Biomass offers a renewable carbon source that could be utilized as a raw material in the chemicals industry. A potential route for the conversion of biomass feedstock’s into industrial chemicals is through the catalytic conversion of biomass sugars (glucose) to furan based compounds through an aqueous reforming process. However, to accommodate the transport of these bulky sugars within the catalytic framework, a new breed of hydrothermally stable catalysts is required with either: a three dimensionally ordered mesoporous (3DOm) or a hierarchical micro-mesoporous pore topology. Zirconia offers a candidate catalytic material due to its hydrothermal stability and surface properties. Additionally, recent synthetic techniques offer the ability to produce monodispersed silica particles, which form a pore size-tunable colloidal crystal template when dried. This work examines the use of sol-gel based zirconia precursors to prepare 3DOm zirconia through a hard templating technique. Dynamic light scattering was used to select a zirconia precursor solution (zirconyl chloride octahydrate) for the infiltration of the pre-formed mesoporous silica templates. The solutions were successfully templated, resulting in monoclinic and tetragonal 3DOm zirconia upon removal of the silica template. Crystallinity was characterized with X-Ray diffraction and Raman spectroscopy; while, nitrogen adsorption provided insight into pore size tunability and resistance to collapse. Transmission electron microscopy was used to assess structural integrity and development at various stages during calcination. Results suggest that the zirconia polymorphism is tunable by controlling the degree of template-induced confinement during nucleation, crystallization, and higher-temperature processing of the zirconia materials. Specifically, apparent stabilization of the tetragonal phase of zirconia (i.e., resistance of tetragonal-to-monoclinic transformation) is achievable on the basis of confinement rather than through doping or the incorporation of additives.
Low Packing Fraction Crystalline Cavitands Exhibiting Molecule-Sized Cavities

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The development of new materials for application in gas storage, separations and sensing has garnered much interest as the power of synthetic organic chemistry has afforded chemists the opportunity to widely optimize the functionality of these materials. Typically, porous materials have been utilized for such roles, including coordination polymers or MOFs, COFs, PIMs, and porous organic cages. [Ultra]microcavity materials – calixarenes, cryptophanes, cucurbiturils, etc., are not formally defined as being porous, however possess molecule-sized void spaces and should therefore afford the ability to optimize sorption/inclusion selectivity much like ultramicroporous materials.

Cavitands are ‘molecular vessels’ that have been widely investigated since Cram’s seminal paper in 1982 and are amenable to structural fine-tuning by appending a variety of functional groups onto the ‘rim’ (R), ‘feet’ (R’) and ‘bridge’ (Y) of the bowl-like moiety (R.R’.Y; Scheme 1). Due to their concave nature, members of this family will be incapable of forming close-packed structures in their pure crystalline state, thus it should be possible to exploit the voids of these materials for various purposes.

The cavitand Me.H.SiMe$_2$ has shown a remarkable ability to bind a wide variety of gases. To probe structural factors at play with respect to enclathration selectivity, x-ray crystal structures of numerous isostructural guest@Me.H.SiMe$_2$ (x ≤ 1) were obtained under ambient conditions or high pressures for more volatile guests (Figure 1). Thermogravimetric analysis (TGA) studies illustrate the cup’s ability to confine certain gases up to 300 °C above their normal boiling points (Ar, Kr, Xe, CH$_3$F).

Single crystals of clathrates containing Kr, CH$_3$F as well as the hydrate of Me.H.SiMe$_2$ have illustrated the ability to be emptied using high temperature in a single crystal fashion without loss of crystal integrity. The sorption of water by Me.H.SiMe$_2$ in a single crystal (SC) fashion has also been performed (k = 1.4 x 10$^{-4}$ hr$^{-1}$), a parameter rarely determined purely by single crystal x-ray diffraction (SCXRD). Other cavitand structures possessing microcavities will also be presented.

