CO_2 in carrier gas argon via pressure trace measurements. Recently, we performed small angle x-ray scattering measurements at the 12ID-C beamline at the Advanced Photon Source at Argonne National Laboratory. Particle sizes were calculated for CO_2 concentrations of 2 to 40 percent by mole. Position-resolved data showed trends of increasing particle sizes and decreasing particle number densities with distance from the throat following the onset of nucleation. At the exit of the nozzle, the CO_2 cluster sizes range from 4.0 to 6.4 nm. From the scattering and pressure data, we have calculated experimental nucleation rates on the order of 10^{16}/s*cm^3. Experimental results will be compared to classical nucleation theory and other models to help mend the gaps between predictive methods and reality.

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