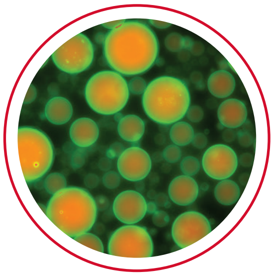
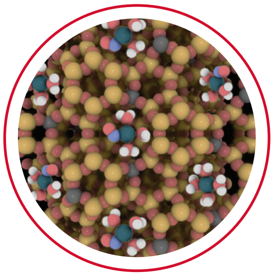
36TH ANNUAL

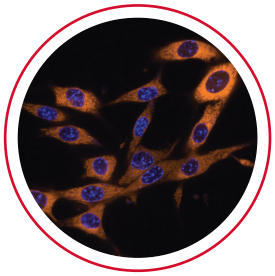
RESEARCH SYMPOSIUM

Presented by:
The Organization of Chemical Engineering Graduate Students
and the William A. Brookshire Deptartment of Chemical & Biomolecular Engineering

> **This symposium provides an exciting opportunity for our department's graduate students to showcase their research in our four fields of biomolecular engineering, catalysis and reactor engineering, energy and environmental engineering, and materials science and engineering.**







Event Features

- Research Presentations
- Poster Sessions
- Faculty Meetings
- Industry Guest Speaker
- Networking Opportunities

Research Areas

- Biomolecular Engineering
- Catalysis & Reaction Engineering
- Energy & Environmental Engineering
- Material Science & Engineering

October 8, 2021
9:00AM – 5:00PM

Virtual Event

Virtual:

Oral Presentation/Keynote Speaker
and Poster Presentations
held through ***Gather.town***

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Welcome Note

On behalf of the Organization of Chemical Engineering Graduate Students and the University of Houston, we would like to thank you for attending the 36th Annual Graduate Research Symposium. Due to the ongoing pandemic, this symposium is being conducted online through Gathertown. Thus, we are very excited for this year's event.

This is an exciting opportunity for our department’s graduate students to showcase their research in fields, including reaction engineering and catalysis, materials engineering, polymer engineering, transport and separations, bio-molecular engineering, petroleum and energy engineering, and computer aided process engineering. Throughout the day there will be student presentations, a poster session, and a keynote speaker. This will allow everyone to enjoy the hard work each student puts into their research project and provides an opportunity for interaction with the graduate students.

We would like to thank the numerous sponsors and their generous contributions for this event. It is with your help that we are able to keep the event going through 36 years of success. We would also like to thank our advisor, Dr. Megan Robertson, who has been there for us every step of the way and provided us with invaluable guidance.

Sincerely,
2021 OChEGS Officers

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Schedule of Events

Introduction	9:00 am – 9:15 am	Welcome from OChEGS, Department Chair
Oral Session I: Materials Science and Engineering	09:15 am – 09:35 am	**Ali Slim -** Nanoparticle Dynamics in Unentangled Polyelectrolyte Solutions
	09:35 am – 09:55 am	**Maninderjeet Singh -** Block copolymer self-assembly for multifunctional applications
	09:55 am – 10:15 am	**Josiah Hanson -** Sustainable Thermoplastic Elastomers Containing Ionic Interactions
Break I	10:15 am – 10:30 am	
Keynote Speech	10:30 am – 11:30 am	**Dr. Jill Martin -** What's Next for Plastics in a Circular Economy?
Poster Session	11:30 am – 01:30 am	Poster Session
Oral Session II: Biomolecular Engineering	01:30 pm – 01:50 pm	**Yixi Wang** – Anaerobic Bio-activation and Conversion of Short-Chain Alkanes
	01:50 pm – 02:10 pm	**David Yang -** Mesoscopic Clusters and Fibril Formation of the Tumor Suppressor p53
	02:10 pm – 02:30 pm	**Atul Goyal** - Continuous monitoring of monoclonal antibody breakthrough from capture columns using immobilized fluorescent reporters
Break II	02:30 pm – 02:45 pm	
Oral Session III: Catalysis and Reaction Engineering	02:45 pm – 03:05 pm	**Meet Shah** - Analysis of temperature patterns in shallow-bed autothermal catalytic reactors
	03:05 pm – 03:25 pm	**Jiakang Chen -** A Global Kinetic Model for the Oxidative Dehydrogenation of Ethane over Mixed Metal Oxide Catalysts at Supra-Ambient Pressures
	03:25 pm – 03:45 pm	**Deependra Parmar -** Spatiotemporal Coke Coupling Enhances Para-Xylene Selectivity in Highly Stable MCM-22 Catalyst
	03:45 pm – 04:05 pm	**Xiaohui Zhao -** Active oxygen sites in ethane oxidation on non-stoichiometric nickel oxide catalysts
	04:05 pm – 04:25 pm	**Abhay Gupta -** Spatiotemporal Features of NO and Hydrocarbons Trapping and Conversion in a PNA+HCT+OC Sequential Monolith Configuration
Symposium Conclusion	04:25 pm – 04:40 pm	Poster Award Presentations and Concluding Remarks
04:40 pm – 05:30 pm		Virtual happy hour/networking

Keynote Speaker:

Dr. Jill Martin

Global Sustainability Fellow at Dow Chemicals

Jill Martin is a Fellow in the Packaging and Specialty Plastics business of The Dow Chemical Company. For the past 27 years, she has served in both research and development (R&D) and technical service and development (TS&D) for the North America Packaging and Specialty Plastics and Hydrocarbons (P&SPH) business. She began her career in R&D working on polyethylene product development including hot melt adhesives, automotive UTH applications, and hygiene absorbent products before moving into a role in New Business Development focusing on technical and commercial evaluation of external technologies. In 2003 she joined the TS&D group working directly with customers and brand owners in the hygiene, rigid and flexible packaging and medical device markets before transitioning into her current role aligned to development of sustainable technologies for packaging markets. In this role she has responsibility for development of packaging materials within the context of a circular economy partnering with R&D and across the entire value chain. Martin is a member of the CalPoly and Clemson Packaging Advisory Boards as well as the ISTA Global Advisory Board and the Great Lakes Energy Institute at Case Western Reserve University. She is a past chair of SPE’s South Texas division’s International Polyolefins Conference.

She received her Bachelor of Science Degree in Chemical Engineering from Carnegie Mellon University in Pittsburgh, Pennsylvania, and a Doctorate in Polymer Engineering and Science from Case Western Reserve University in Cleveland, Ohio. Her thesis focused on structure / property relationships in polyethylenes which she has leveraged into a challenging and long-term career with Dow. She holds over 30 patents and has presented at more than fifteen conferences and workshops on a range of topics from medical devices to innovation in flexible packaging.

Keynote Speech:

Title: What's Next for Plastics in a Circular Economy?

Abstract: The use of plastics across the globe has grown steadily since the mid-20th century due to the broad range of applications for which they may be used. Replacement for other materials such as metal and glass has been driven by the combination of durability, toughness, and lower part weight. Parallel development in the recovery, recycling, re-use, and re-design of plastics has lagged leading to our current challenge of plastics in the environment. Innovation in terms of material design, re-use, and recovery have rapidly been brought to the market to meet the demands of brand owners and NGOs eager to see solutions to address the environmental and societal impacts. However, bringing the most promising circular solutions to scale will require many technical and non-technical skill sets to navigate the complexity of the plastic waste issue. No single company or individual can solve the global challenge but collaborative engagement, with a benefit to all parties, has been demonstrated as an effective way to reduce the impact and create viable economies for communities. In addition to discussing examples of collaborative frameworks, I will also share my experiences in this field and the unique viewpoints that women in the science and engineering disciplines can contribute.

<u>**Presentation Abstracts**</u>

Anaerobic Bio-activation and Conversion of Short-Chain Alkanes

Yixi Wang[a], Nam Nguyen[a], Qinxuan Wang[b], Seung Hwan Lee[c], Ehsan Bahrami[a], Ramon Gonzalez[c], Jeremy A. May[b] and Patrick C. Cirino[a]

[a]Department of Chemical and Biomolecular Engineering, University of Houston; [b]Department of Chemistry, University of Houston; [c]Department of Chemical, Biological, and Materials Engineering, USF

Graduate

This project developed a metabolic engineering platform in *E. coli* whereby short-chain alkanes are enzymatically activated by adding fumarate in the absence of oxygen, for subsequent metabolic conversion into biofuels or other chemicals.

Short-chain alkanes are abundant carbon sources, but their efficient utilization is suffered due to their low energy density and the catalytic challenges associated with controlled functionalization. Biological routes of alkane functionalization are promising, and anaerobic alkane activation avoids the energy and carbon inefficiencies due to aerobic respiration [1].

Functional, heterologous expression of alkylsuccinate synthases which catalyze anaerobic alkane activation has proven difficult [2]. As the first case of functionally expressing alkylsuccinate synthase in *E. coli*, our work should prove useful for further enzymatic hydrocarbon utilization.

Recombinant proteins were codon optimized and expressed in *E. coli*. Short-chain alkanes and fumarate were fed as substrates and corresponding products were detected by GC-MS. Control experiments were designed for subunit analysis and enzymatic alkane activations were confirmed. Key experimental considerations and further enzyme engineering for improved activity and altered substrate specificity will be described.

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1. Haynes, C.A. and R. Gonzalez, *Rethinking biological activation of methane and conversion to liquid fuels.* Nat Chem Biol, 2014. **10**(5): p. 331-9.
2. Salii, I., et al., *Determinants for Substrate Recognition in the Glycyl Radical Enzyme Benzylsuccinate Synthase Revealed by Targeted Mutagenesis.* Acs Catalysis, 2021. **11**(6): p. 3361-3370.

Block copolymer self-assembly for multifunctional applications

Maninderjeet Singh[1], *Alamgir Karim*[1]

Department of Chemical and Biomolecular Engineering, University of Houston

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Block Copolymer (BCP) self-assembly holds immense potential for understanding the fundamentals of polymer self-assembly and generating nanostructures having potential applications in energy storage, nanolithography, and electronics materials. In particular, controlling the orientation and alignment of BCPs opens avenues for their use as electrolytes, lithographic templates, and dielectric capacitors. In this talk, I will present our work on controlling the BCP orientation using thermal gradient-based annealing for mechanically robust ion conduction channels, BCP alignment using thermal gradient-based shear for sub-10 nm patterning, and the use of BCPs and cyclic polymers for dielectric capacitors having high energy density. We show that the thermal gradient-based annealing can generate vertically oriented lamellar BCP channels on non-treated substrates, and these vertically oriented channels can be preferentially swollen with Ionic Liquid post-BCP assembly to generate BCP channels having Ionic Liquid segregated to one polymer domain. We show the template-free alignment of vertically oriented lamellar BCPs having channel dimensions ~9 nm over large areas by using shear stress generated by an elastomer over the BCP films during the thermal gradient-based annealing. This innovative method of generating BCP aligned over wafer-scale areas has direct applications for sub-10 nm patterning for nanolithography. We generate large area aligned unidirectional gold nanowires using these aligned BCP templates. Furthermore, we extend the use of shear-induced assembly to BCP-grafted nanoparticle blend films to generate hybrid nanostructures, which show unique optical properties. We show that the chain-end separation is an important parameter for the use of BCPs in dielectric capacitors, which demonstrates the fundamentals of dielectric breakdown in polymer-based capacitors for determining the upper limit of capacitive energy storage. Motivated by this, we probe the role of chain ends in polymers during the dielectric breakdown by using cyclic polymers having no chain ends and demonstrate significantly higher dielectric breakdown strength in cyclic polymer films as compared to their linear counterparts.

