RESEARCH SYMPOSIUM

Presented by:

The Organization of Chemical Engineering Graduate Students And the UH Department of Chemical & Biomolecular Engineering

🔠 Virtual Event Features

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

Research Areas

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

OCTOBER 23, 2020 9:00AM - 5:00PM Event Held Virtually

For more information, visit: https://ochegs.chee.uh.edu/35thannual-symposium-fall-2020/



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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 35th Annual Graduate Research Symposium. Due to the ongoing pandemic, this symposium is being conducted online through Zoom sessions and LinkedIn Events. 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 35 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 absolutely invaluable guidance.

Sincerely,

2020 OChEGS Officers

Surya Pratap Singh Solanki	President
Shreeyansh Rastogi	Vice President
Melisa Montalvo	Treasurer
Stephanie Sontgerath	Social Chair
Dr. Megan Robertson	Faculty Advisor



Schedule of Events

Introduction	9:00 am – 9:10 am	Welcome from OChEGS, Department Chair
Oral Session I: Catalysis and Reaction Engineering	09:10 am – 09:30 am	Sadia Afrin- On the evolution of ceria surfaces to activate non-oxidative dehydrogenation - a transient kinetic analysis
	09:30 am – 09:50 am	Heng Dai- Finned Zeolite Catalysts
	09:50 am – 10:10 am	Rajat Subhra Ghosh - Activity Enhancement and Kinetics of NH ₃ Oxidation on Pt/Al ₂ O ₃ :Rate Enhancement by Ball Milling and Structure Sensitivity Effects
	10:10 am – 10:30 am	Bhaskar Sarkar- Bifurcation analysis of coupled homogeneous-heterogeneous reactions in monolith, gauze or wire-mesh reactors
Break I	10:30 am – 10:45 am	
Keynote Speech	10:45 am – 11:45 am	Dr. Rob Hart- Can Chemists and Engineers Work Together to Turn Molecular Structures Into Useful Products?
Poster Session (LinkedIN)	11:45 am – 01:45 pm	Poster Session – LinkedIn
Oral Session II: Biomolecular Engineering	01:45 pm – 02:05 pm	Adesola Saba– The Metabolism of Bacterial Persisters
	02:05 pm – 02:25 pm	Victoria Hlavinka- Diabetes Mellitus Screening by Chemiluminescent Enzymatic Detection of 1,5 Anhydroglucitol in Saliva
Break II	02:25 pm – 02:40 pm	
Oral Session III: Materials Science and Engineering	02:40 pm – 03:00 pm	Karun Kumar Rao - Machine Learning the Fundamental Tradeoffs between Conductivity and Voltage Stability in Solid State Electrolytes
	03:00 pm – 03:20 pm	Rajshree Chakrabarti- Weak van der Waals interactions dominate the thermodynamics and kinetics of organic crystallization
	03:20 pm – 03:40 pm	Tzu-Han Li- Polymer Dispersity Affects Conformation of Brushes Grafted on Nanoparticles
	03:40 pm – 04:00 pm	Lakshmanji Verma- Fundamentals Governing Crystal Growth in Organic Solvents
	04:00 pm - 04:20 pm	Wenjie Wu- Solvent induced switchable phase separation of polymer-grafted nanoparticle blends
Symposium Conclusion	04:20 pm - 04:30 pm	Poster Award Presentations and Concluding Remarks
04:30 pm – 05:00 pm		Virtual happy hour/networking



Keynote Speaker:

Dr. Rob Hart

R&D Leader for Inorganics at The Shepherd Chemical Company



He attended University of Wisconsin and earned a B.S. in Chemistry studying interand intra-molecular electron transfer in strained substituted hydrazines with Stephen Nelsen. His Ph.D. in Physical Chemistry is from Indiana University, where he and Joe Zwanziger developed a quantitative description of optical second harmonic generation in glass ceramics. Rob did a post-doc with Chris Benmore at

the synchrotron (APS) and neutron source (IPNS) at Argonne National Lab studying structures and high-pressure behaviors of amorphous (liquid and glass) materials. Rob joined Shepherd Chemical in 2005, and has served in various roles in both R&D and manufacturing. He was the Plant Manager of Shepherd's Middletown, Ohio facility for several years, where they achieved record production levels. Highlights during his time in R&D include developing over 20 new products generating \$100M+ in revenue, and in 2016, receiving an award from the American Chemistry Council for a new, water-soluble, low-toxicity polyurethane catalyst, for which they were also granted Shepherd Chemical's first-ever patent. Rob has long been fascinated by how the microscopic structures of materials determine their properties, and how their structures can be modified with chemistry to change their behaviors and improve the world. Generally speaking, he uses scattering and spectroscopic techniques to determine difficult structures and then deploys that information to make better products.



Keynote Speech:

<u>**Title:**</u> Can Chemists and Engineers Work Together to Turn Molecular Structures Into Useful Products?

Abstract: Yes. All observable material properties are deterministically related to their atomic-level structures. Therefore, considerable power can be wielded to selectively improve material properties when their structures are known. For pure, crystalline materials, a systematic approach (i.e., crystallography) usually yields sufficiently accurate structural models. But many technologically and industrially important materials are amorphous. Determination of molecular structures for materials without long-range order is a challenging goal and a general approach does not yet exist. However, scattering, spectroscopy, computer simulation, reasoning by analogy, heuristics, and good old trial-and-error can be effective in generating predictive models of such compounds and mixtures.

Shepherd Chemical manufactures transition metal based specialty chemicals, many of which are amorphous. In this talk, we will provide examples of where structural determination informs and is informed by product performance and properties. That progress allows opportunities for process improvement including reaction dynamics, and control and automation. Specifically, we will talk about copper-based products for automotive airbags and catalysis, bismuth-based products for lubrication and catalysis, and other cases utilizing zinc, chromium, and cerium chemistry. In all cases, collaboration between chemists and engineers is critical to success and will be emphasized.



Presentation Abstracts



On the evolution of ceria surfaces to activate non-oxidative dehydrogenation a transient kinetic analysis Sadia Afrin, Praveen Bollini

Cerium oxide is commonly understood to exhibit excellent redox properties, in part owing to facile Ce⁴⁺ to Ce³⁺ interconversion facilitated via the formation of oxygen vacancies- a property that has been exploited commercially in three-way catalysis for automotive emission control.¹⁻⁵ Presence of two complementary sets of sites, lattice oxygen and oxygen vacancy, in aerobic redox cycle along with existing evidence of lattice oxygen assisted Mars van-Krevelen and vacancy mediated non-Mars van-Krevelen mechanism for dehydrogenation of alkanes and alkanols over reducible metal oxides in prior literature⁶⁷ motivated us to investigate the possible contribution of MvK half cycles in activating the catalytic non-Mvk route for dehydrogenation under anaerobic condition over bulk ceria. Four distinct types of transient kinetic experiments are used to decipher the evolution of the surface towards non-oxidative ethanol dehydrogenation. Acetaldehyde formation during aerobic to anaerobic switching experiment suggests that ceria is active for both catalytic oxidative and non-oxidative dehydrogenation of ethanol. An induction period has been observed initially while conducting anaerobic dehydrogenation over oxidized ceria and a transition from non-catalytic oxidative chemistry to catalytic non-oxidative chemistry has been identified during this induction period using stoichiometric relationships. O-vacancy estimates calculated from the oxidation products reveal that reduced ceria activates the non-oxidative route catalytically, which we evidenced by a series of anaerobic dehydrogenation experiments over ceria samples, pre-reduced with H₂ at different temperatures- a systematic way to alter the initial degree of reduction of the surface, as both the fractional reduction of the surface during anaerobic reaction and the initial extent of oxidative dehydrogenation decreases with increasing pre-reduction temperature. Finally, we use alpha hydrogen-free oxygenates (in this case phenol) as a titrant, which was capable of annihilating the non-oxidative chemistry completely, for the in-situ quantification of oxygen vacancies. These experiments, while creating a picture of active site requirements for oxidative and non-oxidative dehydrogenation over reducible metal oxides, also demonstrates a methodology for characterizing active site requirements in bulk oxide catalysis that may be more broadly applicable.

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Finned Zeolite Catalysts

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Confined channels and cages of zeolites have been widely used as shape-selective heterogeneous catalysts in the (petro)chemical industry. A common objective in the design of zeolite is to overcome the inherent mass transport limitations of micropores. The advent of two-dimensional¹ or self-pillared zeolites² exhibit superior catalytic performance to conventional zeolites. In this poster, we will describe an alternative approach to reduce the internal diffusion limitations of zeolites via the introduction of fin-like protrusions on zeolite surfaces by secondary growth. We will discuss the synthesis of multiple frameworks with nano-sized fins (size α) which exhibit an identical crystallographic registry with the interior crystal (size β) and show their superior catalytic performance relative to conventional analogues.³

This new class of mass transport enhanced zeolites were synthesized by secondary growth using finely tuned composition that allows for the epitaxial growth of fins on the surface of seed crystals. Here we will discuss examples of several finned zeolites with disparate 3-dimensional pore networks to demonstrate the broader applicability of this approach. We also demonstrate a proof of concept using commercial zeolite samples where finned analogues improve their catalytic performance. Our studies of synthesis and methanol to hydrocarbon (MTH) catalytic testing as benchmark reaction are coupled with state-of-the-art characterization using techniques such as high-resolution electron tomography, operando spectroscopy, novel acid titration methods, and molecular modeling to correlate structural features of finned zeolites and their diffusion properties with enhanced catalyst performance.