References
Supercapacitive Swing Adsorption

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Carbon capture is essential for reduction of carbon dioxide (CO\textsubscript{2}) pollution from flue gas which is emitted during fossil fuel combustion. The flue gas is mainly composed of 15% CO\textsubscript{2} and 85% N\textsubscript{2} and it requires high selectivity for gas purification. Some methods have been developed for carbon capture like Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA). Unfortunately, these techniques use a lot of energy during desorption step what reduces power generation efficiency\textsuperscript{1-3}. An ideally effective carbon capture technique needs to promote CO\textsubscript{2} adsorption and desorption at the proper times during the separation cycles, without incurring a large parasitic energy load. Herein, we present a new gas adsorption technique, Supercapacitive Swing Adsorption (SSA), which can reduce the energy load by an applied electric field to drive the adsorption of CO\textsubscript{2} by switching electric bias on and off. All thermodynamics between adsorbent and adsorbate interactions are constantly modified with external electric field. We show that reversible adsorption/desorption of CO\textsubscript{2} from 15% CO\textsubscript{2} and 85% N\textsubscript{2} gas mixture can be achieved by capacitive charge and discharge of electrically conducting high surface area porous carbon materials in aqueous sodium chloride electrolyte. The amount of adsorbed CO\textsubscript{2} scales proportionally with the mass of the sorbent, which is inexpensive, robust and environmentally friendly.

References


Hierarchically Structured Porous Materials towards High Performance Molecular Separations and Reaction-Separation Technologies

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The ability to rationally design and synthesize porous inorganic particles and thin membranes with hierarchically ordered micro- and/or mesoporosity, controlled morphology, and tunable pore topology stands to impact selectivity and efficiency in catalytic, adsorption, membrane-based separations, and reaction-separations applications. Motivated by applications requiring control over transport and reaction of small to bulky molecules, this poster highlights efforts to identify assembly and templating strategies capable of achieving materials spanning these scales. A facile nanotemplating approach is developed and employed to realize these materials, and involves the synthesis and assembly of size-tunable silica nanoparticles into ordered colloidal crystal structures as hard, sacrificial templates for both direct and indirect porous replica formation. We develop various stages of materials assembly emanating from controlled synthesis of primary inorganic nanoparticle building units with nanometer resolution\textsuperscript{1,2}, and encompassing their multi-modal (i.e., size, function) assembly into hierarchically ordered porous structures\textsuperscript{3-6} and templating of higher-order porous materials\textsuperscript{7}. Specific applications to be highlighted in this poster include the scaffolded growth of ultra-thin microporous zeolite membranes as well as zeolite-inspired, template- and surfactant-free mesoporous materials with tunable three-dimensionally interconnected mesoporosity and pore topology, including multimodal silicas, metal-functionalized mesoporous silica substrates, and multi-modal porous carbons.

References
Assembly and scaffolding strategies for realizing ultra-thin inorganic films with tunable porosity

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Ultra-thin ordered mesoporous and mesopore-supported microporous inorganic films on the order of tens of nanometers in thickness bearing ordered pore topology hold exciting technological implications spanning, among others, membrane separations, devices for integrated reaction-separations, and chemical sensing. Yet control over film thickness and quality (i.e., minimizing defects like cracks and grain boundaries) has been a persistent challenge in the fabrication of inorganic films supported on porous and non-porous substrates. This poster will highlight two hierarchical synthesis strategies in which near-monolayer to multilayer colloidal crystal films composed of size-tunable silica nanoparticles (ca. 5-50 nm in size) are used to template replica films through interstice infiltration by a wide range of carbon sources (e.g., furfural, phenol resin, vinyl alcohol, sucrose). In a first proof-of-concept, pre-assembled colloidal crystal films are employed as a robust framework for liquid and/or vapor-phase infiltration, polymerization and pyrolysis of various carbon sources without pore contraction and/or collapse upon template sacrifice. An alternative approach employs careful control over silica particles in sols containing monomeric and oligomeric carbon precursors such that co-assembly of colloidal template particles and replica material into ordered thin films can be achieved in a single step. The wide range of carbon sources accommodated by this templating strategy can be employed as a handle for tuning final film properties including microporosity, mechanical stability, and graphitic composition, among others. It also underscores the versatility of this approach, and the extension to other classes of materials such as ordered porous metal oxide films (e.g., ZrO2) will be presented. The size tunability of the primary silica particles and ability to control the thickness of multi-layer colloidal crystal film templates translates into respective control over the resulting mesopore structure and film thickness scalability. The result is robust, flexible mesoporous or mesopore-supported microporous films that can be transferred by stamp techniques to various substrates (i.e. porous stainless steel support, FTO glass, conductive polymer sheets) for potential applications as high-sensitivity, high flux membranes and promising counter-electrodes for dye-sensitized solar cells.
Theoretical modeling of the conversion of furan to benzofuran during the catalytic fast pyrolysis of cellulose