Nanoparticle Dynamics in Unentangled Polyelectrolyte Solutions

Ali Slim, Ryan Poling-Skutvik and Jacinta C. Conrad

Nanoparticles are very useful materials in a wide range of industries including oil and gas, materials, and medicine. Nanoparticles are capable of improving extraction efficiency in enhanced oil recovery through mobility control [1], enhancing properties of composite materials [2], and advancing therapeutic treatments for disease [3]. Fundamental understanding of the transport properties of nanoparticles in complex media is required to effectively enhance their performance in these applications. There are three size regimes of interest when studying the dynamics of nanoparticles in polymer solutions. When the nanoparticles radius, R_{NP}, is much smaller than the size or radius of gyration, R_g, of polymer chains, nanoparticle dynamics depend on the void geometry and solvent viscosity with polymer chains acting as barriers. Conversely, when R_{NP} is much larger than R_g, heterogeneities are averaged across nanoparticles surfaces and their dynamics couple to the bulk viscoelasticity of the solution. In the intermediate regime where R_{NP} and R_g are comparable, nanoparticles experience fluctuations in heterogeneities. The dynamics in this regime are not well understood. Recent experiments [4] and theories [5] proposed that nanoparticle dynamics in flexible (neutral) polymers couple to fluctuations of segmental relaxations of polymer chains in the intermediate regime. However, an understanding of the nanoparticle dynamics as polymer conformation changes is still lacking.

Here, we study the dynamics polystyrene nanoparticles in sodium polystyrene sulfonate dissolved in deionized water using fluorescence microscopy. The polymer conformation is tuned by varying the solution ionic strength. We find that particle dynamics remain diffusive across all time scales. The diffusivities of large particles ($R_{NP}/R_g > 1$) follow bulk predictions according to Stokes-Einstien (SE) at all ionic strengths. For smaller particles ($R_{NP}/R_g < 1$), however, we find that their dynamics exhibit non-monotonic deviations from SE within the unentangled semidilute regime. The size-dependent dynamics do not collapse onto a master curve, suggesting that predictions for neutral polymers do not hold for charged polymers that have a non-Gaussian conformation. Moreover, we observe that the non-Gaussian parameter and the scaled particle diffusivity map onto the same concentration dependence, suggesting the rise of confinement effects despite the absence of entanglements. This improved understanding of the dynamics of nanoparticles will allow us to control their transport in complex media enabling application in enhanced oil recovery, composite processing, and drug delivery.

References:

[1] H. ShamsiJazeyi, C. A. Miller, M. S. Wong, J. M. Tour, and R. Verduzco, *J. Appl. Polym. Sci.* 131 (2014) 40576
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[4] R. Poling-Skutvik, J. C. Conrad, and R. Krishnamoorti, *ACS Macro Lett.* 4 (2015) 1169
[5] L.-H. Cai, S. Panyukov, and M. Rubinstein, *Macromolecules* 44 (2011) 7853

Mesoscopic Clusters and Fibril Formation of the Tumor Suppressor p53

David S. Yang[1], Arash Saeedi[1], Weichun pan[1], Michael Sherman[3], Aram Davtyan[2], Mohsen Fathi[1], Olga Samoylova[2], Mohammad S. Safari[1], Anatoly Kolomeisky[2], Navin Varadarajan[1] and Peter G. Vekilov[1]

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[2]Department of Chemistry, Rice University, MS 60, Houston, TX 77251-1892.

[3]Sealy Center for Structural Biology and Molecular Biophysics, University of TexasMedical Branch, Galveston, TX 77555

Cancer is one of the leading causes of death worldwide. The protein p53 is an important tumor suppressor and is known as the guardian of the genome. This protein is a transcription factor that binds to DNA and controls multiple signaling pathway to determine the cell fate. More than 50 % of human cancers are related to mutations in the p53 DNA-binding domain. Recent studies suggest that p53 aggregation is a key factor in cancer development and the majority of the p53 mutants have an exaggerated propensity to aggregate. Mechanistic details on the nucleation and growth of p53 amyloid fibrils, however, are missing. Here we explore the aggregation mechanism of the p53 R248Q mutant by combining immunofluorescent 3D confocal microscopy of breast cancer with light scattering from solutions of the purified protein and molecular simulations to probe the mechanisms of phase behavior and aggregation. We establish that R248Q p53 forms anomalous condensates which host nucleation of amyloid fibrils. We also demonstrate that in contrast to dense liquids of other partially disordered proteins, the p53 clusters are driven by the structural destabilization of the core domain and not by interactions of its extensive disordered region. The proposed two-step aggregation pathway is supported by data on the aggregation of a protein construct in which we removed the disordered domains and left intact the ordered DNA binding domain of p53. Two-step nucleation of mutant p53 amyloids suggests means to control fibrillization and the associated pathologies through modifying the cluster characteristics. In a broader context, our findings exemplify interactions between distinct protein phases that activate complex physicochemical mechanisms operating in biological systems.

Continuous monitoring of monoclonal antibody breakthrough from capture columns using immobilized fluorescent reporters

Atul Goyal

In 2020, the global biopharmaceutical market was valued at over $215 billion, with monoclonal antibody (mAb) therapeutics representing the majority [1]. Currently, 68 mAb therapeutics have been approved by the FDA, with ~570 more in clinical testing for applications ranging from cancer to eczema to COVID-19 [2]. For instance, in November 2020, the US FDA issued an emergency use authorization (EUA) for casirivimab and imdevimab to be administered together to treat mild to moderate COVID-19 in adults and pediatric patients who are at high risk for progressing to severe COVID-19 [3].

Measurement of antibody concentrations is ubiquitous in biopharmaceutical process development and manufacturing. Purification of therapeutic mAbs usually involves a protein A affinity capture step, which has become a gold standard for the industry. Advancements in cell culture technology have enabled very high antibody titers which create incentives for high column loadings, but the imperfect mass transfer in capture columns can risk breakthrough of the valuable product. Conservative under-loading, however, wastes expensive protein A chromatography resin, which can cost $12,000liter [4]. Because column breakthrough of antibody in complex, UV-absorbing culture fluid cannot be readily detected in real-time, processes are conservatively designed and column capacity often is underutilized, wasting adsorbent and reducing productivity.

We previously developed a fluorescence-based monitoring technology which allows mix-and-read mAb detection in cell culture fluid, which may be useful in at-line assays and in clone and culture development. Here we report the use of reporters immobilized on CNBr-activated Sepharose 4B resin for continuous detection of IgG in column breakthrough. The column effluent is continuously contacted with immobilized fluorescein-labeled Fc-binding ligands to produce an immediately-detectable shift in fluorescence intensity. The technology allows rapid and reliable monitoring of IgG in a flowing stream, without prior sample preparation. We observed significant shifts in fluorescence intensity at 0.5 g/L human IgG, sufficient to detect a 5% breakthrough of a 10 g/L load. The fluorescence intensity response at different load concentrations was used to calibrate fluorescence intensity with IgG concentration.

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Spatiotemporal Features of NO and Hydrocarbons Trapping and Conversion in a PNA+HCT+OC Sequential Monolith Configuration

Abhay Gupta and Michael P. Harold

There has been considerable progress in addressing NO_x (x = 1, 2) and CO/hydrocarbon (HC) emissions from diesel vehicles using the respective combination of urea-SCR [1] (selective catalytic reduction) and DOC (diesel oxidation catalyst) [2] technologies. However, the exhaust temperature must exceed ~200 °C to achieve high NO_x and CO/HC conversions. During the "cold start" period a large fraction of the pollutants are emitted to the environment. Precious metal dispersed zeolites (Pd/SSZ-13, Pt+Pd/BEA) have been shown to be effective for trapping NO [3] and HCs at low temperature, followed by their release and subsequent conversion at higher temperature. In this study we investigate the combination of PNA (Passive NOx Adsorber), HCT (HC trap) and OC (oxidation catalyst) to address a number of key questions regarding material selection, device configuration, and operation strategy to achieve emission performance targets. Most previous studies of emission catalysts involve the measurement of the outlet species concentrations and therefore provide only a partial picture of the reactor behavior. Here we utilize spatially-resolved mass spectrometry and temperature to resolve the spatiotemporal features spanning the sequential PNA, HCT and OC configuration. The instantaneous profiles provide detailed insight into the storage and reduction dynamics within each catalyst along with the mass and thermal coupling between the catalysts. The in situ measurement of species concentration profiles spanning the entire PNA+HCT+OC reactor system provide a detailed probe of the coupled trapping, release and conversion of NO_x, CO, and hydrocarbons, with a particular focus on the cold start period. We are using these data to compare serial and layered architectures and to devise optimal operating strategies for the multi-functional catalytic system.

References:

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2. Mukai, K., Kanesaka, H., Akama, H. and Ikeda, T., SAE, 0148, (2004).
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Spatiotemporal Coke Coupling Enhances Para-Xylene Selectivity in Highly Stable MCM-22 Catalyst

*Deependra Parmar, Seunghyeok Cha, Taha Salavati-fard, Ankur Agarwal, Hsu Chiang, Seth Washburn, Jeremy C. Palmer, Lars C. Grabow, and Jeffrey D. Rimer**

Graduate Student

Para-xylene is one of the most important aromatic compounds used in the synthesis of various fine chemicals. Toluene alkylation with methanol (TAM) catalyzed by zeolites is an emerging and commercially attractive route to produce p-xylene; however, this process often suffers from low catalyst stability and requires the use of diluents (hydrogen and/or water), low space velocity, and high toluene-to-methanol ratios, which collectively results in low p-xylene yield. Here, we present a study of the catalytic properties of MWW-type zeolite catalyst for TAM under high pressure conditions (4.2 MPa).

Our findings reveal that under high pressure conditions without any diluents, MCM-22 shows exceptional catalyst lifetime with the highest p-xylene yield reported to date. The increase in operating pressure suppresses the side-reactions such as methanol-to-hydrocarbons and multiple alkylation of aromatic rings, resulting in significant catalyst lifetime improvement. To understand the catalytic behavior of MWW catalyst, we have deconvoluted the structure-function relationship for different topological features (supercages, sinusoidal channels, and external surface pockets), as they can have profound impact on the catalytic performance.

In this presentation, we will discuss the role of these features for TAM reactions over MCM-22, based on a combination of catalyst testing, density functional theory (DFT) calculations, and molecular dynamic simulations. Our findings suggest that active sites in external surface pockets of MCM-22 are unselective and their deactivation is necessary to achieve high p-xylene selectivity. We also show that the nature of coke species in supercages greatly influences catalyst performance through a unique pathway that is referred to as *spatiotemporal coke coupling*. Overall, this study identifies effective zeolite catalysts for p-xylene production as well as the new insights into the role of coking.

A Global Kinetic Model for the Oxidative Dehydrogenation of Ethane over Mixed Metal Oxide Catalysts at Supra-Ambient Pressures

Jiakang Chen, Zhe Sun, Vemuri Balakotaiah, Praveen Bollini**

Ethylene is a key platform chemical used in the production of a variety of bulk chemicals such as polyethylene, ethylene dichloride, and ethylene oxide. Despite the oxidative dehydrogenation of ethane (ODHE) being extensively investigated as an alternative to steam cracking processes currently used to produce ethylene, a plausible kinetic model that can explain experimental data at high pressures hasn’t yet been proposed. In this work, we use a combination of reaction kinetics experiments and mathematical modeling to develop a global kinetic model that extends up to high pressures (6 bar).