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Activity Enhancement and Kinetics of NH₃ Oxidation on Pt/Al₂O₃: Rate Enhancement by Ball Milling and Structure Senstivity Effects

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Ammonia-oxidation(AMOX) over Pt-containing catalysts is an important reaction for eliminating NH₃ in diesel-engine exhaust. Kinetic models have been developed for Pt-single crystals under ultra-high vaccum[1] and for Pt-gauze for HNO₃ production[2,3] but these are of limited value for NH₃-oxidation on Pt-supported catalysts for emission control. Here we describe a kinetic study for Pt/Al₂O₃ at atmospheric pressure and the development of a microkinetic model. We measured reaction-rate(TOF) dependence over wide range of NH₃ concentration from 10 – 40,000ppm for Pt/Al_2O_3 powder and washcoated-monoliths. The data in Figs.1(a) and (b) show the presence of rate-maximum at 500ppm for unmilled-Pt/Al₂O₃ but at 10,000ppm for ball-milled Pt/Al₂O₃ powder and washcoated-monolith. Another unexpected observation is the enhanced activity of Pt/Al₂O₃ samples upon ball-milling, which resulted in lowering of light-off temperature(T₅₀) by 50°C[Fig.1(c)]. Ball-milling reduces particle size, in-turn decreases the extent of diffusionlimitations. However, steady-state AMOX done over ball-milled Al₂O₃ followed by Pt addition did not show the same enhanced activity ruling out diffusion-limitations as the main cause of the activity enhancement. Further characterization of Pt/Al₂O₃ samples using XRD[Fig.1(e)] reveals an alteration in the distribution of Pt crystalline-planes; notably, Pt<211> increased and Pt<111> decreased. These data suggest that the higher activity of ball milled-Pt/Al₂O₃ is a result of this crystalline-plane transformation. Microkinetics by Rebrov[1] assumed Pt<111>plane which predicted no rate variation with NH₃ concentration. This is due to NH₃ and O₂ adsorbing on independent sites 'b' and 'a' respectively. Contrary, experiments showed '+' to '-' NH3 reactionorder variation over wide range of NH₃ concentration indicates site-competition[Fig-1(d)]. The model was modified by introducing site-competition between NH₃ and O₂ on site-a in addition to NH₃ adsorption on site-b which best described the experimental data and kinetics. These findings show the close dependence of kinetics and reactivity on Pt crystal-planes.

References:

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Figure 1: Reaction rate (TOF) against NH₃ concentration over (a) Un-milled Pt($(0.05)/Al_2O_3$ (b) Ball-milled Pt($(0.05)/Al_2O_3$, Pt($(0.05)/Al_2O_3$,



Bifurcation analysis of coupled homogeneous-heterogeneous reactions in monolith, gauze or wire-mesh reactors

Bhaskar Sarkar and Vemuri Balakotaiah

Catalytic partial and deep oxidation processes are some of the attractive technologies for meeting future energy demands and production of intermediate chemicals. Typically, such partial catalytic combustion involves both homogeneous and heterogeneous reaction chemistries with strong thermal and species coupling. Over the past two decades, there have been numerous studies in this field, most of which focused on the hydrodynamic aspects of the system through development of computational fluid dynamics (CFD) models coupled with detailed micro-kinetic reaction mechanisms. Such models are good for predicting product distributions and conversions only in isothermal or small scale systems. Because of their mathematical complexity, they are not amenable for bifurcation analysis and hence not useful to determine non-linear features of scaledup systems (e.g. multiple steady states). In this regard, bifurcation analysis is a very important mathematical tool, which can help in analyzing the multiple steady states and different possible behaviors of the system for various choices of physical parameters. The main goal of this work is to determine the impact of design and operating parameters such as space time, feed temperature, reactor dimensions and feed conditions on the ignition-extinction phenomena of coupled homogeneous-heterogeneous system and to identify an optimum operating window using the bifurcation theory. We start with developing reduced order models with position, flow and kinetic parameter dependent transfer coefficients for coupled homo/hetero reactions in monoliths. The usefulness of these reduced order models is illustrated through determination of ignition-extinction behavior in oxidative coupling of methane (OCM) and catalytically stabilized combustion of lean hydrogen and propane.

For the case of OCM, the computations show that for typical operating conditions, the methane conversion and C_2 product selectivity are non-monotonic on the ignited branch and there exists an optimum point of operation away from the extinction point. The predicted methane, oxygen conversions and C_2 selectivity are compared to reported experimental results in the literature. We also present the various species and temperature profiles along the length of the reactor and examine how these profiles are impacted by the substrate conductivity, space time and heat loss. Phase diagrams in the plane of equivalence ratio and feed temperature are computed for lean combustion of hydrogen and propane. The roles of Lewis number, heat loss, and thermal mixing on the extinction limit of catalytic/thermally coupled homogeneous reactions are investigated.



The Metabolism of Bacterial Persisters

Adesola Saba and Dr. Mehmet Orman

Bacterial cultures are rarely homogenous. Normal proliferating cells are usually the most abundant phenotype, but there are also non-proliferating phenotypes present e.g. viable but non-culturable "VBNC" cells and persisters. Persisters are a small fraction of cells with the ability to temporarily tolerate a super lethal dose of antibiotics. Such cells later exit the persistence state and resume normal growth when the antibiotic challenge is removed; however, their progeny regains antibiotic susceptibility – a key distinction from resistant mutants¹. Persisters have been implicated in the recalcitrance of infections such as pneumonia, tuberculosis, and cystic fibrosis. They have also been shown to serve as a reservoir for the evolution of resistant mutants²³.

For a long time, it was believed that these persisters are metabolically dormant, since they are nonproliferating. However, Orman and Brynildsen recently showed that dormancy is not necessary or sufficient for persistence⁴. In fact, persisters can consume certain carbon sources^{5,6}, harbor electron transport chain (ETC) activities^{5,6}, maintain high ATP levels⁷, and drive the futile production and degradation of RNA⁸. Moreover, certain metabolites entering upper glycolysis induce rapid persister death when treated with gentamycin, whereas most of the metabolites entering lower glycolysis cause little to no potentiation⁵. It has also been reported that persistence is drastically reduced when certain metabolic genes (*ubiF* and *sucB*) are perturbed⁹.

In this study, we sought to understand the precise role that carbon metabolism plays in persistence. We conducted persister assays on single gene mutants of about 300 non-essential genes associated with carbon metabolism, and found that persistence is significantly reduced when certain genes in the TCA Cycle, ETC, and ATP synthase are deleted. Our findings were confirmed in multiple organisms (*E. coli* and *Pseudomonas aeruginosa*), and using multiple classes of antibiotics (β -lactams and fluoroquinolones) for the attack. We further observed that some of the bacterial genes of interest code for enzymes which coincidentally have a different constitution in eukaryotes, thus making them potential targets for anti-persister therapy in humans.

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Diabetes Mellitus Screening by Chemiluminescent Enzymatic Detection of 1,5-Anhydroglucitol in Saliva

Victoria Hlavinka, Binh V. Vu, Federico Ruiz-Ruiz, Patricia Vazquez, Mary A. Crum, Ujwal Patil, Jinsu Kim, Calef Sánchez-Trasviña, Mirna González-González, Katerina Kourentzi, Marco Rito-Palomares, and Richard C. Willson

Diabetes mellitus is a severe, chronic disease that affects over 420 million people worldwide. If left untreated, diabetes can lead to severe complications and death. The onset of complications can be delayed or even prevented when the disease is diagnosed early, but it is estimated that nearly 40% of all diabetes cases are undiagnosed. Screening in communities without adequate access to healthcare can significantly reduce the number of undiagnosed cases of diabetes. The blood concentration of 1,5-anhydroglucitol (AHG), a naturally-occurring six-carbon monosaccharide similar in structure to glucose, falls in concentration during periods of hyperglycemia as glucose outcompetes it for kidney reuptake. Blood AHG is useful for monitoring glycemic control, and saliva AHG has been suggested to be useful for diabetes screening. However, previous efforts to measure AHG in saliva and demonstrated that the assay could distinguish between healthy and treated-diabetic individuals (N=265; p < 0.0001, ROC AUC 0.82). These results suggest that, with further validation, this approach may serve as the basis of a non-invasive tool to screen for diabetes.



Weak van der Waals interactions dominate the thermodynamics and kinetics of organic crystallization

Rajshree Chakrabarti¹, Lakshmanji Verma¹, Viktor G. Hadjiev² Monika Warzecha³, Jeremy C. Palmer¹ and Peter G. Vekilov¹

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In aqueous solutions, solvent structuring at the crystal-solution interface governs the thermodynamics of crystallization and, through the activation barrier for incorporation of solute into the crystal, the kinetics of crystal growth. Whether solvent structuring persists in crystallization from organic solvents and its potential consequences for the molecular-level interactions comprising organic crystallization is poorly understood. Organic solvents, in which the bonds that could support a defined fluid structure are weak and varied, present a particular challenge to understand the effect of solvent structuring and solvent-solute interactions on thermodynamics and kinetics of crystallization.

To understand the thermodynamic determinants of organic crystallization, we characterize the enthalpy and entropy of crystallization of etioporphyrin I (a planar metal-free porphyrin) from five solvents selected to highlight the role of several categories of solute-solvent interactions; etioporphyrin I represent a class of molecules that arrange in low-symmetry crystals suitable for semiconductors and solar panels. To understand solvent structuring at the crystal interface and solute-solvent interactions in solution we employ as molecular probes the crystallization enthalpy and entropy, complemented by UV-Vis absorption spectra of the solutions and electron microscopy and x-ray characterization of the crystal phases. The enthalpy and entropy trends reveal that solvent structuring insignificantly impacts the solution thermodynamics owing to the weak solvent-solvent bonds.

Time-resolved *in situ* atomic force microscopy monitoring of the step dynamics on (010) face of etioporphyrin in two types of solvent, alcohols (octanol, butanol and hexanol) and DMSO, having varying aliphatic chain lengths and subsequent solvent viscosities demonstrate the impact of solute-solvent interactions and solvent viscosity on the barrier for solute incorporation into kinks. The relationship between step kinetic coefficient and solvent viscosity reveals that the crystallization of organic small molecules is governed not only by diffusion limitation but also by solute-solvent interaction at the kinks. The correlation between the step velocity v and the solute concentration C on the (010) face of etioporphyrin I for different solvents reveal that for solvents belonging to the same homologous series, solute incorporation scales with the solute diffusion coefficient. All-atom MD simulation for solvent structuring at the crystal interface emphasizes the importance of solute-solvent interaction at the crystal interface.

These emerging insights offer guidance for polymorph selection, chiral separations, structure design and numerous other open questions relevant to myriad crystallization systems in the pharmaceutical and chemical industries.