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Catalytic fast pyrolysis (CFP) is a promising route to the production of renewable biofuels from cellulosic biomass. Understanding the fundamental zeolite-catalyzed chemistry is crucial in optimizing the process and making it commercially viable. Motivated by this need, we have studied the pathways by which furan is converted into benzofuran in HZSM-5. Furan is one of the products of CFP and is often used as a model feedstock in lieu of cellulose, while benzofuran is recognized as an intermediate on the pathway to desired aromatic compounds like benzene, toluene and xylene. Using embedded cluster models of zeolites and QM/MM calculations with the ONIOM methodology, we explore several gas-phase and zeolite-catalyzed pathways to identify the role of the zeolite catalyst in these pathways. Our results strongly indicate that Diels-Alder cycloaddition between two furan molecules is unlikely to lead to the formation of benzofuran inside the zeolite. Instead, the route to benzofuran is initiated by the protonation and subsequent ring opening of one furan molecule. In addition, we locate transition states for selected steps in the pathway using the climbing image nudged elastic band (CI-NEB) method. Our calculations show that furan can be stably protonated at the oxygen atom in the gas-phase. However, in HZSM-5, this particular protonated species is a transition state, not a stable intermediate. In the protonation of the C2 carbon atom in furan, the zeolite structure is seen to undergo significant structural relaxation in going from the reactant to the transition state to the product.
Mesoporous Aluminosilica with Crystalline Channel Walls

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Mesoporous aluminosilica with crystalline channel walls was synthesized by high pressure and high temperature treatment of a mesoporous aluminosilica/carbon nanocomposite material. The mesoporous aluminosilica was synthesized through soft-assembly of commercially available Pluronic P123 block copolymers as template and aluminosilica precursor followed by calcination under air. It was observed that at a pressure of 4 GPa and temperature of 750 °C for 6 hr, the aluminosilica/carbon nanocomposite was transformed into crystalline phase. The crystalline phase was quartz as seen from XRD analysis. Upon removal of carbon phase by oxidation, the obtained material was mesoporous as confirmed by nitrogen adsorption technique. The mesoporosity was also confirmed by transmission electron microscopy. Further optimization of the synthesis conditions showed that the crystallization could be achieved at a pressure of 2 GPa and somewhat lower temperature. The synthesized material has potential to meet the conditions required for cracking hydrocarbons at high temperature.
When a fluid gets adsorbed by a porous solid, the solid deforms. The character of deformation maybe different: some materials swell, some contract. The magnitude of deformation also varies: for zeolites, activated carbons and mesoporous molecular sieves (MMS) the relative change of a sample volume $\Delta V/V$ is small (~0.1%). For aerogels and metal-organic frameworks $\Delta V/V$ could reach up to 30%. Understanding of mechanisms of this phenomenon is crucial for enhanced coalbed methane recovery by CO$_2$ injection$^1$; it also offers methods for measuring elastic properties of porous materials$^{2,3}$. While adsorption-induced deformation has recently attracted much attention of experimentalists$^{4-6}$, a number of works giving quantitative interpretation of experimental data is very limited.

In the current work we focus on deformation of mesoporous materials. Experimental measurements of deformation for such systems have been known for decades$^7$, but the theory was lacking. Invention of MMS made a revolution in adsorption science and also stimulated the progress in developing adsorption-induced deformation theories. MMS offer unique opportunities for theory verification, thanks to their well-defined pore morphology and narrow pore-size distribution. Using in situ small angle X-ray scattering (SAXS) one can measure how MMS lattice parameter changes during adsorption, and, therefore, obtain a strain isotherm – expansion of a pore as a function of adsorbate pressure.

The force which causes the deformation is so-called solvation pressure – the pressure which is exerted on the pore wall by adsorbed fluid. The solvation pressure can be obtained from the grand potential of the pore with adsorbed fluid. We calculate the grand potential based on two different adsorption theories: macroscopic Derjaguin-Broekhoff-deBoer (DBDB) approach$^8$ and microscopic Quenched Solid Density Functional Theory approach$^9$. Macroscopic approach reveals two different physical mechanisms causing non-monotonic strain isotherms: Bangham effect – effective lowering of the surface free energy; and deformation by Laplace pressure at the curved liquid-vapor interface. We found that the predictions of two approaches perfectly agree for mesopores > 8 nm. We demonstrated also that the theoretical predictions are in good agreement with SAXS experimental data for water adsorption in SBA-15 silica$^5$ (Figure 1). The details of the method could be found in Refs 10 and 11.