A global kinetic model that accurately describes ODHE catalysis between 330 and 430°C and 0-6 bar total pressure on a $MoVTeNbO_x$ catalyst was developed. The reaction scheme contains three primary and three secondary steps. The dehydrogenation of ethane represents close to zero order in oxygen whereas deep oxidation, secondary oxidation and carbon monoxide oxidation are half order. A two site model based on the Mars-van Krevelen model was proposed for the dehydrogenation and deep oxidation of ethane and power-law rate expressions were used for all other reaction steps. Parity plots point to good agreement between model predictions and experimentally measured rates with an accuracy of ± 20%. F-values and t-values as well as confidence intervals were utilized to support the global significance of proposed kinetic models. The results of this study carry important implications for reactor design, and create opportunities for ODHE commercialization in the future.

Sustainable Thermoplastic Elastomers Containing Ionic Interactions

Josiah Hanson, Megan L. Robertson

Thermoplastic elastomers (TPEs) are widely used in electronics, clothing, adhesives and automotive components due to their high processability and flexibility. ABA triblock copolymers, in which A represents glassy end-blocks and B a rubbery midblock, are commercially available TPEs. The most commonly used triblock copolymer TPEs contain glassy polystyrene end-blocks and rubbery polydiene mid-blocks. However, these commercial TPEs are derived from petroleum whose manufacturing and disposal have undesired environmental impacts, motivating the development of TPEs from sustainable sources. Poly(meth)acrylate-based TPEs, which have greater oxidative stability than their polydiene counterparts, can be derived from a variety of renewable resources such as fatty acids from vegetable oils and corn stover. The carbon side-chain length (n) on the poly(meth)acrylate is a critical parameter governing their properties. With increasing n, the lack of physical entanglements in the TPE matrix inhibits mechanical performance. To overcome this limitation, a transient network was incorporated into the sustainably derived midblock through hydrogen bonding and ionic interactions. The midblock was composed of poly(butyl acrylate) (n=4) or poly(lauryl methacrylate) (n=12), with a comomoner capable of hydrogen bonding and ionic interactions (poly(meth)acrylic acid, neutralized with sodium). The endblocks were poly(methyl methacrylate). The effects of acid content (5-10 mol%), ion content (0-5 mol%), and carbon side-chain length (n = 4 and 12) on the properties of the triblock copolymer TPEs were explored. Midblock chain dynamics were characterized through measurement of relaxation time with rheology, while mechanical performance was evaluated with tensile testing. The incorporation of ionic interactions led to a 17 fold improvement in tensile strength and more moderate increase (factor of 1.5) in strain at break. Factors of enhancement were defined for the tensile stress and strain at break, in which the property was divided by that of the triblock copolymer without ionic interactions or hydrogen bonding in the midblock. The factors of enhancement of tensile strength and strain at break each collapsed to a master curve when plotted as a function of the relaxation time of the midblock for triblock copolymers of varying side-chain length, acid content, and ion content. The midblock relaxation time was therefore a critical factor in determining triblock copolymer mechanical behavior. The presence of ionic aggregates was confirmed with wide-angle X-ray scattering, and features associated with the aggregates became more pronounced at higher ion content. An activation energy, providing indirect measurement of the ionic aggregate binding energy, was quantified from the rheological data.

Active oxygen sites in ethane oxidation on non-stoichiometric nickel oxide catalysts

Xiaohui Zhao, Qianyu Ning, Lars Grabow, Jeffrey Rimer, Praveen Bollini**

Graduate Student

Non-stoichiometric metal oxides represent an important class of oxidation, dehydration, and dehydrogenation catalysts for fossil fuel conversion. The lack of characterization techniques for identifying or quantifying surface oxygen entities has led to open questions regarding the role of (non)-stoichiometric oxygen (NSO) in mediating these reactions [1]. Particularly, the ambiguous nature of NSO over NiO and its availability under ethane oxidative dehydrogenation (ODHE) reaction conditions have prevented an in-depth understanding of reaction kinetics and the effect of thermal treatment on catalyst selectivity [2].

In this study, we use a quantitative analysis of CO_2 adsorption isotherms toward investigating surface oxygen sites on NiO catalysts. Equilibrium adsorption isotherms, Fourier-transform infrared spectroscopy (FTIR) measurements, and reversibility assessments all provide evidence of two surface oxygen species: non-stoichiometric oxygen and lattice oxygen, the binding with CO_2 of which can be described by a dual-site Langmuir model. Non-stoichiometric oxygen binds CO_2 more strongly than lattice oxygen and the resultant carbonate species irreversibly adsorbs at 25 ℃, but reversibly adsorbs at higher temperature (e.g. 300 ℃).

Leveraging CO_2 as an exclusive and reversible titrant for non-stoichiometric oxygen, we have demonstrated for the first time the activity of non-stoichiometric oxygen in both ODHE and total oxidation. Reaction rates subjected to change by CO_2 co-feeds correspond with non-stoichiometric oxygen density under steady state and transient conditions, whereas residual rates can be attributed to surface lattice oxygen or the formation of surface carbonate species that are less active. Turnover frequencies over non-stoichiometric oxygen were found to be ten times higher than lattice oxygen, and the former were also more selective to ODHE. These observations help rationalize the detrimental effect of thermal annealing on ethene selectivity and activity by reducing surface non-stoichiometric oxygen density. These observations are further supported by density functional theory (DFT) calculations on three sites, showing non-stoichiometric oxygen to be the most favorable for C-H activation of ethane. The present data sheds light on the functionality of oxygen species in partial oxidation reactions, and can help guide future developments and kinetic inquiries of bulk metal oxide catalysts.

References:

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[2] X. Zhao, M. D. Susman, J. D. Rimer, & P. Bollini, *Catalysis Science and Technology*, 11(2) (2021) 531–541

Analysis of temperature patterns in shallow-bed autothermal catalytic reactors

Meet Shah, David West, Vemuri Balakotaiah

Graduate

Transverse temperature patterns have been observed in shallow-bed catalytic reactors with high adiabatic temperature rise at both lab and industrial scale. Fluid physical property variations [1] and different rates of heat and mass transport [2] have been analyzed as possible mechanisms of pattern formation utilizing continuum models. Particle level multiplicity may result in stable pattern formation due to different regions of reactors being at different steady state. We show that continuum models with uniform averaged bed properties (e.g. effective radial conductivity) ignore the impact of thermokinetic multiplicity at the particle level and are unable to predict stable pattern formation. We reason that cell models that incorporate the appropriate physical phenomena can predict stable patterns due to particle level multiplicity. We analyze the bounds for stable and unstable pattern formation and region of attraction for various patterned states for adiabatic operation of the reactor. The general cell models analyzed incorporate physical property variations and are applicable to packed-bed as well as monolith reactors. Our analysis shows that the inclusion of physical property variation compounds the impact of multiple mechanisms on pattern formation.

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Poster Abstracts

CH_4 Steam Reforming on Pt+Pd/Al_2O_3 Monolith Catalyst: Impact of $Mn_{0.5}Fe_{2.5}O_4$ Spinel Addition

Pak Wing Chen, Debtanu Maiti, Ru-Fen Liu,

Lars C. Grabow, Michael P. Harold

Graduate

For stoichiometric natural gas vehicles (NGV) emission control, a four-way catalyst containing platinum group metal (PGM) and spinel is used to simultaneously convert CH_4, CO, NOx and other hydrocarbons. Spinel oxides (AB_2O_4) have been reported to be excellent oxygen storage materials and can reduce the required PGM loading [1]. The combination of lean/rich feed and spinel addition allows for improved CH_4 conversion [2]. Our recent work includes the investigation of the role of water and spinel in reducing atmospheres. Flow experiments, post-reaction characterizations and density functional theory (DFT) were used to examine the catalyst activity on methane steam reforming (MSR).

Dual-layer PGM+spinel (30/100/25) and PGM-only (30/100a) monolith catalysts [30 g PGM/ft^3 monolith, 100 g spinel (25w% on Al_2O_3)/L or 100 g Al_2O_3/L monolith] were provided by CDTi Inc. Flow experiment results with lean/rich feed reveal O_2 depletion at temperature above 350ºC, suggesting that MSR becomes the primary pathway for the remaining ~20% CH_4 conversion. Full CH_4 conversion was achieved by 475ºC in the MSR reaction over the PGM-only catalyst. However, MSR activity is inhibited by spinel addition. Enrichment of Mn and Fe species was observed near the surface PGM layer of the PGM+spinel catalyst from the SEM/EDS analyses and DRIFTS data, indicating possible base metal migration and encapsulation of the PGM active sites. DFT calculated results also indicate favorable base metal and/base metal oxide layer formation on the PGM layer.

Our study provides fundamental and practical insight into the CH_4 abatement in rich conditions at high temperatures, which paves the path for optimizing catalyst formulation and operation of NGV emission control.

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Density Functional Theory Study of Methane-to-Methanol Conversion under Dynamic Electrochemical Conditions

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Graduate

Methane, an abundant energy resources in the U.S., has very strong C-H bonds, which are energy consuming to be activated. Current catalytic processes used to upgrade methane to higher value products are facing two major issues: (i) high temperatures (ca. 900 K) are required, and (ii) the lifetime of the catalyst is limited due to sintering and coking. We aim to address these challenges and pursue a novel low temperature process, which leverages a molten carbonate electrochemical cell to convert methane to methanol [1]. The main advantages of this process are that the rate of CO_3^{2-} delivery can be controlled by adjusting the cell potential, the cell potential can be dynamically varied, and CO_3^{2-}, as an oxidant, delivers one oxygen atom at once, preventing the overoxidation of methane.

Various reaction pathways were studied by performing density functional theory (DFT) calculations over Ni(111) and NiO(100) surfaces using the Vienna Ab-initio Simulation Package (VASP). On Ni(111) surface, results show that the two mechanisms studied, CO_3-assisted and O-assisted methane activation, are competing with each other. Both mechanisms have to go through the step of methanol formation from CH_3 and OH, which has a high activation barrier. However, on the NiO(100) surface, a direct formation of methanol was observed when studying the O-assisted mechanism. Thus, the O-assisted mechanism is likely to dominate over the CO_3-assisted mechanism, which has high activation barriers for both methane activation and methanol formation steps. The effect of dynamically applied electric fields was studied for the reaction on NiO(100) surface. Results show that the forward reaction can be promoted by a positive electric field, while the surface refreshment is favored by a negative electric field. The fact that the two parts of the reaction cycle are promoted by distinct electric fields shows great potential to dynamically increase the overall reaction rate by applying an oscillating potential. By optimizing the potential and the frequency of oscillation, the reaction rate is expected to be increased [2].