Fundamentals Governing Crystal Growth in Organic Solvents

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

Graduate

Crystallization from solution underlies myriad processes in nature and industry. Solvents crucially determine the crystal habit and solvent-surface interactions impose distinct crystal morphologies. The association of solute molecules to crystal growth sites drives away solvent associated to solute and structured in the vicinity of growth sites. Thus, insight into the solvent structure and dynamics at the crystal-solution interface is an essential prerequisite for understanding of growth mechanisms. In recent years, the crystallization of organic materials from the organic solvents has been a focus of attention as a major step in the manufacture of pharmaceuticals and fine chemicals. Despite extensive efforts, a molecular perspective of the fundamental thermodynamics and kinetics aspects of the growth mechanisms remain elusive. We employ all-atom molecular dynamics simulations and advanced sampling techniques to investigate the structure, dynamics, and energetics that govern the molecular behaviors during organic crystal growth. We address the solvent structuring at the interface, solute oligomerization in the solution and the adsorption of the solute monomers and oligomers on the crystal surface, processes that run parallel to crystallization and largely determine its rates and outcomes. We found that the weak intermolecular bonds between organic solvents and the crystal surface did not preclude the build-up of layered solvent structure along the surface. The degree of order in the solvation layer is determined by the chemical and topological features exposed on the crystal surface. A solvation layer nearest to the surface may impeded or promote the solvent and solute dynamics and the layer characteristics drive disparate growth rates on the anisotropic faces of β -hematin crystals, a central part of the survival of malaria parasites. Furthermore, despite common beliefs, a majority species of solute in the solution may or may not be the incorporating species for the crystal growth. The (010) faces of etioporphyrin crystals, an organic semiconductor, grow by direct incorporation of the dimers with dimers present in the solution as the majority component. On the other hand, the (002) face of olanzapine, an antipsychotic drug for schizophrenia, grows by the surface diffusion with incorporation of the dimers even though dimers represent a minority component in the solution. We show that growth by dimers is preferred owing to their preferential adsorption on the crystal surface, complemented by additional dimerization on the surface. These findings are crucial for molecular-level understanding of the fundamental thermodynamic and kinetic parameters of growth that guide the optimization of crystallization from the organic solvents.



Machine Learning the Fundamental Tradeoffs between Conductivity and Voltage Stability in Solid State Electrolytes

Karun K. Rao, Michael Nikolaou, Yan Yao, Lars C. Grabow

Solid state batteries provide many safety advantages over traditional lithium-ion batteries by replacing the combustible organic liquid electrolyte with a ceramic solid-state electrolyte (SSE). However, reported SSEs with ionic conductivities approaching that of liquid electrolytes are unstable in contact with a lithium anode leading to increased internal cell resistance, and poor cyclability. Conversely, compounds stable at the anode or cathode interfaces do not exhibit useful bulk ionic conductivities. Although *ab initio* methods exist to study each ionic conductivity and voltage stability range, there is no established theory to connect these two properties. Here, we leverage machine learning (ML) to investigate the role of crystal structure in the tradeoff between voltage stability and ionic conductivity. To this end, we trained a partial least squares (PLS) machine learning algorithm using the valence electronic density as a descriptor of 60 known solidstate electrolytes along with their corresponding ionic conductivity, anodic voltage limit, and cathodic voltage limit. The trained model has an 80% prediction accuracy and suggests that within the search space of crystal structures, the voltage stability and ionic conductivity are inherently inversely correlated. A multi-objective optimization also suggests that materials with positively correlated ionic conductivity and voltage stability may be highly anisotropic. Our PLS machine learning model, compared to the more popular neural network, has the benefit of being able to predict and explore the relationship between multiple properties and retains a high level of interpretability versus other 'black box' models. The PLS model successfully identifies a BCC anion substructure and channels as effective descriptors. Using this model, we screened through a database of ca. 14,000 materials and identified five new promising solid-state electrolyte candidates to have conductivities greater than 16 mS/cm. The model predictions were subsequently verified with *ab initio* molecular dynamics simulations. The proposed ML model and electron density descriptor may be used in future studies to elucidate structure-property relationships for other applications with high accuracy and without sacrificing interpretability.



Polymer Dispersity Affects Conformation of Brushes Grafted on Nanoparticles

Tzu-Han Li, Vivek Yadav, Jacinta C. Conrad, and Megan L. Robertson

The efficacy of polymer-grafted nanoparticles in applications such as drug delivery, reinforced composites, and water purification can be controlled, in part, by conformation of the grafted polymers. Although parameters affecting the conformation of spherical polymer brushes such as polymer grafting density σ and chain length have been well-studied, the polymer brush dispersity D (i.e. the breadth of the molecular weight distribution) remains underexplored. Theory and simulation suggest that increase in D can markedly alter chain conformation with long chains extended outward from and short chains compressed toward the grafted surface.^{1,2} Experimental studies that quantify the conformation of disperse polymer brushes grafted on nanoparticles, however, remain scarce. Here, we show that the effect of D on the conformation and stimulus response of spherical polymer brushes depends on the brush molecular weight. We synthesized poly(tert-butyl acrylate) PtBA grafted silica nanoparticles with varying Đ via atom transfer radical polymerization with addition of a chain terminating agent. As Đ of the PtBA brushes was increased from low-D (D = 1.03 - 1.25) to high-D (D = 1.49 - 1.96), the average brush length (as assessed by hydrodynamic radius using dynamic light scattering) could be collapsed onto a master curve as a function of weight-average degree of polymerization Nw, for brushes of length greater than 27 nm. By contrast, the high-Đ PtBA brushes with shorter lengths were up to twice as thick as the low-D PtBA brushes. In the semidilute polymer brush regime, the brush lengths of PtBA and polymers from earlier literature studies could be collapsed onto a master curve as a function of Nw1/3. In the concentrated polymer brush regime, the brush lengths bifurcated as a function of Nw1/2, where the lengths of the high-D brushes were greater than the low-D brushes at low, but not high Nw1/2. We also demonstrated that long poly(acrylic acid) PAA brushes with different D exhibited similar pH-responsive behavior, but the pH-dependent thicknesses of short brushes were dependent on D. Variations in brush length, originating from changes in chain conformation, and in brush response to environmental stimuli via control in D can be leveraged to improve dispersion in complex media.

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Solvent induced switchable phase separation of polymer-grafted nanoparticle blends

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Polymer-grafted nanoparticles (PGNPs) have attracted great attention in the past few years for the application of nanoelectronics [1], photonic devices [2], and enhanced mechanical properties [3]. However, these applications require the particles to form well-controlled structures [4]. We developed a method to switch the phase-separated structures of poly (methyl methacrylate) silica (PMMA-SiO₂) and poly(styrene) silica (PS-SiO₂) blends by using direct solvent immersion annealing (DIA). Our results show that by varying the solvents in the DIA solution, two different and switchable morphologies are formed in the PMMA-SiO₂/PS-SiO₂ blends. By repeating the process for over 10 times, it reveals that the switchable process is stable. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was also conducted and reveals that the switchable phase separation is not just on the surface but also inside the films. Kinetic study also shows that the process is efficient, which stabilizes within 5 minutes with a correlation length at around 1.2 um.

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Poster Abstracts



Exploring Degradation as a Viable End-of-Life Process for Thermoset Polymers

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There is a great need to recycle polymers to minimize their environmental impact, as the majority of produced polymers end up in landfills after their useful lifetime. Linear polyesters degrade rapidly, and their degradation behavior has been well studied. By contrast, thermoset polymers normally require harsh degradation conditions due to their highly crosslinked structures.¹⁰ We have explored the incorporation of cleavable hydrolytic linkages into the crosslinked network, to determine if thermoset polymers can be also degraded under benign conditions. Epoxy resins are thermoset polymers widely used in composites, coatings and adhesives, with applications spanning automotive and aerospace industries, structural components, and wind turbine blades, among others. The standard precursor to epoxy resins, the diglycidyl ether of bisphenol A (DGEBA), is derived from petroleum and lacks functional groups which can promote degradation under benign conditions. Epoxidized vegetable oils, phenolic acids, and vanillic acid, which contain ester linkages were investigated as sustainable sources to produce degradable epoxy resins. The resulting phenolic acid-based and vanillic acid-based epoxy resins exhibited comparable thermal and mechanical properties to conventional DGEBA-based epoxy resins. The accelerated hydrolytic degradation behavior of the ester-containing epoxy resins was explored, through monitoring of the polymer mass loss after exposure to a basic solution at moderate temperatures. ¹² The biobased epoxy resins exhibited rapid degradation in the basic solution, in contrast to the slow degradation rate of the traditional DGEBA-based epoxy resin. A degradation model was proposed to describe the degradation behavior and mass spectrometry confirmed the mechanism was surface erosion through ester hydrolysis. For comparison purposes, accelerated hydrolytic degradation behavior under mild acidic conditions was also explored. It showed that bio-based epoxy resins exhibited bulk erosion in acidic solutions, in agreement with the behavior of linear polyesters. An autocatalysis model was proposed to describe the degradation behavior under mild acidic conditions. Various factors which affected the degradation rates were also discussed.

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Destabilization of p53 core domain by mutation drives the nucleation of p53 fibrils

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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 R2480 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.



Phase Behavior of Colloids with Polymer-Mediated Attractions

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Mixtures of micron-sized colloidal particles and polymers 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]. Understanding the effects of interactions between the colloidal particles due to the presence of the particles is critical for designing formulations for these applications. Polymers that do not adsorb to the surface of the particles induce entropic depletion attractions, whose strength and range can be tuned through the concentration and size of the polymer. The phase behavior of depletion mixtures has been systematically investigated [3]. By contrast, polymers that adsorb to the particle surface can generate attractive bridging interactions between two particles. The physical bridges between the particles can lead to the formation of clusters or flocs. Bridging attractions are prevalent in separation processes such as waste treatment [4], but how the phase behavior, structure, and dynamics depends on the strength of bridging interactions remains incompletely understood. Here, we investigate the phase behavior of a model system for bridging interactions in which the strength of the polymer adsorption can be tuned through the pH of the system. We induced bridging interactions between trifluoromethyl methacrylate-co-*tert*-butyl methacrylate (TtMA) particles by adding poly(acrylic acid) (PAA). The bridging attraction is likely driven by hydrogen bonding between PAA by either or both of the steric and electrostatic stabilizers on the surface of the particles. The steric stabilizer on the particles, poly(vinylpyrrolidone), forms hydrogen bonds with PAA at low pH [5]. Likewise, the electrostatic stabilizer, dimethylacrylamide, can strongly hydrogen bond to PAA in acidic conditions [6]. These bonds weaken as the pH is increased, which we expect will affect the structure of the flocs formed through bridging attractions. We present preliminary data on the structure and dynamics of the TtMA particles as a function of solution pH and polymer concentration. The fundamental understanding of the effects on bridging strength on suspension properties is expected to improve the efficacy of flocculation processes in wastewater treatment and create dense markers for indirect detection of specific cell surface molecules [7].