Figure 1: Deformation induced by water adsorption on SBA-15 silica at 293 K. Experimental strain isotherm (points) is derived from SAXS data. Theoretical predictions (line) are calculated using the macroscopic theory based on DBDB approach. Figure is adapted from Ref. 10.

References
Promising alternative energy systems such as photosynthetic water splitting and carbon dioxide conversion to liquid fuels both require the use of efficient water oxidation catalysts (WOC’s). Currently, one of the major limitations preventing the practical development of these systems is the expense of rare earth metal WOC’s such as \( \text{IrO}_2 \). Relatively inexpensive, first row transition metal oxide WOC’s have shown promise as a possible alternative to noble metal catalysts. Of the most active of these materials, is the spinel \( \text{Co}_3\text{O}_4 \).[1] We have recently shown that nanostructured cobalt oxide catalysts supported in mesoporous silica have been able to oxidize water with efficient turnover rates and costs approaching practical use.[2] Of particular interest to current research is how the structure of the cobalt oxide spinel correlates to its impressive activity. Understanding the importance of the spinel may lead to the rational development of better transition metal based catalysts.

Plants or more specifically the complex photosystem two, which is responsible for the oxidation of water in plants, has been studied as a source of inspiration in the development of inexpensive WOCs. Past research has shown that a manganese oxide cubane core found in photosystem two is the active site for water oxidation.[3] This cubane core found in plants closely resembles cobalt octahedral sites found in the spinel \( \text{Co}_3\text{O}_4 \). Additionally, the spinel structure contains tetrahedral sites, which may affect the activity the catalyst by changing the electronic or structural properties of the spinel material.

Our research has focused on understanding the importance of both sites on WOC activity by replacing some of the cobalt with other transition and alkaline earth metals. Recently, we have successfully synthesized, characterized, and photocatalytically tested several mesoporous metal-substituted cobalt oxide spinel materials in near neutral conditions. Our results indicate in substitution of different metals into the spinel structure can strongly affect the activity, stability, and structure of these catalysts.

References

The hydrothermal instability of conventional catalyst supports, therefore, demands the development of next generation materials for high-selectivity catalytic conversions in the biofinery (e.g., dehydration/oxidation chemistries, isomerizations). Specifically, hydrothermally stable heterogeneous catalysts bearing three-dimensionally ordered mesoporous (3DOm) and hierarchical (i.e., macro-mesoporous) pore structures are sought in order to accommodate diffusion of bulky sugar molecules, polysaccharides, and their derivatives. The enhanced hydrothermal stability and reducible structure of titania establishes its promise as a robust substrate for liquid phase biofuel catalysis. A sacrificial nanotemplating strategy involving the infiltration of colloidal crystals composed of size-tunable (ca. 10 nm and larger) silica nanoparticles with titania precursor solutions followed by confined hydrolysis therein enables the fabrication of three-dimensionally ordered mesoporous (3DOm) titania structures with controlled pore body size in the range of nanometers to tens of nanometers. The hard silica template enables calcination-induced improvement in titania crystallinity, with the templated pores robust to collapse upon template removal. This approach results in 3DOm titania materials with attractive textural properties, including surface areas (ca. 289 m$^2$/g) and pore volumes that are up to four times and more than an order of magnitude larger, respectively, then commercially available titania. Fundamental insight into titania polymorphism (i.e., rutile, anatase, or fraction thereof) has been elucidated as it relates to its sensitivity to the degree of titania confinement imparted by the template as well as the template surface chemistry. Specifically, increasing confinement helps to stabilize the active anatase polymorph, while tuning the density and type of surface silanol groups on the template enables fine control over fractional polymorphism, the latter having potential implications on inherent reactivity. Functionalization of these materials with inorganic (Pt) moieties has been studied for the purpose of creating multifunctional dehydration-oxidation catalysts for processing of sugars. Template transfer techniques are under investigation as a means for realizing uniformly distributed functionality and possible partial embedment within the 3DOm titania structures for enhancing catalyst stability.
Synthesis, Structures and Photoluminescence Properties of a Series of Alkaline Earth Metal-Based Coordination Networks Synthesized Using Thiophene-Based Linkers