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Design of antibiotic dosing regimen to eradicate persistent bacteria

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Persister bacteria are a major threat to human health as they are responsible for relapse of infections and chronic illnesses, such as tuberculosis and recurrent urinary tract infections, to name a few. They often act as precursors for development of antibiotic resistant strains. Persisters are a sub-population of bacteria which survive very high antibiotic exposures by staying in a growth-repressed state during the antibiotic attack and cannot be killed unless they recommence growth. Once the antibiotic is removed, they regrow to form a fresh infection. Developing anti-persister therapies is a challenge due to insufficient knowledge about persisters and the-state-of-art is prolonged treatment with antibiotic hoping for eventual eradication with patient's immune system. This is undesirable even when successful due to antibiotic overdose. Our hypothesis is that persisters can be eradicated by an alternating antibiotic dosing regimen, as follows: Expose persisters to a repeated cycle of (a) high enough antibiotic concentration that kills a number of persisters "before" they become dormant, and (b) a low antibiotic concentration at an appropriate time within the cycle, enticing persisters to recommence growth.
We have confirmed the hypothesis by computer simulation and results of pre-liminary *in vitro* testing are highly encouraging. The suggested pulse dose strategy is more effective compared to the conventional strategy of prolonged treatment with complete eradication of persisters with three dosing cycles. The kill rate increases by several orders of magnitudes when the persisters at the end of one cycle are reinoculated in fresh media and allowed to grow for a short duration of 1-2 hours. The next step, is to fine tune and calibrate mathematical models to find optimal dosing regimens and establish guidelines that can be used for a broad range of antibiotic-bacteria combinations.

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Mechanisms for Additive Promotion Effects on Direct Air Capture Using Amino-Silica Sorbents

Xiaowei Wu, Ramanan Krishnamoorti, Praveen Bollini**

Graduate

Direct air capture (DAC) is a novel CO_2 capture technology that holds the key to achieving negative emissions if widely applied. Amino-silica sorbents, a class of organic-inorganic hybrid materials, have been researched widely and verified as strong candidates to capture CO_2 under atmospheric conditions due to stable CO_2-amine interactions. However, one of the key limitations of this system is that some amine sites are not utilized by CO_2, likely due to the diffusion barrier from dense aminopolymer film located in the mesoporous silica pores and CO_2-induced crosslinking during adsorption. The incorporation of non-amine additives into the amino-silica system have been researched as a potential way to improve amine efficiency [1], however, different hypotheses have been proposed in the prior literature to explain the promotion effect without strong evidence supporting most of these hypotheses [2]. Herein, we used different additives (polyethylene glycol (PEG200), diethylene glycol (DEG) and hexyl ether (HE)) in this study in order to explain promotion effects in DAC with changing additive chemical structures. PEG modified samples provide much higher amine efficiency at room temperature than polyethyleneimine(PEI)-only samples at both intermediate and low PEI loading ratios, while a relatively small improvement was observed at 48℃, due to the reduction in diffusion barrier after PEG addition, as reported in previous literature. DEG generally provides similar promotion trends as PEG but less effectively, suggesting that larger molecule sizes of additives favor reduction of the diffusion barrier. HE, an additive without hydroxyl groups, surprisingly also increases the amine efficiency at intermediate PEI loading ratios, but not at low PEI loadings, suggesting different promotion mechanisms for PEG and HE. Thermal gravimetric analysis and infrared spectroscopy were used to provide more insights chemical properties changes after additive incorporation. The improved understanding of mechanisms underlying promotion effects discussed herein is critical in the design of high working capacity DAC sorbents, and may help dramatically reduce cost of temperature swing-based DAC processes.

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Characterizing a cAMP/Crp mediated metabolic futile cycle in bacterial persisters

Han G. Ngo, and Mehmet A. Orman

Graduate

Persisters are a small subpopulation of cells that survive antibiotic treatment and resume growth after antibiotic is removed from the environment [1]. Some variants of persisters can grow in the presence of antibiotic [1], but these types are rare and not as abundant as type I persister variants, which are formed by passage through the stationary phase [1]. In this study, type I persisters will be our main focus because (i) they are formed by many bacterial species, (ii) they are tolerant to a wide range of antibiotics, and (iii) their eradication presents a huge challenge [1-4, 5]. From our previous experiments, we discovered that type I persisters have high respiratory activities that are maintained by endogenous proteins and RNA degradation products [6]. The intracellular degradation occurs in the stationary phase due to cells' self-digestion mechanism [7]. Self-digestion produces self-inflicted damage that transiently repressed the cellular functions targeted by antibiotics [6]. Also, this process facilities persister cell survival in stationary phase by recycling essential energy molecules in cells. We think that type I persistence is facilitated by a Crp/cAMP-mediated metabolic futile cycle in stationary phase, wherein energy derived from catabolism is dissipated through the continuous degradation of cellular components. This hypothesis will be verified by using persistence assays, gene deletions, flow cytometry, redox sensors, cell division reporters, and mass spectrometry analysis.

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Phase Behavior of Colloids with Polymer-Mediated Attractions

Mariah J. Gallegos, Diego D. Soetrisno, Nayoung Park, and Jacinta C. Conrad

Colloidal particles and polymers mixtures are widely used in applications such as paints, consumer products, and pharmaceuticals [1], and more recently have been employed as feedstocks for extrusion-based additive manufacturing [2]. Tailoring the interaction between colloidal particles and polymers in solution can result in different types of attractions between particles, thereby affecting phase behavior which is critical for designing formulations for applications. Polymers that adsorb to the particle surface create physical bridges between the particles, which can drive the formation of clusters through bridging interactions. These bridging attractions are prevalent in separation processes such as waste treatment [3], but how the phase behavior, structure, and dynamics of the suspension depend on the strength of bridging interactions remains incompletely understood. Here, we investigate the phase behavior of a colloid-polymer mixture with attractive bridging interactions in which the strength of the polymer adsorption can be tuned through the pH of the solution. Bridging interactions were induced between trifluoromethyl methacrylate-co-*tert*-butyl methacrylate (TtMA) by introducing poly(acrylic acid) (PAA) to the system. The bridging attraction is driven by hydrogen bonding of PAA with either or both of the steric and electrostatic stabilizers on the surface of the particles. The steric stabilizer on the particles, poly(vinylpyrrolidone), forms strong hydrogen bonds with PAA at low pH [4]. Likewise, the electrostatic stabilizer, dimethylacrylamide-co-sulfopropyl acrylamide, can strongly hydrogen bond to PAA in acidic conditions in the presence of a co-polymer [5]. The formation of hydrogen bonds between TtMA particles and PAA decreases as pH is increased. The structure and dynamics of the TtMA particles as a function of solution pH and polymer concentration were quantified using confocal microscopy and particle-tracking algorithms for particle volume fractions $\Phi = 0.15$ and 0.40 and polymer concentrations of 0, 0.7, and 2.4 mg mL^{-1}. We find that the particles form flocs and networks at low pH but largely remain dispersed at high pH. By quantifying the dynamics (mean-square displacement and van Hove correlation) and structure ($g(r)$ and number density fluctuations), we confirmed that the bridging system exhibited gel and fluid phases at pH 3.8, 4.7, and 5.6 with PAA concentrations of 0.7 and 2.4 mg mL^{-1}. This model system is expected to be useful for fundamental studies of effects of bridging strength on suspension properties, which can lead to improvements in efficacy in flocculation processes such as wastewater treatment and creation of dense markers for indirect detection of specific cell surface molecules [6].

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Solute Incorporation into Crystal Kinks Sites from Organic Solvent: A Molecular Simulation Study

Lakshmanji Verma, Rajshree Chakrabarti, Jeremy C. Palmer, and Peter G. Vekilov

Graduate

Crystallization from solution is ubiquitous. Solvents play a crucial role in the determination of the crystal habit and solvent-surface interactions lead to distinct morphologies for a crystal. During crystallization, solvents structured on the solute as well as growth sites are removed. Therefore, solvent structure and dynamics at the crystal-solvent interface, which depends on crystal-surface interactions, become essential for understanding the growth mechanisms. Experiments have been crucial in understanding the crystal growth from the solution, but the molecular perspective of the fundamental thermodynamics and kinetics which drive these growth mechanisms still evade the community. We employ atomistic molecular dynamic (MD) simulations and advanced sampling techniques to investigate the structure, dynamics, and energetics that determine the growth mechanism of the molecular crystals. We studied the crystallization of organic crystals from the organic solvents which recently attracted a lot of attention to obtain better crystals for pharmaceutical and fine chemicals. We also addressed the growth mechanism of etioporphyrin-I, an organic semiconductor candidate, from pure organic solvents. We found that irrespective of the solvents used the incorporation of the etioporphyrin-I happens in two steps through an intermediate state and this intermediate state is stabilized by the solvent-solute as well as solvent-crystal interaction. The proposed two-step scheme of molecular incorporation presents a new paradigm for solution crystallization that may contribute to understanding crystallization in nature and expedite the selection of solutes and solvents in the crystallization process design of organic pharmaceuticals and advanced materials.

Morphology Dependent Microstructural Deformation and Structure-Property Relationship Studies on Styrenic Thermoplastic Elastomer Films

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Thermoplastic elastomers (TPEs) containing polystyrene (PS) hold a special class of molecular chain arrangements of the hard and soft segments giving rise to many well-defined nanostructures. The orientation and ordering of these nanodomains affect the mechanical properties of TPEs to a very large extent. Accordingly in this work, we investigated this behavior and characterized the impact of different morphologies on the uniaxial tensile properties as well as the deformation of PS domains within the rubbery matrix. A cylindrical poly(styrene-b-(ethylene-co-propylene)-b-styrene) (SEPS) TPE was chosen in this project. Various phase-separated morphologies have been obtained by solution casting bulk films of different thicknesses using four different solvents. The extent to which PS domains order and orient have been varied from 70 - 92 nm in grain sizes and parallel to vertical orientations. The domain periodicities also range from 22 nm to 26 nm. This has been correlated to the interactions of polymers and solvents and the solvent volatilities. Further, the elastic modulus decreased with increase in ordering of the films whereas their tensile strength increased. Deformation resulting in anisotropic Small Angle X-ray Scattering (SAXS) has been evaluated along equatorial and meridional axes for strains until 500%. The degree of deformation (inter-domain spacing, domain distortion) swifts linearly for small strains (less than 100%) as the polystyrene cylinders deform in a non-affine manner throughout the extension. The study of such property dependencies play an important role in designing materials needed to withstand the requirements of specific applications.

Lon Deletion Impairs Persister Cell Resuscitation in *Escherichia Coli*

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Bacterial persisters are non-growing cells that are highly tolerant to bactericidal antibiotics. However, this tolerance is reversible and not mediated by heritable genetic changes. Lon, an ATP-dependent protease, has repeatedly been shown to play a critical role in fluoroquinolone persistence. Although *lon* deletion (Δ*lon*) is thought to kill persister cells via accumulation of the cell division inhibitor protein SulA, the exact mechanism underlying this phenomenon has yet to be elucidated. Here, we show that Lon is an important regulatory protein for the resuscitation of the fluoroquinolone persisters in *Escherichia coli*, and *lon* deletion impairs the ability of persister cells to form colonies during recovery, without killing these cells, through a *sulA*- and *ftsZ*-dependent mechanism. Notably, this observed non-culturable state of antibiotic-tolerant Δ*lon* cells is transient, as environmental conditions, such as starvation, can restore their culturability. Our data further indicate that starvation-induced SulA degradation or expression of Lon during recovery facilitates Z-ring formation in Δlon persisters. Calculating the ratio of the cell length (L in µm) to the number of Z-rings (Z) for each ofloxacin-treated intact cell analyzed has revealed a strong correlation between persister resuscitation and calculated L/Z values, which represents a potential biomarker for Δ*lon* persisters that are transitioning to the normal cell state under the conditions studied here.

Revised activity descriptor for recombinative hydrogen desorption

Chenghao Wang
Graduate

The widespread adoption of water electrolysis using renewable energy for the sustainable production of H_2 is partially hindered by the scarcity and high price of Pt, the catalyst of choice for the hydrogen evolution reaction (HER). The high catalytic activity of Pt for HER has been attributed to its optimal binding strength of hydrogen. The empirical correlation between the metal-hydrogen binding strength and HER activity was first reported by Trasatti in 1972 and later popularized by Nørskov et al by providing a theoretical basis within the framework of the volcano curve.