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Partial Oxidation of Methane to Methanol through the Homogeneous Contribution of Tri-Iron Nodes in a Metal-Organic Framework Material

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The direct oxidation of methane to methanol is an inspiring process which has the potential to create new avenues for the utilization of widely available natural gas resources. Although not yet realized on an industrial scale, this reaction is capitalized with ease within the metabolic pathway of methane-oxidizing bacteria. Specifically, oxoiron(IV) moieties in methane monooxygenase enzymes¹¹ have inspired the development of synthetic catalysts with similar active centers, however, the inability to capture the exactly defined active sites and environments of these enzymes is a major limitation of current synthetic materials. Metal-organic frameworks (MOFs) are a class of crystalline materials with extended porous structures that have the potential to overcome existing limitations of biomimetic catalysts due to their well-defined structures and endowment with metal centers uniform in nuclearity and oxidation state. In particular, MIL-100 (MIL = Materials of Institut Lavoisier) is a framework which has attracted recent attention as a catalyst for the partial oxidation of light alkanes.^[2,3] The inorganic metal node of this framework consists of three octahedrally coordinated metal atoms sharing an oxygen vertex (M3IIIO). Thermal activation, which removes terminally coordinated species including water molecules and anionic ligands, leads to the formation of a mixed-valence node (M2IIIMIIO) when fully activated. Results of our work indicate that N₂O promotes the oxidation of CH₄ to CH₃OH over MIL-100(Fe) at low temperature (≤ 473 K) and ambient pressures. Through isotopic tracer experiments, it was elucidated that H₂O is essential to the generation of CH₃OH by reaction with surface methoxy intermediates. Characterization by infrared spectroscopy and complementary in-situ titrations with NO and H₂O revealed that Feⁿ and Fe^m sites are responsible for CH₃OH and CO₂ formation, respectively. Moreover, in the fully activated catalyst, it was demonstrated that every Fe₃O node is involved in methanol formation, providing a significant advantage over previously identified synthetic iron catalysts that consist of a distribution of both inactive and active iron moieties. As demonstrated here for MIL-100(Fe), the high degree of structural homogeneity that can be attained in MOF materials may facilitate their more extensive evaluation as biomimetic catalysts for breakthrough chemical processes.

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Irreversible Inhibition of Barite Crystallization: A Unique Mechanism for Treating Scale Formation

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The mineralization of sparingly soluble compounds in process equipment may result in corrosion, equipment damage, and cause reduction or loss of finished product for oil and gas production, wastewater treatment, and manufacturing processes. Conventional treatments rely on the use of caustic solutions that pose a negative environmental impact. Designing effective biodegradable chemical treatments to reduce or eliminate scale formation requires an understanding of the molecular-scale interactions of chemical additives in supersaturated environments at the crystal interface. Here we implement a cooperative approach to design and test environmentally friendly chemical treatments for scale formation using a combination of surface science techniques and microfluidic technology. Crystallization can be suppressed in highly supersaturated solutions using dilute quantities of modifiers. These studies focus on barium sulfate (barite), a highly insoluble and common scaling mineral. In this presentation we will describe the effect of organic acids on barite crystallization in bulk assays under flow and in quiescent conditions. Using *in situ* scanning probe microscopy, we explore the interfacial interactions between the modifiers and different surfaces of barite over a range of supersaturated conditions to elucidate the role of these inhibitors during crystal growth. Our findings identify unique crystal-modifier interactions that suppress barite crystallization via an irreversible inhibition mechanism. Collectively, these studies provide new fundamental understanding of crystal growth modifier action towards the design of improved scale treatments.



On the evolution of ceria surfaces to activate non-oxidative dehydrogenation a transient kinetic analysis Sadia Afrin, Praveen Bollini

Cerium oxide is commonly understood to exhibit excellent redox properties, in part owing to facile Ce⁴⁺ to Ce³⁺ interconversion facilitated via the formation of oxygen vacancies- a property that has been exploited commercially in three-way catalysis for automotive emission control.¹⁻⁵ Presence of two complementary sets of sites, lattice oxygen and oxygen vacancy, in aerobic redox cycle along with existing evidence of lattice oxygen assisted Mars van-Krevelen and vacancy mediated non-Mars van-Krevelen mechanism for dehydrogenation of alkanes and alkanols over reducible metal oxides in prior literature⁶⁷ motivated us to investigate the possible contribution of MvK half cycles in activating the catalytic non-Mvk route for dehydrogenation under anaerobic condition over bulk ceria. Four distinct types of transient kinetic experiments are used to decipher the evolution of the surface towards non-oxidative ethanol dehydrogenation. Acetaldehyde formation during aerobic to anaerobic switching experiment suggests that ceria is active for both catalytic oxidative and non-oxidative dehydrogenation of ethanol. An induction period has been observed initially while conducting anaerobic dehydrogenation over oxidized ceria and a transition from non-catalytic oxidative chemistry to catalytic non-oxidative chemistry has been identified during this induction period using stoichiometric relationships. O-vacancy estimates calculated from the oxidation products reveal that reduced ceria activates the non-oxidative route catalytically, which we evidenced by a series of anaerobic dehydrogenation experiments over ceria samples, pre-reduced with H₂ at different temperatures- a systematic way to alter the initial degree of reduction of the surface, as both the fractional reduction of the surface during anaerobic reaction and the initial extent of oxidative dehydrogenation decreases with increasing pre-reduction temperature. Finally, we use alpha hydrogen-free oxygenates (in this case phenol) as a titrant, which was capable of annihilating the non-oxidative chemistry completely, for the in-situ quantification of oxygen vacancies. These experiments, while creating a picture of active site requirements for oxidative and non-oxidative dehydrogenation over reducible metal oxides, also demonstrates a methodology for characterizing active site requirements in bulk oxide catalysis that may be more broadly applicable.

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Density Functional Theory Modeling of NO_x Trapping in Pd-exchanged ZSM-5 and SSZ-13 Passive NO_x Adsorbers (PNAs): Effect of Zeolite Pore Size

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Vehicles are the major sources of worldwide NO_x emissions that have adverse impacts on climate, ecological balance and human health. Lean-burn designs have considerably lowered temperatures of exhaust emissions from diesel engines leading to higher efficiency. However, leading emission control technologies available to reduce NO_x, CO and hydrocarbon (HC) emission levels have operating temperatures typically above 200 °C. Significant amounts of the mentioned pollutants get released into the atmosphere during the time taken to reach this light-off temperature. In recent years, passive NO_x adsorbers (PNAs) and hydrocarbon traps (HCTs) have attracted much attention to abate the release of these pollutants. A required feature of these materials is to trap NO_x, CO and HC at low temperatures and release them at higher temperatures so that they can be converted downstream once the light-off temperature is reached.

Both small and medium pore ion-exchanged zeolites have shown great promise in trapping and releasing NO_x at low temperatures. Particularly, Pd-exchanged SSZ-13 and ZSM-5 have been shown to trap NO_x at temperatures below 150 °C and release them above 200 °C.^{1,2,3} Our Density Functional theory (DFT) results indicated Z_2Pd^{II} to be a stable storage site for both zeolites. However, the high energy ZPd^I sites seem to bind NO the strongest. In this work, we present a comparison of NO binding among different plausible active sites for the zeolites mentioned. Under relatively dry conditions, we investigated various pathways that dynamically form ZPd^I sites in response to the reducing agents NO, CO and C₂H₄ present in the exhaust, and compared the effect of zeolite pore size on the pathways. We also qualitatively considered possible effects of the DFT functionals that may influence the high NO binding on ZPd^I sites in ZSM-5.

The elementary steps we considered provide detailed mechanistic insights into the conversion between different active sites during NO trapping. For both SSZ-13 and ZSM-5, adsorbed NO stabilizes ZPd^I sites, thus making their existence feasible under PNA conditions. This knowledge helps us build the basis for predicting possible NO trapping behavior in zeolites of different pore sizes.

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C-H Bond Activation on Nickel Oxide Surface: A Density Functional Theory Study

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Natural gas is one of the most abundant energy resources in the U.S. It's main components, methane and ethane, have very strong C-H bonds, which makes them energy consuming to be activated. Thus, the development of efficient catalysts to upgrade methane and ethane to higher value products is both, challenging and very desirable.

Two major issues that current catalysts for methane activations are facing are that high temperatures (up to 900K) are required, and the lifetime of the catalysts is limited due to sintering and coking. Inspired by the work of Spinner and Mustain we aim to address these challenges and pursue a novel low temperature process, which leverages the use of an electrochemical cell to convert methane to methanol. The envisioned process uses carbonate anions (CO_3^{2-}) that are produced from CO_2 and O_2 at the cathode and transferred to the anode through the electrolyte. At the anode, carbonate ions serve as activator for methane and the transfer of a single oxygen atom that can selectively oxidize methane to methanol. By simultaneously controlling the concentration of CH₄ at the anode and the rate of CO_3^{2-} delivery by adjusting the cell potential and current density, we anticipate that the over-oxidation of methane can be prevented, such that a high yield of methanol can be achieved.

Ethylene, as a major building block for chemical industry, is produced by steam cracking of naphtha or ethane, which is energy consuming. Ethane oxidative dehydrogenation (ODH), which is an exothermic reaction, is a promising alternative. The challenges are to activate the strong C-H bond, and to minimize the total oxidation of ethane and increase the selectivity of the ethylene product. NiO with doped Nb has been reported to lower the activation barrier of ethane ODH reaction. Furthermore, surface defects or doping help with the selectivity of ethene product.

To obtain fundamental insights into the C-H bond activation of methane and ethane, we have performed density functional theory (DFT) calculations on NiO(100) in VASP. The effects of applied electric fields were accounted for the methane activation. Our results indicate that the interaction between the externally applied electric field and the dipole moment generated between the surface and adsorbates plays the dominant role in altering the binding behavior. The reaction enthalpy and activation energy of certain elementary steps exhibit a strong dependence on the applied electric field, suggesting that a tunable electric field in an electrochemical cell offers unique advantages for selectively upgrading methane to value-added products. Several surface terminations of NiO(100) were studied for ethane ODH and the results indicate that an O-enriched NiO(100) surface contributes to the C-H bond activation of ethane.