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Three alkaline earth metal (Ca, Sr) based coordination networks were synthesized using 2,5-thiophenedicarboxylic acid (TDC) under solvothermal conditions and characterized by single crystal X-ray diffraction, thermal and photoluminescence methods. Two different solvents, namely DMF and ethanol, were used to synthesize the networks, while keeping the synthesis temperature constant. The photoluminescence measurements reveal strong correlations between luminescence properties, the crystal packing and coordinated solvent molecules.
Synthesis of Transition Metal Phosphate Frameworks

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Transition metal phosphates made from Fe, Mn and Co are of interest because they possess unique catalytic and electrochemical properties compared to metal oxides. To date, very few framework structures based upon these metals have been successfully synthesized using traditional hydrothermal or solvothermal syntheses. In this presentation we will discuss our results using ionothermal synthesis to make transition metal phosphates.¹ Using the deep-eutectic solvent of choline chloride and N,N'-dimethylurea we have made 4 pure cobalt phosphate phases: DEL-1 (novel), DEL-2 (novel), CoPO₄-ABW and CoPO₄-HEX. While investigating these materials we were able to study how temperature, reaction time, and molecular amounts of water determine the recovered cobalt phosphate phase. By slightly changing the deep-eutectic solvent to choline chloride and 2-imidizolidone we were able to synthesize isostructural Co, Mn, and Fe phosphates with a DFT framework structure.

References
High pressure cracking of n-hexane over H-ZSM-5

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The cracking of n-hexane over H-ZSM-5 has been studied at pressures from 0.03 to 137 bar, between 558 and 633 K, for application to endothermic reforming. The rates showed the effects of saturated adsorption for n-hexane in the zeolite, with the reaction being first-order at low pressures and zeroth-order at high pressures. The activation energy also changed with increasing pressure by an amount equal to the heat of adsorption of n-hexane in ZSM-5, going from 170 kJ/mol to 90 kJ/mol. The selectivity for C-7+ products varied only with temperature and conversion.
Metal-Organometallic Frameworks Incorporating Metallocyclopentadienyl Moieties

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Metal-organic frameworks (MOFs), or porous coordination polymers (PCPs), are a rapidly growing class of porous materials with potential for various applications, including gas storage, separation, and catalysis. The rigidity and tunability of MOFs allows for modification of the framework and consequently the functionality of the pores in the material, particularly via choice of ligand. We have developed a series of new facially-metallated aryl carboxylate ligands incorporating precatalytic metallocyclopentadienyl moieties. Using these ligands, we anticipate the ability to photolytically activate catalytic [CpM]n+ species inside the parent framework. We have demonstrated that such η⁶-metallated carboxylic acid ligands sustain the porosity of a framework, and can result in materials with large pore volumes.1 Several of these ligands have been reticulated into known MOF architectures (e.g. MIL-type, UIO-type), resulting in isostructural metal-organometallic frameworks (MOMFs) with the ultimate goal of post-synthetic activation for heterogeneous catalysis.

References
An Adamantane-Based 3D Covalent Organic Framework as HF-Resistant Ultra-Low Dielectric Constant Material

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The continuing downscaling of microprocessor features demands the timely development of ultra-low dielectric constant (ultra-low-k) materials to reduce resistive-capacitive (RC) delay, lower power dissipation, and alleviate interline crosstalk.1,2 Known approaches to reduce the k value of a material include incorporation of porosity and use of light constituent atoms. Here we show for the first time that covalent organic frameworks (COFs)3,4 are a promising new class of porous crystalline ultra-low-k materials with higher porosity and lighter constituent atoms than zeolites. A simple design strategy herein is employed for a 3-D porous COF with ctn net, denoted as ACOF-1, based on an adamantane derivative, 1,3,5,7-tetrakis(4-(dihydroxy)borylphenyl)adamantane (TBPA). This new class of highly porous materials are shown to have ultra-low-k value (1.91-1.24) by both experiment and calculation. To the best of our knowledge, the k value of 1.82 at 1 MHz represents one of the lowest k in all of low-k materials reported. Specifically, the ultra-low-k value has already met the target after the next decade proposed by the National Technology Roadmap for Semiconductors (NTRS) in 2010 (k = 1.7-2.0, 2024). ACOF-1 also has excellent HF resistance, and it remained unchanged in terms of weight, color, and morphology in HF solution for at least 24 hrs, which suggests that ACOF-1 is superior to silica based low-k materials in terms of HF-resistance. Nanoindentation results show a elastic modulus of 7.0 GPa. These results combined suggest that porous COFs are a promising new class of low-k materials.

References