Despite its widespread adoption, however, the optimal activity requirement of $\Delta G=0$ has shortcomings. Zero coverage values are often unrealistic and attempts to estimate ΔG near saturation coverage are futile, because thermodynamics dictate $\Delta G=0$ at equilibrium. Figure 1a confirms that the activation barriers (E_a) for recombinative H_2 desorption from a near equilibrium surface plotted against ΔG collapse to a vertical line. The small deviations from $\Delta G=0$ originate from the finite size of the unit cell used in the density functional theory (DFT) calculations.

We observed that the two H* atoms involved in the Tafel step on equilibrated surfaces typically bind in two different types of sites, e.g. top and fcc on fcc(111) surfaces. When using the binding energy difference ($\Delta\Delta G$) between the weaker and stronger binding sites as descriptor instead, we show in Figure 1b that it linearly correlates with E_a for pure transition metals, near surface and some single atom alloys (SAA). Notably, we identified several deviating SAAs which have significantly lower E_a than expected and could be interesting candidates for further investigations.

Overall, the kinetics of the Tafel step are more rigorously captured by $\Delta\Delta G$ as alternative descriptor, as it conforms to thermodynamic principles and removes ambiguity in choosing surface coverages for DFT calculations.

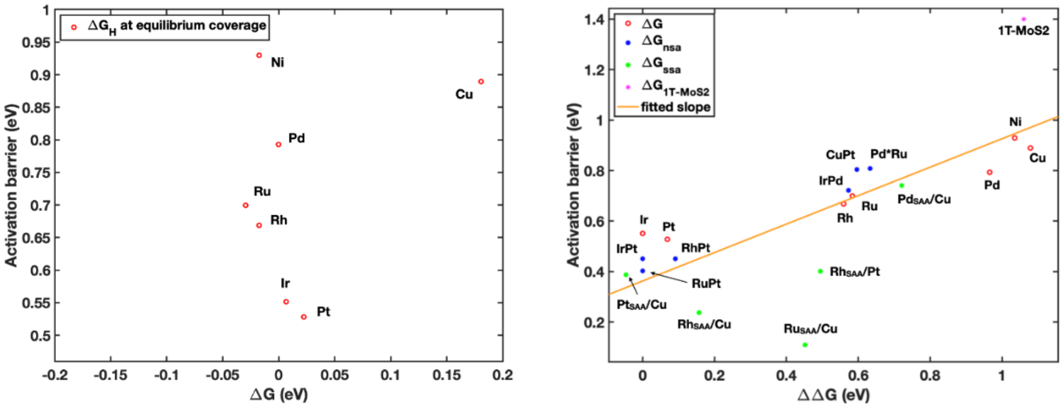

Figure 1. a) Activation energies plotted against the hydrogen free binding energy (ΔG) of pure transition metals under equilibrium coverages. b) Activation energies plotted against the binding energy difference ($\Delta\Delta G$) for pure transition metals, NSAs, SAAs and 1T-MoS_2

Mechanistic Insight into N_2O-Mediated Oxidation over a Mixed-Valent Iron Metal-Organic Framework Catalyst

Jacklyn N. Hall, Praveen Bollini

Graduate

The direct oxidation of methane to methanol is a process which has the potential to create new avenues for the utilization of widely available natural gas resources yet has not been developed at an industrial scale. Metal-organic frameworks (MOFs) are a class of crystalline materials with extended porous structures that have attracted recent attention as catalysts for the partial oxidation of light alkanes. Specifically, their well-defined structures and endowment with high densities of uniform metal centers offer an advantage over previously identified supported catalysts, including most prominently iron or copper-exchanged zeolites, that suffer from heterogeneity in site structure [1]. Recently it has been identified that the MOF material MIL-100 (MIL = *Materials of Institut Lavoisier*), featuring trinuclear iron nodes, oxidizes methane to methanol selectively with nitrous oxide at low temperatures (423 – 473 K) and ambient pressure [2]. Clarity into the steps facilitating the oxidation, however, is limited by the stoichiometric nature of this transformation, as methanol is captured as a surface-bound methoxy intermediate. Furthermore, carbon monoxide is applied as a reductant to further elucidate reaction steps that mediate redox turnovers with nitrous oxide over MIL-100(Fe). Steady state kinetic experiments evidence that elementary reaction steps in the oxidation half-cycle are kinetically relevant, with nitric oxide in-situ titrations indicating that turnovers effectuated by divalent iron sites involve the near complete (91%) and uniform involvement of every iron node. At elevated N_2O/CO molar ratios (≥ 20) at 473 K, increased rate dependence on the CO partial pressure is consistent with significant fractional surfaced coverages (> 0.2) of metal-bound oxo intermediates, the predicted values of which correlate linearly with isotopic exchange rates between the surface ^{16}O and gaseous $^{18}O_2$ co-fed during reaction. Overall, the results of this study provide novel insight into the kinetic relevance of reaction steps facilitating N_2O-mediated oxidation chemistries over MIL-100(Fe) for the broad purpose of improving atomic-level efficiencies of MOFs for light alkane conversion.

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A Global Kinetic Model for the Oxidative Dehydrogenation of Ethane over Mixed Metal Oxide Catalysts at Supra-Ambient Pressures

Jiakang Chen, Zhe Sun, Vemuri Balakotaiah, Praveen Bollini**

Ethylene is a key platform chemical used in the production of a variety of bulk chemicals such as polyethylene, ethylene dichloride, and ethylene oxide. Despite the oxidative dehydrogenation of ethane (ODHE) being extensively investigated as an alternative to steam cracking processes currently used to produce ethylene, a plausible kinetic model that can explain experimental data at high pressures hasn’t yet been proposed. In this work, we use a combination of reaction kinetics experiments and mathematical modeling to develop a global kinetic model that extends up to high pressures (6 bar).

A global kinetic model that accurately describes ODHE catalysis between 330 and 430°C and 0-6 bar total pressure on a $MoVTeNbO_x$ catalyst was developed. The reaction scheme contains three primary and three secondary steps. The dehydrogenation of ethane represents close to zero order in oxygen whereas deep oxidation, secondary oxidation and carbon monoxide oxidation are half order. A two site model based on the Mars-van Krevelen model was proposed for the dehydrogenation and deep oxidation of ethane and power-law rate expressions were used for all other reaction steps. Parity plots point to good agreement between model predictions and experimentally measured rates with an accuracy of ± 20%. F-values and t-values as well as confidence intervals were utilized to support the global significance of proposed kinetic models. The results of this study carry important implications for reactor design, and create opportunities for ODHE commercialization in the future.

Morphology Transitions in Lamellar Block Copolymer Films between Direct Solvent Immersion Annealing and Thermal Annealing for Accelerated Assembly

(Kshitij Sharma, Ali Masud, Aman Agrawal, Guangcui Yuan, Sushil Satija, John Ankner, Jack Douglas, and Alamgir Karim)

Thin polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) diblock-copolymers (BCP) films with symmetric volume fractions assume parallel lamellar microstructure with respect to a Silicon oxide surface owing to the preferential segregation of PMMA molecules to the surface [1]. Thin BCP films can be processed using thermal annealing (TA) and direct solvent immersion annealing (DIA) to achieve this lamellar self-assembly. DIA methodology involves immersion of BCP films into a solvent environment composed of a good/intermediate/bad solvent to cause rapid self-assembly and has been reported to produce microdomains sizes (~L_o/2) that are nearly 50% smaller compared to those produced by TA (L_o) [2]. We report a switchable transition between the two domain sizes observed for the two processes. Further, we find a large asymmetry in the kinetics of these reversible processes due to the distinct molecular mechanisms involved in the two different techniques. We use atomic force microscopy and neutron reflectivity to characterize the surface topography and bulk film structure, respectively, with successive annealing treatments to capture intermediate stages of the transition process. The interesting structural crossover between the two distinct states and the underlying kinetics of the process by thermal annealing/DIA will be discussed in terms of chain swelling, diffusion, and in-plane vs. out-of-plane chain junction density evolution.

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Controlling Formic Acid Decomposition Through Alloy and Ensemble Effects on PdCu Catalysts

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Formic acid (FA) is a promising hydrogen carrier, because it can be formed through CO2 hydrogenation and subsequently release hydrogen under moderate conditions. To effectively use FA as hydrogen carrier, however, a catalyst with high selectivity to CO_2 and H_2 is needed. The periodic table contains just over 10 transition metals that have practical uses as supported metal catalysts. With very few exceptions, these pure metals rarely provide active sites with both high activity and selectivity towards the desired product, but designer alloys can often circumvent these limitations.

For FA decomposition, Pd is known for its activity but lacks selectivity and is easily poisoned by the by-product CO. Cu, on the other hand, exhibits good selectivity but with much lower turnover frequencies (TOFs). Using density functional theory and microkinetic modeling, we show that the selectivity of Cu can be combined with the activity of Pd over dilute PdCu alloys. An upshift of Cu's d-band center upon alloying greatly increases the reactivity of Cu , without compromising its selectivity [1]. Isolated and unselective Pd sites at low Pd/Cu ratio can be fully poisoned by trace amount of CO, without negatively affecting surrounding Cu sites. Increasing the Pd content, however, causes the formation of larger Pd ensembles, which cannot be passivated by CO and provide active sites for unselective reaction pathways. Our results and their interpretation are consistent with TPD, TEM, and EXAFS characterization, and reaction studies.

Our detailed structure-function relationship for FA decomposition over PdCu alloy catalysts suggest that by carefully balancing alloy (electronic) and ensemble (geometric) effects it may be possible to rationally design metal alloy catalysts with exceptional activity and selectivity.

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Simulation of Finite-sized Particle Transport through Porous Media

Deepak Mangal, Jacinta C. Conrad, and Jeremy C. Palmer

Understanding the transport of finite-sized particles comparable to pore or throat diameter through a porous medium is important in many industrial and natural processes, including oil recovery, drug delivery, the dispersion of nutrients, minerals and contaminants through soil, and separations using techniques such as gel electrophoresis and chromatography. One of the key aspects influencing particle transport is the nature of their interactions with the porous medium, including steric repulsions and hydrodynamic interactions, that in turn are affected by the structure of the medium. Here, we perform Stokesian dynamics simulations to investigate the effect of steric and hydrodynamic interactions and system dimensionality on particle diffusion and dispersion over a broad range of flow rates in nanopost arrays. Whereas both types of interactions hinder particle diffusion under quiescent conditions, they are found to enhance longitudinal particle dispersion under flow. Longitudinal dispersion, however, is similar in two- and three-dimensional models of nanopost arrays. We also examine the effects of array structure and flow orientation on particle diffusion and dispersion in three-dimensional square and hexagonal nanopost arrays. We find that quiescent diffusion decreases as the volume fraction of nanoposts is increased, as expected, and is approximately independent of array geometry. Dispersion under flow depends on the direction of the incident flow relative to the array lattice vectors. For flow oriented along the lattice vectors, the longitudinal dispersion coefficient approximately recovers Taylor-Aris scaling behavior at high Péclet number (Pe). For other flow orientations, however, the qualitative behavior of the longitudinal dispersion coefficient depends on the nanopost volume fraction and flow angle. Specifically, at large nanopost volume fractions, we observe non-monotonic dependence of the longitudinal dispersion coefficient on Pe when the flow orientation is slightly perturbed from certain lattice vectors.