CO₂ adsorption over bulk NiO catalysts: determining active oxygen species over NiO catalyst for ethane oxidative dehydrogenation reaction

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Bulk metal oxides represent an important class of catalysts for oxidation, dehydration, dehydrogenation reactions. Studying the nature, density, and the strength of sites present on oxide surfaces at a molecular level forms the fundamental basis for bridging the materials structures with its catalytic activity. NiO-based materials are promising catalysts for ethane oxidative dehydrogenation (ODH) for ethylene formation. Surface lattice oxygen and adsorbed oxygen ions have been proposed to abstract protons and assist C-H bond cleavage, therefore acting as the active site for ODH reaction. However, this hypothesis has not been proved experimentally as the heterogeneous nature of solid surface and the complex surface structures under reaction condition have posed enormous challenges to accurately measure the active sites in working condition.

In this work, two surface oxygen sites of NiO have been probed by CO_2 molecules using FTIR spectroscopy. Two surface carbonate species form upon CO_2 adsorption, which exhibit distinct behaviors against temperature and CO_2 pressure: the formation of carbonate I is negligible above 150 °C and desorbs completely after purging CO_2 , while the formation of carbonate II is substantial up to 300 °C and is stable even after removing gaseous CO_2 . These differences are attributed to the energetics of different adsorption sites and resultant carbonate structures. DFT calculation of CO_2 adsorption over NiO (100) surface suggests two possible stable carbonates: a monodentate carbonate formed over a (100) lattice oxygen and a bridging carbonate formed over a (100) oxygen adatom. The relative binding energy and the predicted C-O vibrational frequencies of each structure are in agreement with carbonate I and II determined by FTIR, respectively. CO_2 interactions with two types of oxygen sites, 1) lattice oxygen and 2) oxygen adatom, are further studied by fitting the adsorption isotherm into a dual-site Langmuir model. Site densities of lattice oxygen and oxygen adatom are calculated to be 4.29 and 1.04 µmol/m². CO_2 heat of adsorption are 30 kJ/mol over lattice oxygen and 38 kJ/mol over oxygen adatom, which are consistent with carbonate I.

The role of oxygen adatom in ethane ODH reaction is studied by cofeeding CO_2 with ODH reactant at 280-450 °C. The fractional decrease in ethene formation rate becomes more prominent at higher CO_2 pressure and lower temperatures, which is consistent with the formation of carbonate II that titrates oxygen adatom for ODH turnover. The re-exposure of oxygen adatom upon removing CO_2 from ODH reactant also causes the recovery of ODH rate. Correlating the ethene formation rate with surface density of vacant oxygen adatom results in a constant turnover frequency as a function of time on stream.

Together, this works applies CO_2 adsorption as a technique for probing surface oxygen sites and their energy distributions over NiO catalysts, and establish the activity of surface oxygen adatom during ODH reaction, which can be extended to other metal oxides catalyzed reaction systems.



Controlling Formic Acid Decomposition Through Alloy And Ensemble Effects On PdCu Catalysts

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Formic acid is a potential hydrogen carrier for mobile energy needs, but the kinetics of H2 storage and release at moderate condition need to be improved. For example, hydrogen release may occur in a direct formic acid fuel cell (DFAFC) where an efficient HCOOH decomposition catalyst is needed at the anode to satisfy the increasing power density demands. 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. For formic acid decomposition, Pd is known for its activity but lacks selectivity towards the desired product CO2. Pd is also easily poisoned by the by-product CO. Cu, on the other hand, exhibits great selectivity but with much lower turnover frequencies. Using density functional theory and microkinetic modeling, we show that the high selectivity of Cu can be combined with the good activity of Pd over dilute PdCu alloys. Charge transfer from Cu to Pd and an upshift of Cu's dband center upon alloying greatly increase 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 deactivating surrounding Cu sites. Increasing the Pd content, however, leads to 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 characterization and reaction studies carried out by our experimental collaborators. Our atomic-scale structure-function relationship for formic acid decomposition over PdCu alloy catalysts suggest that by carefully balancing alloy (electronic) and ensemble (geometric) effects it

[1] "Oxygenate Reactions over PdCu and PdAg Catalysts: Influence of Electronic and Geometric effects." Tanmayi Bathena et al. under review.

may be possible to rationally design metal alloy catalysts with exceptional activity and selectivity.



Solvent structure and dynamics 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 catalysis¹, shape-selective transport, electrode design², and aqueous separation³. Recent studies have shown that the silicalite-1 crystals can provide a promising route for extraction of 1-butanol (a gasoline additive) from dilute fermentation broths⁴⁵, with high selectivity over water. Fundamental understanding of the key factors governing selective adsorption and transport remains limited, however, particularly the influence of solvent structure and dynamics near the surface. We study the crystal-water interface for silicalite-1, a siliceous analogue of the widely used industrial ZSM-5 zeolite. 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 role of solvent mediation and external membrane surface on the separation ability.

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Bacteria motility enhances adhesion to oil droplets

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Many bacteria species are known to degrade various hydrocarbons. In an oil spill scenario, chemical dispersants are used to break the larger oil droplets into smaller droplets thereby providing larger surface area for bacteria to adhere. Predicting the extent of biodegradation in an oil spill scenario requires improved understanding of the factors that affect the interactions of bacteria with dispersed hydrocarbon droplets. Because more than 80% of bacteria species are known to be motile, we examined the effect of bacteria motility on adhesion of bacteria to oil droplets. Hexadecane droplets were stabilized in synthetic seawater through addition of dioctyl sodium sulfosuccinate [DOSS], a major component of the Corexit EC9500 surfactant used in the 2010 Deepwater Horizon oil spill in the Gulf of Mexico.¹ Subsequently, we characterized the adhesion of a motile bacterium, an environmental isolate of Halomonas titanicae, and a nonmotile bacterium, Marinobacter hydrocarbonoclasticus SP17, to the DOSS-stabilized droplets over time.²⁻³ We also carried out control experiments on *H. titanicae* bacteria that were rendered nonmotile chemically (through addition of carbonyl cyanide 3-chlorophenylhdrazone) or mechanically (through shearing to remove flagella). We found that the interfacial cell density of both motile and nonmotile bacteria increases with time and follows first-order Langmuir adsorption. Increasing the concentration of DOSS reduces the interfacial tension and thereby leads to a decrease in the interfacial cell density of both nonmotile and motile bacteria. Motile bacteria exhibit higher interfacial cell densities on all time scales and for all surfactant concentrations. Understanding how motility and surfactant affect adhesion may give insight to more efficient use of dispersants in future oil spills.

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Towards Extensional Rheology of Colloid-Polymer Mixtures with Depletion and Bridging Attractions

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Extensional deformation of complex fluids is ubiquitous in industrial processes such as fiberspinning, extrusion, and injection molding [1] and plays a vital role in applications including agrochemical spraying, inkjet printing, turbulent drag reduction, or enhanced oil recovery [2]. Some of these applications, such as printing inks and paints, use mixtures of colloids and polymers as their feedstock. Polymer additives can induce depletion or bridging attractions, depending on whether they adsorb on the particles surface. Interesting rheology behavior, such as shearthickening, can be observed in these attractive systems [3,4]. Few studies, however, examine the extensional rheology of colloid-polymer mixtures compared to shear rheology even though extensional deformations also impact these processes. An improved understanding of the extensional rheology of these dispersions is important to improve their processing.

Here, we study the extensional rheology of colloid-polymer mixtures with dripping-onto-substrate (DoS) protocol [5]. In this protocol, we characterize the capillary-driven thinning and pinch-off dynamics of the liquid bridge neck formed between a nozzle and a sessile drop. From the filament-thinning dynamics, we can extract the extensional viscosity and suspension relaxation time of our solutions. We calibrate our setup using a poly(acrylic acid) solution in 70 v/v% glycerol-water and compare the results with literature [6]. Our calibration allows us to optimize our imaging setup using either a smartphone or high-speed camera and improve our edge-detection algorithm analysis. With this protocol, we will investigate the extensional rheology of colloid-polymer mixtures with different interactions and, more broadly, inform the design of complex fluid suspensions for advanced manufacturing.

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Dual Role of Polyphosphates as Potent Inhibitors of Struvite Nucleation and Crystal Growth

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The crystallization of struvite (MgNH4PO4·6H2O) is relevant for nutrient (nitrogen and phosphorus) recovery in water purification and scale formation in pipelines, and it is a primary component of so-called infection stones arising from urinary tract infections. Research efforts have focused on understanding the effects of different parameters (e.g., supersaturation, pH, inhibitors) on crystallization of struvite; however, prior studies have only focused on the use of bulk techniques and have not provided mechanistic insights into these controls.

Herein, we present a comprehensive approach to evaluate struvite formation at both macroscopic and microscopic length scales in the absence and presence of various inhibitors. We conducted *in situ* kinetic measurements to estimate the extent of inhibition posed by each inhibitor on struvite formation. To this end, we employ a microfluidic platform to track the anisotropic growth rates of struvite crystals under various conditions, including comparisons of solutions with and without the presence of modifiers¹. Furthermore, we elucidate the mechanism of inhibitory action by probing the surface dynamics in real time via *in situ* atomic force microscopy (AFM), which has proven to be a powerful technique to elucidate molecular level details of crystallization^{2,3}. The results reveal unique mechanisms facilitating complete inhibition of growth and in select cases the unprecedented suppression of nucleation, which is not commonly observed for even the most potent modifiers of mineralization⁴. Collectively, our findings identify highly efficient and commercially available modifiers that inhibit struvite formation. This study also uncovers a new class of inhibitory mechanisms for the prevention of commercial scale.

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Zinc-Incorporated FAU Zeolite: Simultaneous Control Over Crystallization Kinetics, Interzeolite Conversions, and Physicochemical Properties

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Zeolites with isomorphically-substituted elements (e.g. zinc, tin, and gallium) are materials of growing importance for commercial applications. Here, we discuss our recent work surveying FAU syntheses in the presence of transition metals, which are known to alter the nanoscopic structure of zeolite growth solutions. We have used a facile study on the crystallization kinetics of FAU and GIS to elucidate the effects of heteroatomic species on amorphous growth solutions and crystalline product phases. Specifically, we have demonstrated the ability of zinc to modify the kinetic pathway of a zeolite growth solution regardless of when it is added to the mixture. Through the mechanistic insights gleaned from these studies, we have developed a range of facile techniques for controlling both phase purity and the physicochemical properties of zeolites. Furthermore, we have elucidated the link between FAU and GIS zeolites. These findings have further implications for the development of fundamental understandings of zeolite synthesis, most notably in the preparation of transition metal-substituted zeolites.