Molten Salt Synthesis of NiO, MgO, and their Mixed Oxides: Designing New Methods to Control Crystal Morphology

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In several catalytic and absorption processes of industrial relevance, the crystal morphology and surface terminations of metal oxides play an important role; however, controlling these surface properties and studying their different behaviors in order to rationally optimize catalyst performance is not always feasible. In this presentation, we will discuss methods of preparing rock-salt metal oxides like MgO,[1] NiO,[2] and their solid solutions, (Mg,Ni)O,[3] by molten salt synthesis (MSS), Our findings reveal that MSS enables a high level of morphological control by altering the pathways of metal oxide crystallization. We will show that polar MgO(111) can be prepared using either alkali nitrates or chlorides.[1] For NiO, the morphological diversity is much wider, including NiO octahedra and trapezohedra exposing NiO(311) and (611) facets in alkali chlorides. These high-index facets have not been previously reported for this material.[2] Our findings also reveal that NiO(311) trapezohedral particles grow through a nonclassical crystallization pathway, and are stable under steaming and retain catalytic activity in oxidative dehydrogenation of ethane over long time on stream, indicating high morphological stability at reaction conditions without evidence of sintering.[2] We will show that the judicious selection of alkali nitrates allows for the synthesis of NiO cubes, cuboctahedra, and octahedra. Moreover, we have discovered that the formation of (Mg,Ni)O solid solutions is distinctively favored in alkali chlorides whereas in nitrates segregation of the oxides takes place.[3] The crystallization process in chlorides is mediated by the formation of molten phases comprised of K3NaMCl6 (M=Mg, Ni) from which solid metal oxides form. Collectively, our findings reveal that diverse morphologies can be achieved through crystal engineering, thus allowing for the establishment of structure-performance relationships in a wide range of industrial catalytic processes.

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Investigating the effects of Density Functional Theory (DFT) functionals on NO binding to ZPd^{I} active sites in Pd-exchanged/SSZ-13 Passive NO$_x$ Adsorbers

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Relevant to passive NO$_x$ adsorbers (PNAs) in diesel engine emissions control technology, NO binding on ZPd^{I} active sites of Pd-exchanged SSZ-13 is predicted to be highly exothermic (-2.51 eV) by the BEEF-vdW exchange-correlation functional, leading to a strong stabilization of the otherwise unstable Pd cation with +1 oxidation state. While investigating condition-dependent Pd speciation, we also tested the PBE-D3(BJ)vdW and HSE06-D3(BJ)vdW functionals and calculated binding energies of -2.82 eV and -1.81 eV, respectively. Clearly, the stability of the ZPd(NO) complex is a strong function of the exchange correlation functional. Since we have invoked this metal-nitrosyl motif within the zeolite framework as NO$_x$ storage site and as intermediate during NO oxidation, we have investigated NO and CO binding to ZPd^{I} with different exchange-correlation (XC) functional types incorporating higher levels of theory using plane wave (PW) and Gaussian basis sets in order to assess the reliability of calculated binding energies, incorporating the empirical van der Waals correction terms as well as the Hubbard *U* term and used bond analysis tools such as crystal orbital hamilton population (COHP) analysis to identify the electronic structure level differences that cause the large range of calculated energies. In addition, we considered experimental gas phase NO and CO vibrational frequencies and the reaction enthalpy of CO oxidation by NO$_2$ as benchmarks and calculated residual mean absolute error (RMAE) of scaled DFT frequencies and error in reaction enthalpy. Our benchmarks indicate that TPSSh has closest agreement with experimental known reaction enthalpy for model reaction in gas phase. Pure GGA functionals predicted higher binding energy than hybrid functionals for both NO and CO on ZPd^{I} active site but closer frequency for experimental known values. Hybrid functional (HSE06) predicts more ionic nature of Pd-N bond than pure GGA (PBE) which results in weaker binding of NO on ZPd^{I}. Our in-depth study has provided a better picture of the reliability and robustness of DFT functionals for PNA and is paramount in understanding the dynamic changes of active sites during NO$_x$ trapping.

Harnessing heteroatom effects in zeolite synthesis: a kinetic trap for organic-free FAU

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Graduate

Heteroatom-modified zeolites have emerged as fascinating materials owing to their potential to improve both catalyst performance and stability. However, optimizing these properties is challenging in part because zeolite crystallization is not well-understood, particularly when the addition of heteroatoms obfuscates molecular phenomena and/or prolongs crystallization times. In this presentation, we will discuss our studies of faujasite (FAU) crystallization in organic-free media containing heteroatoms. Faujasite is a metastable zeolite heavily utilized as a fluid catalytic cracking catalyst. FAU commonly undergoes mid-synthesis interzeolite transformation to more thermodynamically stable phases (e.g. GIS) according to the Ostwald rule of stages. To this end, we have surveyed the effects of multivalent heteroatoms on FAU and GIS crystallization and identified metals such as zinc to be useful elements for controlling crystal growth and interzeolite transformation.

In this presentation, we will discuss how experiments and modeling have been used to characterize zincoaluminosilicate growth solutions throughout stepwise crystallization processes wherein we elucidate the challenges associated with heteroatom-incorporated zeolite synthesis and evaluate the efficacy of zinc on suppressing zeolite crystallization. We additionally reveal the mechanisms responsible for this effect; namely, soluble zincate species bind silicate oligomers, which effectively increases the energetic barrier to GIS nucleation. Furthermore, we will show that it is possible to take advantage of suppressed kinetics to control phase purity and kinetically trap metastable zeolites. Our work further demonstrates the lack of an epitaxial relationship between parent (e.g. FAU) and daughter (e.g. GIS) zeolites, which underscores possible pathways for interzeolite conversions between two frameworks lacking common structural building units. Lastly, we will describe how a molecular level understanding of heteroatom effects is critical for ensuring the optimal properties of zeolite catalysts. Collectively, these experimental and modeling studies have demonstrated a novel technique for studying zeolite crystallization phenomena by suppressing growth kinetics using soluble transition metal species.

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Therapeutic Approach to Eradicate Methicillin-resistant *Staphylococcus aureus* Persisters

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Graduate

Persister cells are a small fraction of non-proliferating variants in a cell population that can tolerate lethal doses of antibiotics. These cells can resume their growth upon removal of antibiotics. In this study, we aim to identify therapeutic strategies to eliminate persister cells of Methicillin-resistant *Staphylococcus aureus* (MRSA) strains. MRSA remains one of the main virulent pathogens responsible for serious hospital-acquired infections including bloodstream infections and ventilator-associated pneumonia [1]. Because of their emerging resistance to all current antibiotic classes, it is becoming increasingly difficult to eradicate MRSA persisters. Previous studies have shown that proton motive force (PMF), an essential survival mechanism in bacteria, can be a good target for developing anti-persister strategies [2], [3]. Small drug molecules can disrupt PMF by changing the electrochemical potential or the proton concentration gradient across cellular membrane. Perturbing PMF can also permeabilize cell membrane and enhance antibiotic uptake. Here, by screening a small chemical library, we found several drugs, Nordihydro Guaiaretic Acid, Gossypol, Diclofenac, Celastrol and Alexidine, that can significantly dissipate PMF of MRSA strains. Our subsequent assays further verified that these drugs can efficiently eliminate MRSA persisters, highlighting their potential clinical applications.

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Identity of Active Sites and Inhibiting Species in the Catalytic Dehydration of Methanol over MIL-100(Cr)

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Graduate

Metal-organic frameworks (MOFs) have recently received extensive attention as promising materials in catalysis research, an example of which is MIL-100(Cr) (MIL = Materials of Institut Lavoisier), a type of chromium based MOF material with isolated, uniform, and tunable metal Cr_3O nodes [1], as well as accessible acid sites without the creation of defects [2], offers a unique opportunity to develop an improved understanding in structure-property relationship in heterogeneously-catalyzed reactions. Herein, we used methanol dehydration as a probe reaction to identify active sites, establish reaction mechanism, and determine inhibiting species over MIL-100(Cr) nodes. We performed in-situ titrations using pyridine and 2,6 Di-tert-butylpyridine, and identified methanol dehydration mainly proceeds on Brønsted acid sites. The active site density is directly related to the number of Cr nodes, where residual activity is due to the difference in kinetic diameters of the two titrants. Spectroscopy and isotopic studies suggest the dehydration of methanol to DME is kinetically limited by the decomposition of methanol dimer. A negative, larger than -1 order dependence of measured DME formation rates on water partial pressure (0.5-2.5 kPa), and a positive, less than first order dependence on methanol partial pressure (0.2-2 kPa) at 478 K, 493 K and 508 K can be rationalized by the competitive adsorption of methanol – water dimer at high water to methanol partial pressure ratio, which was further evidenced by the dependence of the reaction rates on residence time at constant methanol partial pressure. The titrations described in this study allow for a characterization of active site speciation in MIL-100 catalysts, and the proposed reaction mechanism accounts for the observed kinetic measurement over MIL-100(Cr), which provide guidance on future MOF catalyst design and our eventual goal of tuning them for advanced catalytic applications.

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A Transient Metabolic State in Melanoma Persister Cells Mediated by Chemotherapeutic Treatments

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Graduate

Persistence is a transient state that poses an important health concern in cancer therapy. The mechanisms associated with persister phenotypes are highly diverse and complex, and many aspects of persister cell physiology remain to be explored. We applied a melanoma cell line and panel of chemotherapeutic agents to show that melanoma persister cells are not necessarily preexisting dormant cells or stem cells; in fact, they may be induced by cancer chemotherapeutics. Our metabolomics analysis and phenotype microarray assays further demonstrated a transient upregulation in Krebs cycle metabolism in persister cells. We also verified that targeting ETC activity can significantly reduce melanoma persister levels. The reported metabolic remodeling feature seems to be a conserved characteristic of melanoma persistence, as it has been observed in various melanoma persister subpopulations derived from a diverse range of chemotherapeutics. Elucidating a global metabolic mechanism that contributes to persister survival and reversible switching will ultimately foster the development of novel cancer therapeutic strategies.

Mechanistic role of water in the storage and oxidation of NO on Pd/CHA

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Graduate

Palladium exchanged zeolites have been extensively studied as passive NO_x adsorbers (PNA) to store NO_x at low temperature and release it at higher temperature to a downstream selective catalytic reduction (SCR) catalyst which converts NO_x to N_2. PNA occurs with complex exhaust feed compositions and the observed NO_x uptake is a strong function of the reaction conditions and Pd speciation [1]. Notably, the presence of water leads to solvated and mobile Pd complexes that behave drastically different from the cationic species anchored to the zeolite framework under dry conditions [2]. As secondary function Pd-zeolites also catalyze the oxidation of NO to NO_2.

Herein, we use periodic, van der Waals corrected density functional theory (DFT) to propose a complete reaction mechanism for NO storage and oxidation on dynamically hydrated isolated Pd within chabazite (CHA) zeolite. We report the effect of water solvation on binding preference of adsorbates on various monomeric Pd active sites, and find that NO preferentially binds to the $[Pd(H_2O)_4]^{2+}$ site and facilitates the activation of one of the water molecules coordinated to Pd. The water activation step results in the formation of the key intermediate HONO, which subsequently disproportionates to NO, NO_2, and H_2O. In the process of HONO formation Bader charge analysis indicates a reduction of Pd, which serves as a storage site for NO. NO desorption at high temperature requires re-oxidation of Pd using either NO_2 or O_2 as oxidant.

Our proposed mechanism predicts the role of water in oxidizing NO at low temperature and is consistent with experiments resulting in low temperature NO_2 formation even without oxygen. Our findings suggest that the presence of water plays a major role in active site transformation, thus, opening up an interesting avenue for catalyst performance improvement.

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Simulation of Weak Polyelectrolyte Brush

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Graduate

Weak polyelectrolyte brushes consist of end-grafted polymer chains with various degrees of ionization that depend on environmental conditions such as pH and salt concentration. This feature enables unique stimuli-responsive behavior that can be utilized in many applications, including targeted drug delivery and nanofluidic circuits, among others. However, it is currently challenging to rationalize the behavior of weak polyelectrolyte brushes with current theoretical and experimental approaches due to the complex interplay of reaction equilibria and electrostatic interactions. Here, we address this challenge by employing advanced molecular simulation techniques to model the behavior of planar weak polyampholyte brushes containing both acidic and basic monomers. Specifically, the effect of pH, polyampholyte sequence, and grafting density on brush characteristics such as brush height and degree of ionization were investigated by combining advanced Monte Carlo (MC) methods (reaction ensemble and grand canonical ensemble) with classical molecular dynamics (MD) simulations [1]. The simulation results indicated that both degree of ionization and brush height for a weak polyampholyte brush exhibit non-monotonic behavior with respect to solution pH. The minimum brush height occurs at neutral pH, where degree of ionization is at its maximum. Polyampholyte sequence also plays a significant role in brush conformation, with brush height increasing as the sequence block size decreases. In contrast, grafting density's effect on brush height is not as significant: higher grafting density results in a slightly higher brush height, which agrees with expectations based on the behavior of neutral polymer brushes. We anticipate that improved understanding of these effects will facilitate rational design of advanced stimuli-responsive surfaces for myriad engineering applications.

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Dynamics of Flexible Viruses in Semidilute Polyelectrolyte Solutions

Farshad Safi Samghabadi, Ali H. Slim, and Jacinta C. Conrad

Phages are nanoscale viruses that can infect bacteria without harming animal or plant cells [1]. Initially recognized as antimicrobial agents, they are now widely used in applications such as drug and vaccine delivery [2], phage therapy [3], and phage display [4]. Understanding the transport properties of phages in real medical samples, which are mainly charged biopolymers, is essential to effectively enhance their performance in these applications. Previous studies have investigated the nanoparticle dynamics decoupling from the Stokes-Einstein prediction [5], effects of different length scales on the dynamics of anisotropic viruses [6], and interactions between the nanorod and the polymer matrix [7]. The dynamics of nanoparticles, especially highly anisotropic particles like phages, are not well studied in charged polymer solutions. Although different theories have been developed to predict the diffusion of nanoparticles in homogeneous neutral polymer solutions and melts [8], these theories are not expected to be readily applicable to the transport of anisotropic particles in charged polymers that adopt distinct chain conformations.

Here, we study the dynamics of flexible M13 bacteriophage in aqueous solutions of semidilute sodium poly (styrene sulfonate) (NaPSS) with varying ionic strength using fluorescence microscopy. We observe approximately diffusive dynamics but non-Gaussian distribution of displacements for all polymer concentrations. Moreover, the non-Gaussian parameter, as an indicator of the degree of heterogeneity in the system, shows temporal evolution. The dynamics of phage are faster than spheres of the same hydrodynamic radius. Available scaling theories for neutral polymers cannot predict the behavior of the system in the whole range of accessible polymer length scales. These results suggest that the observed dynamics arise from multiple diffusive modes due to the anisotropic structure of the filamentous viruses or the presence of confining time and length scales. These findings also indicate that predictions for the diffusion of nanoparticles in neutral polymers do not hold for charged polymers with non-Gaussian conformations. This improved understanding of the dynamics of phages in complex media will enable us to better design phage-based systems for different applications, including phage carriers, phage diagnostics, and phage display.

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New Classes of Zeolite Catalysts with Improved Diffusion Properties

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Designing zeolites with reduced diffusion limitations is critical to improving catalyst activity and stability in commercial applications such as methanol-to-hydrocarbon (MTH) reactions. Hierarchical and nanosized zeolites have been explored in this regard, but preparation of such materials requires complex organics and/or non-trivial synthesis techniques that have been demonstrated for relatively few framework types. Here, we will present an alternate approach to achieve nanosized zeolites via the growth of small protrusions (or “fins”) on the external surfaces of zeolite seeds. We have prepared finned zeolites for multiple structures, such as ZSM-5 and ZSM-11 [1], and demonstrated their enhanced mass transport properties relative to conventional materials. Notably, we have shown that finned zeolites have superior performance in the MTH reaction with respect to catalyst lifetime and total turnovers. Here we will show how finned zeolites with tailored properties (e.g. Si/Al ratio) impact catalyst performance relative to a broader set of well-known hierarchical materials, which include self-pillared pentasils [2], ultrasmall crystallites (i.e. 3Dom) [3], and two-dimensional nanosheets [4].

A second class of materials that will be discussed are zeolites with elemental zoning wherein a thin siliceous shell is epitaxially grown on the external surfaces of zeolite (seed) crystals [5]. These core-shell configurations have been extensively studied for zeolite ZSM-5 where it has been shown that the incorporation of a siliceous shell via facile secondary growth enhances mass transport, leading to MTH catalysts with markedly improved lifetime. In this presentation we will summarize our recent studies of ZSM-11@silicalite-2 core-shells prepared with different shell thicknesses. Moreover, we will compare these materials against the performance of a reverse core-shell configuration, silicalite2@ZSM-11, wherein the active zeolite shell layer is epitaxially grown over the siliceous (passive) shell. Preliminary studies of silicalite1@ZSM-5 have revealed a five-fold increase in catalyst lifetime, a five-fold increase in turnover number, and a product selectivity that differs from both homogeneous and core-shell analogues.

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Directed evolution of a protein-based sensor for Anaerobic Biological Methane Activation

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Graduate

An Escherichia coli strain that can activate short-chain alkanes (C3-C6) by adding fumarate has been designed in the Cirino lab. The resulting alkylsuccinate products can be metabolically converted into “building block” precursor metabolites for the biosynthesis of biofuels or other valuable chemicals, coupled with fumarate regeneration [1, 2]. A biochemical conversion process of this kind, using methane or other natural gas liquids as substrates, has potential to significantly reduce capital and operating expenses compared to existing alkane “gas-to-liquid” technologies [3]. Here, we aim to engineer the substrate specificity of this alkylsuccinate synthase system to achieve methane activation and hence the biosynthesis of methyl succinate (MS). A primary goal is to design a protein-based sensor/reporter system, which will be used for high-throughput screening of alkylsuccinate synthase variant activities to detect the addition of fumarate to methane. This will be accomplished by engineering the inducer specificity of regulatory protein ItcR (from Y. pseudotuberculosis), which naturally responds to itaconic acid (methylene succinate, IA) with high sensitivity. Whereas 5mM IA efficiently relieves transcriptional repression by ItcR, the same concentration of MS, differing by only one carbon-carbon bond (methyl vs. methylene), shows a 100-fold reduced transcriptional response [4]. To isolate ItcR variants with higher sensitivity and specificity toward MS, one round of fluorescence-activated cell sorting (FACS) screening was applied, resulting in increasing the ItcR specificity toward MS and decreasing the background. This obtained variant is used to make a new library to run the next round of the screening, to get more responsive variants.
It must be noted that the final obtained variants will be used as sensors and reporters of MS biosynthesis, by placing reporter and/or selection genes under the control of the ItcR cognate promoter (pccl).

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Quantitative *In-situ* FTIR analysis of Ce^{3+} densities and the role of oxygen vacancies in catalysis over ceria surfaces

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Cerium oxide catalyzes a range of redox and acid catalyzed reactions, with the facile reduction of Ce^{4+} to Ce^{3+} and concurrent oxygen vacancy formation purported to play a key role in many of these reactions [1]. Characterization of oxygen vacancies (or Ce^{3+} densities) is critical in most cases to the interpretation of catalytic phenomena involving the same. Spectroscopic techniques employed in prior literature to probe oxygen vacancies, however, each have specific limitations, such as complex and overlapping X-ray photoelectron spectra peaks corresponding to Ce^{3+} and Ce^{4+} ions, and the effect of particle size on Raman quantification [2]. In this work, we show, using group and crystal-field theory, that not only do La Porte forbidden electronic transitions of free Ce^{3+} ions from $^2F_{5/2}$ to $^2F_{7/2}$ electronic states [3] become symmetrically allowed through the action of electrostatic field of crystalline CeO_{2-x}, but that these transitions, coincidentally, appear in the infrared region at a wavenumber of approximately 2150 cm^{-1} [4]. Integrated molar extinction coefficients measured for this transition were found to be insensitive to both the identity of the reductant (H_2, CO, and C_2H_5OH) as well as the temperature range of measurement, and were used to decipher active site requirements for two separate reactions. Firstly, H_2-D_2 exchange rates per oxygen vacancy at 373K were found to be independent of degree of reduction, suggesting the exclusive occurrence of exchange over reduced metal sites. Secondly, inverse trends between isobutene formation rates and the density of vacancies resulting from CO_2 formation during tert-butanol dehydration suggest the sole involvement of oxidized ceria domains in catalyzing isobutene formation, the rates of which can be controlled using ethanol co-feeds. The analysis of this electronic transition may be more broadly applicable to other bulk metal oxides, and could provide a means for clarifying the mechanistic function of understoichiometric domains in oxide catalysis more generally.

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The Spatiotemporal Examination of Coupled Endo-Exo Reactions: A study of Tri-Reforming of Methane

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The main principle governing the tri-reforming of methane, is to use excess heat generated by the complete oxidation of methane in situ to drive highly endothermic reactions in dry and steam reforming. This allows for the consumption of greenhouse gases and subsequent production of syngas. The synergistic combination allows for optimal utilization of the strengths of each reaction while mitigating their negatives. To optimize this system, knowledge of the inter-reaction dynamics is required via understanding of the spatiotemporal phenomena.

To obtain both spatial concentration and temperature, a unique experimental array was used. Temperature was obtained via laser pulses into an optical fiber, where the resulting signal is transformed from time domain into a spatial result. This technique relies on the principle of optical frequency domain reflectometry(OFDR). The spatial concentration is determined via a SpaciMS(spatially resolved inlet mass spectrometer), which has a moveable inlet capillary that feeds into a mass spectrometer.

The spatial temperature and concentration profiles show that there are two regions of dominant reaction behaviors present. The first spatial regime is the oxidation zone. In this section of the catalyst, oxygen is still present allowing for the complete oxidation of methane to dominate. The SpaciMS shows rapid consumption of both methane and oxygen in this region as well as a mirrored production of CO_2. The OFDR shows a rapid increase in temperature near the entrance of the catalyst, where this oxidation region is located.

Once the oxygen is depleted, the dominant chemistries change to that of the reforming reactions. The temperature increase observed near the inlet of the catalyst is quickly diminished via steam and dry reforming. Once the excess energy from oxidation is consumed, the reforming reaction rate tapers off. The OFDR shows a gradual plateauing of temperature drop and SpaciMS has a reduction in the rate of methane consumption. The later section of the catalyst, after the oxidation temperature spike is consumed, is a mixture of water-gas shift reaction and trace amounts of steam reforming.