Oxidative Dehydrogenation of Ethane over M1 Phase Catalysts: Autothermal or Cooled Tubular Reactor Design?

Jiakang Chen, Praveen Bollini*, Vemuri Balakotaiah*

Ethylene is a platform chemical used in the production of polyethylene, ethylene dichloride and ethylene oxide. Oxidative dehydrogenation of ethane (ODHE) represents a potential alternative that is less capital and energy-intensive compared to steam cracking processes currently used to produce ethylene. Most current research is focused on developing new catalysts and interpreting catalytic function over heterogeneous catalysts that demonstrate high performance, an example of which are Mo-V-Te-Nb based bulk mixed metal oxides. Despite extensive catalysis-focused research, to date, there hasn't been a single reactor design proposed that can be plausibly implemented on an industrial scale. In this work, we show that ODHE can be operated autothermally with ambient temperature feeds and no external heat input.

An ODHE kinetic model developed using lab-scale kinetic data was used to compare autothermal and multitubular reactor designs. The results show that the autothermal reactor configuration is more favorable than the multi-tubular one for this highly exothermic reaction, and becomes even more so with increasing catalyst activity. The autothermal reactor designed as part of our study, unlike multitubular ones, takes advantage of multiple steady-states and falls close to the extinction point on the ignited branch. We also discuss, for the first time, a bifurcation analysis of an ODHE system based on ignition and extinction behavior discussed as a function of adiabatic temperature rise, catalyst activity, and oxygen reaction orders, thereby providing additional insights into strategies for successfully operating these processes on an industrial scale.



Strontium Ions Function as both an Accelerant and Structure-Directing Agent of Chabazite Crystallization

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Zeolite crystallization often requires the presence of an organic structure-directing agent (SDA) to facilitate the formation of nanoporous cages and channels. Among the limited number of zeolites that can be synthesized in organic-free media, alkali metals are most commonly employed as inorganic SDAs. Many alkali metal zeolites are usually prepared under moderate conditions using temperatures less than 100 °C and synthesis times on the order of hours. One notable exception is zeolite chabazite (CHA), which is prepared from potassium ions and requires atypically long crystallization times on the order of weeks. Attaining practical synthesis times on the order of days necessitates an alternative approach, such as the use of zeolite crystal seeds. In this study, we show that growth solutions prepared via the partial substitution of potassium with strontium generate purely-crystalline chabazite within hours without the need for either organics or crystal seeds. Studies of strontium inclusion in seed-assisted syntheses also reveal shorter synthesis time. Notably, we show that strontium has a pronounced impact on the kinetics of chabazite formation, leading to 14- and 3-fold reductions in crystallization time compared to pure potassium syntheses in the absence and presence of crystal seeds, respectively. Using a combination of ²⁹Si and ²⁷Al MAS NMR spectroscopy, we also show that strontium functions as a SDA based on its ability to alter $Q^4(nAl)^{29}Si$ speciation, thereby redistributing tetrahedral Al sites in the framework. Given the widespread application of chabazite in adsorption and separation processes, designing facile and efficient synthesis approaches with concomitant control of physicochemical properties is commercially relevant.



Elucidating Active Site Requirements over Well-Defined Active Sites in Metal-Organic Framework Materials

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Chromium-base catalysts, such as Phillips catalysts, are of great industrial value in large-scale processes such as ethylene polymerization and oligomerization.¹ Due to the complexity of structure, low percentages of active chromium species, and the interference of the metal aggregation, there are still ongoing debates on the source of catalytic activity, the oxidation states of active chromium, and the mechanism for ethylene polymerization for the past 50 years.²⁻⁵ Recently, metal-organic frameworks (MOFs) have recently received extensive attention as promising materials in heterogeneous catalysis research due to their well-defined structures and their ability to incorporate diverse metallic nodes and organic ligands in the same framework.⁶ More specifically, MIL-100(Cr) (MIL = Materials of Institut Lavoisier), a type of chromium based MOF material with isolated, uniform, and tunable metal Cr₃O nodes⁷ compared to its metal oxide counterparts, offers a unique opportunity to develop an improved understanding in structure – property relationships in heterogeneously-catalyzed reactions. In this work, two vapor phase reactions, methanol and ethanol dehydrations, were used as probe reactions, and insitu titrations involving pyridine and 2, 6 di-tert- butyl pyridine (2, 6 DTBP) were employed to quantify active sites as well as to identify their nature (Lewis vs. Brønsted)⁸ under reaction conditions. We have found that the catalytic activities of both reactions decreases as pyridine pressure increases in the reaction stream, where the reduced turnover rates of dimethyl ether and diethyl ether in biomolecular alcohol dehydrations follow the same trend, indicating they both react on the same type of active site. Introduction of more titrant in the co-feed results in the complete loss of activity with pyridine, while the formation rates of diethyl ether and ethylene reduced 57.6% and 85.1%, respectively, with 2, 6 DTBP. The difference in kinetic diameters of the two titrants might possibly be responsible for the observed residual activity. Moreover, the total acid site density was estimated to be between 0.29 to 0.48 mol/mol Cr by assuming 1:1 titrant to acid site ratio. The titration data described in this study allow for a characterization of active site speciation in MIL-100 catalysts, and provide guidance on future MOF catalyst design and our eventual goal of tuning them for advanced catalytic applications.

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Biological activation of short-chain alkanes

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Natural gas liquids (NGLs) are short-chain hydrocarbons produced during crude oil extraction. Vast NGL reserves and large production capacity in the US have generated great interest in using these compounds as fuels and chemical feedstocks. However, NGLs remain under-utilized due to difficulties in transportation and their low energy density [1]. To solve these problems, the hydrocarbons must be activated and converted to higher energy density-and/or higher-value chemicals. Controlled catalytic activation of hydrocarbons has been long sought but remains inefficient, currently requiring multiple pressure and temperature shifts and large-scale facilities to offset expenses (up to \$20 billion for a Fischer-Tropsch plant) [2]. In contrast, biological activation can potentially be operated at much smaller scales and with moderate conditions. *In vivo* activation of alkanes has been documented under both aerobic and anaerobic conditions, but oxygen-dependent bioactivations are inherently energy and carbon inefficient, with CO₂ as a significant byproduct.

In this project, we are harnessing a metabolic pathway found in certain denitrifying or sulfate reducing bacteria, whereby C-H bonds of short-chain alkanes (less than C7) are activated anaerobically, via fumarate addition. A key challenge to exploiting this chemistry lies in the functional expression of the "alkylsuccinate synthase", along with its partner activating enzyme, in a suitable host organism. To confirm functional expression based on GC-MS analysis of extracted culture broth, authentic standards of the anticipated alkylsuccinate products were first synthesized. Using E. coli as host, we have established for the first time the functional expression of enzymes that catalyze fumarate addition to hexane and propane. Studies with substrate isotopes confirmed these syntheses. We are optimizing conditions to increase product titer, as well as improving / streamlining sample work-up procedures amenable to high-throughput screening. These steps will enable use of a directed enzyme evolution approach to isolate variants having higher activity on smaller alkane substrates.

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Colloidal Model for the Study of Non-Classical Nucleation and Crystallization

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Crystallization is a ubiquitous phase transition that is of great importance for various areas of applications: from the controlled precipitation of chemicals and pharmaceuticals. to imaging and data storage in electronics. Decades of intense studies have built a framework of knowledge illuminating crystal nucleation and growth from concentrated phases, such as melts, which is well described by classical nucleation theory (CNT). In contrast to nucleation from melts, crystals in solution had been reported to nucleate and grow using multi-step pathways that deviate from classical mechanisms; and factors that control crystallization from solution still remain poorly understood. In situ observation methods, including scanning probe and transmission electron microscope (TEM), are often applied when studying crystal growth in solution at atomic scale. However, these methods have their limitations to observe, in real time and in 3-D, interactions between monomers that lead to nucleation and association of monomers to crystals that lead to growth. Thus, there remain fundamental open questions on how the interactions between monomers affect nucleation and growth from solution.

The objective of this study is to test whether tuning the shape of interaction potentials will control the choice of pathways by which crystals nucleate and grow from solution. As an alternative to atomic systems, we formulate suspension of submicron particles (i.e. colloidal particles) that can be tracked in 3-D using fast scanning confocal microscopy and imaged over time. We synthesized 2,2,2-trifluoroethyl methacrylate-*co-tert*-butyl methacrylate copolymer with a modification of the protocol described by Kodger et al. The particles were suspended in a mixture of thioglycerol and water that nearly matched their density and refractive index. The interactions between charged particles can be manipulated by adding salts (to screen the electrostatic repulsion) and non-absorbing polymers (to induce an attractive depletion interaction). Using fast-scanning confocal microscopy, we imaged the particles in 3-D and identified their centroids using computational methods. Analysis of the particle positions allowed us to calculate the radial distribution function g(r). For salt concentrations above 100 mM, g(r) exhibited a modest local maximum at the particle diameter, i.e. r/2a = 1, indicative of some particle aggregation.

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Highly Stable MCM-22 Catalysts with Enhanced Para-Xylene Selectivity

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Para-xylene (pX) is one of the most important aromatic compounds that is used to synthesize various fine chemicals. An emerging and commercially attractive route to produce pX is toluene alkylation with methanol. Many zeolite-based shape selective catalysts have been considered for this process; however, these catalysts often suffer from short catalyst lifetime and low feed utilization. Here we report on the performance of MCM-22 (MWW type) zeolite for toluene alkylation with methanol under high reactants pressures (4.2 MPa), showing exceptional catalyst stability (> 30 days) while maintaining high toluene conversion (25%), without the use of hydrogen/water diluents.

Our findings reveal that increasing reaction operating pressure results in a multi-fold improvement in catalyst lifetime due to the suppression of side reactions, such as methanol-to-hydrocarbons and multiple alkylation of aromatic rings. Notably, during the course of the reaction, pX selectivity increases from its thermodynamic composition (23%) to a steady value of 58%, leading to the highest mass time yield ever obtained for this reaction.

To understand the origin of high pX selectivity and catalyst stability, we used a combination of experimental testing, density functional theory and molecular dynamics. With these techniques, we have deconvoluted the role of three different topological features in the MCM-22 catalyst: sinusoidal channels, surface pockets, and supercages. We have found that the sinusoidal channels are very selective towards pX with both transition state selectivity and diffusion limitations favoring pX formation, while surface pockets are unselective in nature and their deactivation is essential for high pX selectivity. Interestingly, the supercages play a crucial part for high catalyst lifetime and pX selectivity. Even though the supercages partially deactivate at the beginning of the reaction by coke deposition, they are responsible for turnovers at long time on stream. Furthermore, the deposited coke species in the supercages promote coke formation on the surface pockets, leading to high pX selectivity. The nature of coke species in supercages greatly influence the rate of coke deposition on the external pockets. This sequential coke evolution in MCM-22 is referred to as "spatiotemporal coke coupling" between supercages and surface pockets. Overall, this study provides a commercial viable route for pX production as well as the new insights into MCM-22 reaction chemistry, which can have profound impact on the various alkylation reactions.



Structure-Property Relationships in Ion Containing Sustainable Thermoplastic Elastomers

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, commercial TPEs are derived from petroleum whose manufacturing and disposal have undesired environmental impacts, motivating the development of TPEs from sustainable sources. Vegetable oils and their fatty acid derivatives are attractive alternatives to petroleum due to their abundance and low cost. Our group has previously reported replacing polydienes in commercial TPEs with sustainable polyacrylates derived from fatty acids. However, polymers with bulky constituents, such as the long alkyl side-chains of fatty acid-derived polymers, typically exhibit poor mechanical performance due to lack of entanglements in the rubbery matrix. To improve the mechanical properties, transient networks were incorporated into the fatty-acid derived midblock through either hydrogen bonding or ionic interactions which can act as a transient network. In this work ABA triblock copolymers were synthesized with poly(nbutyl acrylate - co - acrylic acid) random copolymer midblocks (~5 mol % acrylic acid) and poly(methyl methacrylate) endblocks. This system was chosen to act as a model system with alkyl acrylate midblocks since it can be sustainably derived from renewable feedstocks while also having a short alkyl side chain. In the *n*-butyl acrylate model system, the triblock copolymer tensile strength increased linearly with the logarithm of relaxation time of the midblock, with more than 5-fold improvement, without losing extensibility.



Enhanced CH₄ Conversion over Pt+Pd/Al₂O₃ + Mn_{0.5}Fe_{2.5}O₄ Spinel catalyst: Impact of Oxygen Storage Material

Pak Wing Chen, Kyle Karinshak, Debtanu Maiti, Ru-Fen Liu, Lars C. Grabow and Michael P. Harold

Natural gas vehicles (NGV) have gained interests because they use inexpensive domestic fuel and produce less CO_2 emissions compared to gasoline or diesel vehicles. The remaining NGV emissions containing CH₄, CO, NOx and other hydrocarbons can be controlled with a four-way catalyst containing platinum group metal (PGM) and spinel oxides (AB₂O₄). Spinel oxides have been reported to be excellent oxygen storage materials and can reduce the required PGM loading [1]. A previous study has also shown that the combination of spinel addition and lean/rich feed modulation allows for a lower methane conversion temperature [2]. In this study, the contribution of $Mn_{0.5}Fe_{2.5}O_4$ spinel on CH₄ conversion over PGM catalyst is investigated using flow reactor experiments and dynamic oxygen storage capacity (DOSC) measurements. In addition, several new spinel materials were identified and evaluated based on the formation energy of oxygen vacancies using ab initio density functional theory calculations.

Monolith catalysts [30 g PGM/ft³, 100 g spinel (25% on Al₂O₃)/L monolith] and supported powder samples [1 wt% PGM/Al₂O₃, 25wt% spinel/Al₂O₃] were provided by CDTi Inc. Experimental results show that $Mn_{0.5}Fe_{2.5}O_4$ spinel has a beneficial impact on CH₄ oxidation. The enhancement is mainly attributed to the high DOSC of the spinel component. The addition of spinel, however, has a detrimental effect on CH₄ steam reforming, which occurs at high CH₄ conversion when O₂ has been depleted. Temporal analysis of products (TAP) experiments and post-reaction characterization are underway to further explore the distinct trends seen in CH₄ oxidation and steam reforming. Based on computational screening studies several new spinel compositions were identified to be promising candidates for enhancing CH₄ conversion at lower temperature.

Our study provides fundamental and practical insight into the function of spinel on CH_4 conversion over PGM catalyst, which paves the path for optimizing catalyst formulation and operation of NGV emission control.

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Simulation of Finite-sized Particle Transport through Porous Media

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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, and ground water contamination and remediation. Theoretical and computational studies of pore-scale transport have often focused on the dispersion of infinitesimally small particles in which steric and hydrodynamic interactions of particle with the porous medium do not play an important role in the dispersion. Here, we employ the Stokesian dynamics method to investigate the effect of steric and hydrodynamic interactions on flow-driven transport of finitesized nanoparticles within a porous medium. We model the porous medium as an ordered array of nanoposts. We vary the flow conditions to access Péclet numbers from 0 to 40 and the spacing between nanoposts to access dimensionless confinements from 0.05 to 0.5. Using this model, we calculate diffusion coefficients in quiescent conditions and dispersion coefficients in flow conditions. Under quiescent conditions, the diffusivity of particles that interact with the posts only through steric exclusion linearly decreases with increasing confinement due to the higher frequency of collisions with nanoposts. Inclusion of lubrication and far-field hydrodynamic interactions (HI) further reduces particle diffusivity, largely for strong confinement due to increased viscous drag from nanoposts. Under flow conditions, with steric interactions alone, the longitudinal dispersion coefficient increases slightly as a function of Pe due to increases in collision frequency with nanoposts and in the width of collision frequency distribution. Inclusion of lubrication and far-field HI, however, leads to a power-law increase in the longitudinal dispersion coefficient as a function of Pe, due to spatial variations in the fluid velocity induced by nanoposts. Improved understanding of the effects of steric and hydrodynamic interactions on particle transport under quiescent and flow conditions will help to improve the design of particles for transport through porous media and the design of periodic microstructures for separations of nanomaterials.



Dynamics of Filamentous Phage in Polymer Solutions

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Bacteriophage ("phage"), viral nanoparticles that infect bacteria, are widely used as uniform, anisotropic building blocks for applications in electronics [1] and sensing [2]. These applications often require phage to be controllably transported through complex fluids that contain polymers, macromolecules, or proteins. For example, phage used as reporter particles in ultrasensitive lateral-flow assays must be transported through biological fluids to binding sites on a functionalized membrane. The assay sensitivity then depends in part on the efficient transport of the phage [3,4]. How nanoparticle anisotropy affects transport in complex fluids at a comparable particle and matrix characteristic length scales remains incompletely understood. Here, we investigate the dynamics of phage with varying aspect ratios in semi-dilute polymer solutions using fluorescence microscopy.

We found that phage diffuse faster than predicted by the Stokes-Einstein relation using the bulk viscosity of the polymer solutions. The normalized diffusivity of the phage remains approximately constant at low polymer concentration and then decreases as the polymer concentration is further increased. Normalized length scales based on the ratio of phage scales (radius, length) to the polymer correlation length were unable to collapse the diffusivities onto those of spherical particles. This result suggests that an intermediate length scale, between phage length and radius, controls phage diffusion through a crowded medium. These results provide insight into the transport behavior of anisotropic nanoparticles and, more broadly, would guide the development of applications that exploit particle anisotropy to generate unique functional properties in composite materials.

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Reviewing Non-classical Pathways of Cholesterol Crystallization regulated by cluster Precursors

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Cardiovascular disease (CVD) is the leading cause of death in the United States. Dietary cholesterol was implicated n increasing blood cholesterol levels leading to the elevated risk of CVD. Cholesterol in body is carried by two main particles: low- density lipoprotein (LDL) and high-density lipoprotein. The harmful cholesterol-filled plaques grow inside arteries when the number of LDL largely increased and the system lost the balance between two particles. Such plaques are responsible for angina, heart attacks and most types of stroke.

Precipitation of solid cholesterol crystals from supersaturated bile has an essential role in cholesterol gallstone formation. Crystallization of cholesterol in bile is a rather complex process and poorly understood. For now, two main different morphologies were observed in the experiments. The physiological pathway that illustrates the evolution of cholesterol microcrystalline could be a key to understand and regulate the process.

Our recent work firstly succeeded in monitoring the growth of cholesterol crystals at atomic level by applying atomic force microscopy. we showed the existence of an intermediate precursor in the solution, and demonstrate how the precursor land on the crystal surface and lead to significant different precursor-crystal interaction that's alter the modes of crystal growth. Our research provided insights in explaining the complex crystallization of cholesterol in bile and fundamental platform for investigation of controlling the formation of cholesterol crystals in the human arteries.



A DFT Study for the Mechanistic Understanding of Passive NO_x Adsorption on Pd/H-BEA Under Dry Conditions

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With constantly changing fuel sources and improvements in engine technology the treatment of vehicle emissions at low temperature poses a formidable challenge. Although there has been a success in addressing NO_x emissions at temperatures above 200°C with the aid of selective catalytic reduction (SCR) technology, emission control during vehicle cold start (temperatures < 200°C) remains arduous. Metal-exchanged zeolites functioning as passive NO_x adsorbers (PNA) have been proposed as a possible solution. Their role is to adsorb NO_x from the engine exhaust at low temperature and release them when the downstream SCR reaches operating temperature.

In the present work, wWe have used density functional theory (DFT) to gain a mechanistic understanding of NO_x adsorption on Pd/H-BEA, and have proposed a sequence of feasible elementary steps that can explain observations from flow reactor experiments for NO_x trapping.¹ Due to the complex nature of palladium speciation in zeolite pores, the structure of the active site remains elusive. For zeolites with atomically dispersed Pd in the absence of water the most likely active sites are [Z₂Pd^{II}], [ZPd^{II}OH], and [ZPd^I]. On the [Z₂Pd^{II}] site NO can be stored by reversible molecular adsorption or in the form of nitrate. The [ZPd^{II}OH] site catalyzes low energy pathways for NO and also CO oxidation, while [ZPd^I] can be dynamically formed and provides the strongest NO binding site. The presence of CO as stronger reductant was found to be beneficial for NO_x storage. The active site assignments are corroborated by vibrational analysis and comparison to observed experimental diffuse reflectance spectra.⁴

Capturing the temperature dependent evolution and role of active sites in Pd/H-BEA upon NO exposure will expedite the development of suitable PNA materials to achieve desired emission control performance at low temperature.