Variations in the concentration of oxygen were also tested to determine the impact on the spatial patterns seen previously. The location at which the maximum temperature was observed and the oxygen was depleted did not move. With the decreasing quantities of oxygen, there was less excess heat produced via oxidation, resulting in decreased conversion of methane. This dual region behavior presents multiple different methodologies to optimize the reaction system. Such as using a specially designed reactor layout which utilize the endo-exo behavior in a more advantageous manner. The combination of this reaction network along with the robust experimental monitoring utilized, allows for strong efforts to be made on optimization of carbon consumption in the tri-reforming of methane.

Sustainable Epoxy Resins Derived From Syringic Acid

Rosalie S Berg, Megan L Robertson, Venkatesh Balan

Graduate

Composites made of epoxy resins are high strength, yet lightweight alternatives to traditional metal components used in automotive, windmill, and electronics industries. Traditionally, epoxy resins are produced from petroleum-derived bisphenol A (BPA), which is epoxidized and cured with an amine or anhydride hardener. Unfortunately, BPA-based epoxy resins are derived from a non-sustainable resource and are not easily recycled, and BPA itself is a known endocrine disruptor. Lignin, a component of biomass with rigid aromatic structures, offers potential as a more sustainable and less toxic replacement for BPA in epoxy resins. Here we present for the first time the use of syringic acid, a product of catalytic depolymerization of lignin, as a precursor for producing biobased epoxy resins. Syringic acid was epoxidized and cured with an anhydride curing agent, and the structure determined via NMR. We have examined the curing chemistry of epoxidized syringic acid with an anhydride curing agent and studied the properties of the cured resins. This study, in combination with previously published work, has helped us understand how the chemical structure of individual lignin monomers impact epoxy resin properties which in turn can help produce targeted epoxy resins with superior properties to petroleum derived resins.

Mechanistic Characterization of Homologous Recombination in BRCA Mutant Cancers

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Graduate

The American Cancer Society estimates that over 50,000 women will die from either breast cancer or ovarian cancer in the United States in 2021 [1]. Mutations in the tumor suppressor genes, BRCA1 and BRCA2, lead to lifetime risks of 50-80% and 30-50% for developing breast and ovarian cancer, respectively [2]. BRCA mutations impair homologous recombination (HR), an important mechanism for repairing double-strand breaks (DSBs) in DNA. Cancer cells with BRCA mutations have deficient levels of the BRCA2 protein, but HR is still achieved through a RAD52-dependent backup pathway. We aim to develop a novel biochemical assay to detect DNA strand invasion and exchange (key steps in HR), and use this assay to probe the importance of various nuclear proteins in HR. The proposed method includes dual-labeling of complementary oligonucleotides using a fluorophore and a black hole quencher (BHQ). Labeling the oligonucleotides in this way will allow us to monitor which oligonucleotides are annealed to one strand or another. Once this assay has been validated, we will use it (and subsequent validation experiments) to identify the nuclear proteins that are both sufficient and essential to perform the RAD52-dependent HR pathway.

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Nanoparticle dynamics in semidilute polymer solutions: rings versus linear chains

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Understanding the dynamics of nanoparticles in polymer solutions is immensely important for their applications in targeted drug delivery, enhanced oil recovery, and polymer composite processing. The dynamics of nanoparticles are well described by the generalized Stokes-Einstein (GSE) relation, when the nanoparticles are much larger than the polymers. However, deviation from the GSE is observed when the nanoparticle's size is comparable to the length scale in polymer solutions.[1] We investigate the microscopic origin of this anomalous behavior using multiparticle collision dynamics (MPCD) simulations [2], an advanced algorithm for rigorously modeling solvent-mediated hydrodynamic interactions in coarse-grained, mesoscale simulations. We apply hybrid MD-MPCD simulations to study dynamics of nanoparticles in semidilute solutions of ring and linear polymers in the presence of many-body hydrodynamic interactions.[3] The dynamics of the monomers, the polymer centers-of-mass, and the nanoparticles coincide for these two architectures for solutions of the same monomer concentration. The long-time diffusivities of the nanoparticles follow the predictions of a polymer coupling theory,[4] suggesting that nanoparticle dynamics are coupled to segmental relaxations of both ring and linear polymer architectures. At intermediate time scales, the nanoparticle dynamics are characterized by subdiffusive exponents, which markedly deviate from coupling theory and closely follow those of the polymers. Instead, the nanoparticle dynamics are strongly coupled to the polymer center-of-mass motions for both architectures rather than their segmental dynamics.[5] We show that this disagreement is due to the tight coupling of the translational motions of the nanoparticle and polymer centers-of-masses, which is not accounted for in current theories. We also investigate the influence of polymer morphology on this coupling behavior. Surprisingly, we find that the dynamic coupling observed in ring and linear polymer chains solutions is remarkably similar, even in systems with large fractions of ring concatenation defects. However, it leads to a slight decrease in the subdiffusive exponents of the nanoparticles and the polymer center-of-mass.

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Elucidating Pathways of Crystallization through In-Situ Atomic Force Microscopy

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Graduate Student

Understanding growth mechanisms is crucial to guide the rational design of materials for diverse applications. Despite significant efforts to identify the fundamental pathways of nucleation and crystal growth for materials such as zeolites and metals, these processes are not well understood owing in part to the inherently complexity of crystallization. It is increasingly evident that many crystalline materials exhibit nonclassical mechanisms involving the assembly and attachment of precursors that range from oligomers to amorphous particles and small crystallites. These process involve disorder-to-order transitions governed by dissolution and reprecipitation of amorphous precursors, which takes place in parallel with a classical pathway involving monomer addition.

Here, we will discuss how atomic force microscopy (AFM) can be used to track the dynamics of faujasite (FAU) zeolite and Cu nanosheet surface growth – two materials heavily utilized as commercial catalysts. The growth media used for FAU studies are supernatant solutions extracted at periodic times of synthesis to generate a range of supersaturation. The growth media examined for Cu nanosheet surface growth were prepared by different approaches to achieve a range of supersaturation. *In situ* AFM measurements at variable conditions reveal multiple modes of surface growth that range from classical molecule-by-molecule addition to nonclassical pathways, wherein time-resolved analysis allows for direct visualization of layer propagation and particle attachment during crystal growth.

In this presentation, we will present *in situ* studies of both FAU zeolite and Cu nanosheet crystallization. Using time-resolved AFM images, we observe precursor attachment to crystal surfaces, accompanied by structural rearrangement and three-dimensional growth. We also confirm that FAU growth occurs via a nonclassical mechanism, while Cu growth occurs by the addition of both molecules and precursors, thus bridging classical and nonclassical mechanisms.

Understanding solvent behavior near the surfaces of silicalite-1

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Interfacial processes at solid-solvent interface are relevant to a variety of applications such as catalysis[1], corrosion mitigation, electrode design[2], and pharmaceutical precipitation. We study the crystal-water interface for silicalite-1[3], a siliceous analogue of the widely used industrial ZSM-5 zeolite catalyst. Recent studies have shown that the size and shape of silicalite-1 crystals can be controlled synthetically using growth modifiers[4,5], which are small molecules that adsorb and selectively bind to different crystallographic faces to influence anisotropic rates of growth. Fundamental understanding of the key factors governing modifier adsorption remain limited[6], however, particularly the influence of solvent structure and dynamics near the surface. We use molecular dynamics simulations to investigate solvent structuring and dynamics near the (010), (100), and (101) crystallographic faces of silicalite-1. We find that the three surfaces strongly influence solvent properties, altering structure and dynamics within the ~1 nm interfacial region. This behavior is found to depend sensitively on the specific chemical and topographical features presented on each crystallographic face, suggesting that the anisotropic rates of growth observed in experiment may arise from differences in solvent structure at each surface. Implications of interfacial solvent structuring on the adsorption of solutes are also discussed.

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A Solution to Polyolefins Waste: Tunable Functionalization and Repurposing

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Graduate

By 2050 the accumulation of plastic waste is projected to reach 12,000 Mt, where 18% are recycled, 24% incinerated, and the rest 58% are either landfilled or enter the natural environment. The main contributor to this waste is polyolefins, constituting roughly 59% of all plastic waste [1] [2]. Momentum has shifted towards looking for a solution for polyolefin waste and move to a circular economy. A tunable functionalization has shown promising results to upcycle polyolefins, remove the limitation of inertness and improve the final physical properties of the material [3][4]. Subsequently, this functionalized polyolefin can be repurposed on a wide variety of applications including polyurethanes, foams, coatings, films, among others [5][6][7]. In this work, polypropylene was functionalized by a two-step reaction. First, isotactic polypropylene (iPP) was compounded with maleic anhydride (MAH) at 190°C for 20 mins, then it was reacted with ethanolamine in solutions at 190°C for 6h to synthesize a hydroxylated polypropylene (PP-OH). Characterization showed a grafting percentage of MAH on the polypropylene (PPgMAH) between 0.16%-1.36% and a final hydroxyl value of 119.12 mgKOH/g for the highly grafted polypropylene. For future work, it is desired to increase the functionalization of PPgMAH, to achieve higher hydroxyl values (>300 mgKOH/g) and, eventually, incorporate the PP-OH for polyurethanes synthesis.

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Discerning in vitro Pharmacodynamics from OD Measurements: A Model-Based Approach

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Abstract

Time-kill experiments can discern the pharmacodynamics of infectious bacteria exposed to antibiotics in vitro, and thus help guide the design of effective therapies for challenging clinical infections. This task is resource-limited, therefore typically bypassed in favor of empirical shortcuts. The resource limitation could be addressed by continuously assessing the size of a bacterial population under antibiotic exposure using optical density measurements. However, such measurements count both live and dead cells and are therefore unsuitable for declining populations of live cells. To fill this void, we develop here a model-based method that infers the count of live cells in a bacterial population exposed to antibiotics from continuous optical-density measurements of both live and dead cells combined. The method makes no assumptions about the underlying mechanisms that confer resistance and is widely applicable. Use of the method is demonstrated by an experimental study on *Acinetobacter baumannii* exposed to levofloxacin.

Keywords: Mathematical modeling, Pharmacodynamics, Multi-drug resistant bacteria, Combination therapy

Simultaneous in vitro simulation of multiple antimicrobial agents with different elimination half-lives in a pre-clinical infection model

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Abstract

Background: Combination therapy for treatment of multi-drug resistant bacterial infections is becoming increasingly common. In vitro testing of drug combinations under realistic pharmacokinetic conditions is needed before a corresponding combination is eventually put into clinical use.

Objectives: The current standard for in vitro simulation of the pharmacokinetics of two drugs with distinct elimination half-lives cannot be extended to combinations of three or more agents, thus creating a growing need. To address that need this study is focused in the development of a general method to design an in vitro model for simultaneous simulation of the kinetics of an arbitrary number of N drugs with different half-lives.

Methods: The method developed entails two possible configurations: (a) An in-series configuration, which generalizes the standard two-drug design for N drugs and offers new flexibility even for two drugs, and (b) an in-parallel configuration, which is new, and offers yet additional flexibility over the in-series configuration.

Results: Corresponding design equations for sizing and operation of each configuration are rigorously developed and are suitable for immediate use by experimenters. These equations were used for experimental verification using a combination of three antibiotics with distinctly different half-lives (meropenem, ceftazidime, and levofloxacin).

Conclusions: While experimental verification involved antibiotics, the method is applicable to any anti-infective or anti-cancer drugs with distinct elimination pharmacokinetics. With increasing importance of in vitro simulation of the kinetics of an arbitrary number of drugs in combination, the methods developed here are an important new tool for the design of such in vitro models.