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Spatial Features of Coupled Endo-Exo Reactions: A Study of Tri-Reforming of Methane

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The Tri-Reforming of Methane combines the complete oxidation of methane to drive steam and dry reforming to convert potential waste gases into a value-added commodity. This system uses a mixture of one highly exothermic reaction with two strongly endothermic reactions. This combination results in distinctive spatial patterns to be observed within the catalyst. These spatial regimes are detected through a mixture of optical frequency domain reflectometry (OFDR), allowing for temperature as a function of position, and spatially resolved mass spectrometry. These techniques allow for the observation of operative regimes within the monolith catalyst. Oxidation of methane and a corresponding temperature increase happen in the front section of the reactor. This is followed by a sharp reduction in temperature and production of carbon monoxide via steam and dry reforming. The overall reaction behavior provides incentive to pursue specialized reactor designs, to maximize the conversion of methane and carbon dioxide.



Particle transport in solutions of ring and linear polymer chains

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The dynamics of nanoparticles in complex fluids are of great interest for applications in drug delivery, oil recovery, and materials processing. Particle mobility is well described by the generalized Stokes-Einstein (GSE) relation when the nanoparticles are much larger than the polymers. Violations of GSE predictions are observed, however, when the size of nanoparticles is comparable to or smaller than length scales in polymer solutions [1]. We investigate the microscopic origin of this anomalous behaviour using multi-particle collision dynamics (MPCD) [3], an advanced algorithm for rigorously modelling solvent-mediated hydrodynamic interactions in coarse-grained, mesoscale simulations. We apply MPCD to study transport in solutions of nanoparticles and linear polymers, and the effects of many-body hydrodynamic interactions on dynamic coupling in these systems. We demonstrate that the translational centre-of-mass motions of both nanoparticles and linear polymers are sub-diffusive on short times before transitioning into a diffusive regime on longer time scales [2]. The long-time diffusivities of nanoparticles collapse according to scaling predictions [4], in accord with recent experiments [1]. The sub-diffusive behaviour predicted by MPCD simulations, by contrast, agrees with experiments [1], but significantly deviates from theoretical predictions. We show that this disagreement is due to tight coupling of the translational motions of the nanoparticle and polymer centres-of-masses, which is not accounted for in current theories. We also investigate the influence of polymer morphology and flexibility [5] on this coupling behaviour. Surprisingly, we find that the dynamic coupling observed in solutions of ring and linear polymer chains are remarkably similar, even in systems with large fractions of ring concatenation defects. For both ring and linear polymer systems, however, the nanoparticle dynamics become more subdiffusive and decouple from the dynamics of the polymer chain centre-of-mass.

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Amyloid-β Suppression by Drug-promoted Polymorph Transformation

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The accumulation of the protein fragment amyloid- β (A β) outside neurons in the brain is one of the main hallmarks of Alzheimer's disease. Aß peptides can aggregate into both soluble oligomers and insoluble fibrils and plaques. Despite recent interest in neurotoxic A^β oligomers, the structure and mechanism of AB fibril formation are still actively explored. As nearly all treatment development efforts to date have been largely unsuccessful, deeper understanding of the Aß fibrillization and its response to Alzheimer's drugs can guide us to more efficient treatments. Bexarotene, an FDA approved drug for cutaneous T cell lymphoma, is one of several small molecules that show promising results in reducing Aß aggregates in the brain but its mechanism of action remains elusive. The bulk kinetics of fibrillization reveals that bexarotene delays the primary nucleation of fibrils without impacting secondary nucleation and growth. For molecular level insight on how bexarotene operates, we monitor the response of fibril growth to bexarotene by time-resolved in situ atomic force microscopy. The fibril growth rates are indifferent to bexarotene as high as 1 µM, concurrently with bulk fibrillization results. We find that Aβ fibrils generated in presence of bexarotene engage in two surprising behaviors. First, the distribution of the thickness of the bexarotene fibrils diverges from that of normal AB fibrils, suggesting that bexarotene may enforce a distinct fibril polymorph. Second, the rate of growth of bexarotene seeds from pure AB solutions correlates sublinearly with the peptide concentration, in contrast to the linear correlation obtained with normal seeds [1]. We hypothesize that this nonlinear behavior manifests a unique activated complex for growth of the polymorph promoted by bexarotene, which, in addition, varies in response to the $A\beta$ peptide concentration. Urea, known to impair hydrophobic contacts both in the fibril structure and in the activated complex, increases the solubility of fibrils generated in presence of bexarotene, as expected. Surprisingly, urea stimulates the growth rate discriminately, only at specific AB peptide concentrations, and ratifies that the activated complex employed by bexarotene seeds is unique and varies with AB concentration. The suggested polymorph transformation driven by bexarotene presents a novel mode of action of drugs that suppress pathological aggregation not only in Alzheimer's, but also for myriad distinct pathologies that originate with protein condensation.

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Local Confinement Controls Diffusive Nanoparticle Dynamics in Semidilute Polyelectrolyte Solutions

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Nanoparticles are used in a wide range of industries including oil and gas, material manufacturing, and medicine. Nanoparticles can improve extraction efficiency in enhanced oil recovery through mobility control [1], enhance properties of composite materials [2], and advance 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. The diffusive dynamics depend on the size of nanoparticles relative to characteristic length scales in the polymer solution. When the nanoparticle radius R_{NP} is much smaller than the radius of gyration Rg of polymer chains, the polymer chains act as barriers and the nanoparticle dynamics depend on the void geometry and solvent viscosity. Conversely, when R_{NP} is much larger than Rg, the nanoparticles dynamics couple to the bulk viscoelasticity of the solution. In the intermediate regime where R_{NP} and Rg are comparable, however, the polymer solution is heterogeneous on length scales relevant for nanoparticle transport. 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 the segmental relaxations of polymer chains in the intermediate regime. A deeper understanding of the nanoparticle dynamics and their controlling parameters in charged polymer solutions, where the electrostatic interactions between the polymers can modulate the polymer flexibility, however, is still lacking.

Here, we study the dynamics of polystyrene nanoparticles in a model polyelectrolyte, sodium polystyrene sulfonate, dissolved in deionized water at different solution ionic strengths using fluorescence microscopy. In dilute polymer solutions, nanoparticles diffuse according to solution viscosity. As polymer concentration is increased into the semidilute regime, the dynamics of large nanoparticles remain coupled to bulk viscosity across all nanoparticle sizes and ionic strengths. The dynamics of small nanoparticles, however, exhibit a non-monotonic dependence on polymer concentration. Further, the extent to which nanoparticle displacements deviate from the Gaussian distribution, expected for a Brownian diffusion mechanism, exhibits the same non-monotonic dependence. These results suggest that the difference of nanoparticle dynamics in neutral versus charged chains arises from the local conformation of polyelectrolytes, which generates a confining force on local chain length scales. This improved understanding of the dynamics of nanoparticles is expected to allow better control over their transport in complex media, enabling more effective application in enhanced oil recovery, composite processing, and drug delivery.

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Design of antibiotic dosing regimen to eradicate persistent bacteria

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The issue: A small fraction of bacteria use persistence as a strategy to survive exposure to antibiotics. Persistence is conferred by dormancy (non-growth): while bacteria remain dormant they cannot be killed by conventional antibiotics, unless they leave dormancy (recommence growth) and become susceptible to antibiotics again.

Why the issue is important: Persisters are implicated in many chronic infections such as recurrent urinary tract infection, cystic fibrosis and are difficult to eradicate with existing antibiotics. Moreover, prolonged persistence usually leads to complete bacterial resistance to antibiotics.

The state-of-the-art: Prolonged treatment of persisters with antibiotics, hoping for eventual eradication with the help of a patient's immune system; undesirable, even when successful. An opportunity to advance the state of the art: Hypothesis: Persisters may 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.

Remaining challenges: The key is to ensure net bacterial population reduction in each cycle, thus ensuring complete eradication after a number of cycles, therefore timing of antibiotic dosing and withdrawal is crucial. Related experimental studies in literature show encouraging yet inconclusive results.

Current work: We have confirmed the hypothesis by computer simulation. The hypothesis will be tested *in vitro*, in a high throughput microfluidic device. Combining experiments and mathematical modelling, the effect of antibiotic dosing strategies on bacteria killing effectiveness will be tested. The microfluidic device has been fabricated and tested, and time-kill experiments are currently underway.

Benefits: An effective strategy for (a) eradication of persisters using antibiotics that would otherwise be ineffective, and (b) reduced amount and duration of antibiotic usage for persistent infections, thus help to prevent the emergence of antibiotic resistance due to its overdose.



Elucidating the mechanisms of the rapid ordering of block copolymers

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The self-assembly of Block Copolymers (BCPs) provides a facile and cheaper alternative to produce nanostructures for next-generation nanomanufacturing via directed self-assembly. The rapid and continuous processing of BCPs is a necessity to realize their full potential for use in industrial applications. Additionally, the underlying molecular mechanisms involved in BCP selfassembly are not completely understood. We are trying to understand the molecular mechanism governing self-assembly of BCPs and use the acquired knowledge to devise innovative processes for rapid and template-free self-assembly of BCPs. In this work, we demonstrate a way for rapid ordering (~10 sec) of BCPs using pre-nucleated grains in as-cast films imparted by judicious choice of casting solvent and film casting method. The rapid solvent evaporation results in the formation of short-range ordered BCP nanostructures which act as nuclei for the subsequent ordering of BCP to larger grains during thermal annealing. The solvent evaporation quenches the BCP morphology in a weakly segregated state. These weakly segregated domains undergo a transition to equilibrium segregation in the melt state. The time dependence of the increase of domain spacing in weakly segregated as cast morphology to the equilibrium state shows a nonlinear trend. Controlling the as-cast morphology followed by Cold Zone Annealing allows the rapid fabrication of perpendicularly oriented poly(styrene)-block-poly(methyl methacrylate) lamellar structures in 20-500 nm thick films. This rapid self-assembly approach may pave the way for use of BCP self-assembly in industrial applications. Additionally, we study the effect of different solvent and film casting methods to understand the phase separation and nucleation in ascast films.

