

FINAL Program for NECZA 2005
December 9, 2005
University of Pennsylvania, Philadelphia

Poster Session 8:30 am – 9:30 am

Steve Wilson, 9:30-10:10 "Methanol-to-Olefins Process and the Role of
SAPO-34: a Review of Recent Advances" UOP

Scott Auerbach 10:10-10:40 "Modeling Spontaneous Formation of Precursor
Nanoparticles in Clear-Solution Zeolite Synthesis", University of Massachusetts

Break 10:40-10:50

Israel Wachs 10:50-11:20 Smart Combinatorial Operando Molecular
Spectroscopy of Catalysts: Application to CH₄ Aromatization over Mo/ZSM-5, Lehigh
University)

Frank Hursey, 11:20-12:00 An Entrepreneurs Dream---QuikClot
(Quik-Clot)

Lunch 12:00-1:00

Poster Session II 1:00-1:30 pm

Business Meeting 1:30-2:00 pm

Clare Grey 2:00-2:40 pm O¹⁷ NMR Spectroscopy of Zeolites
(SUNY at Stony Brook)

Mark Snyder 2:40-3:20 pm Non-destructive, quantitative characterization of
zeolite thin film polycrystallinity for elucidating structure-properties relations" (U. of
Delaware)

Break 3:20-3:30 pm

Student Minitalk I 3:30-3:40

Student Minitalk II 3:40-3:50

Student Minitalk III 3:50-4:00

Adjourn 4:00 pm

Poster Abstracts to the 2005 NECZA Meeting in Philadelphia, PA.

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Manipulating Lanthanide Luminescence in Metal-Organic Frameworks

Daniel T. de Lill and Christopher L. Cahill

Dept. of Chemistry

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The inclusion of lanthanides within Metal-Organic Framework (MOF) systems has been explored for a variety of reasons, including high coordination numbers and hard acidic properties. Still more interesting perhaps is the fact that lanthanides possess unique luminescent properties (i.e. – sharp emission peaks), which may lead to a variety of useful applications. However, the process by which lanthanides undergo luminescence is highly inefficient due to forbidden transitions as defined by Laporte selection rules. A common way to circumvent this problem is to sensitize the lanthanide luminescence via an unsaturated organic molecule conjugated to the metal center. We recently published a three-dimensional structure where a conjugated organic molecule, 4,4'-dipyridyl, resides in the channels uncoordinated to the metal. We explored the luminescence of this material and have shown that the 4,4'-dipyridyl does indeed sensitize lanthanide luminescence. We have explored and thus report herein the luminescence of GWMOF-6 ($[\text{Ln}_2(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2] \cdot (\text{C}_{10}\text{H}_8\text{N}_2)$) ($\text{Ln} = \text{Eu}^{3+}$ and $\text{Eu}^{3+}/\text{Tb}^{3+}$ (50/50)), and a Tb-only structure believed to be similar to GWMOF-6. Structural and synthetic details will also be reviewed.

Synthesis of Novel Uranium-Containing Compounds in the Pyridinedicarboxylic Acid System

Mark Frisch and Chris Cahill

Self-assembly under hydrothermal conditions has been employed to synthesize several novel uranium-containing extended framework materials in the pyridinedicarboxylic acid (PDCA) systems. Syntheses involving several pyridinedicarboxylic acids with varying positions of the carboxylic acid functional groups resulted in the formation of a family of novel compounds. In attempts to synthesize bimetallic uranium based compounds, the pyridinedicarboxylic acids were chosen as starting materials due to the multifunctional groups of the ligands. We have recently shown in the U-3,5-pyrazoledicarboxylic acid (H₃pdc) compound the uranium metal centers are bound to the H₃pdc in a bidentate fashion through the nitrogen of the pyrazole ring and one of the carboxylic acids to form a connectivity consisting of a five-membered ring. Herein we explore an expansion of this philosophy to include pyridinedicarboxylic acids. An example of this same connectivity is demonstrated upon combining uranium and 2,3-pyridinedicarboxylic acid to form the two-dimensional sheet structure of compound **1** ((UO₂)(C₇H₃NO₄), monoclinic, *P*2₁/*n*, *a* = 6.5288(7) Å, *b* = 15.4692(15) Å, *c* = 9.5211(10) Å, β = 95.512(2)° and *Z* = 1). Presented will be the syntheses, crystal structures, thermal and fluorescence properties of these uranium-containing compounds.

Synthesis and Structural Characterization of Novel Metal-Organic Frameworks

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Studies of structurally and chemically diverse open framework solids have been flourishing in the recent years in an attempt to increase and improve applications of such materials in areas such as catalysis, sorption and ion-exchange. Our research is aimed at finding new 3-dimensional porous frameworks, which may possess interesting physical properties. We report the solvothermal synthesis and structural characterization of several new metal-organic hybrid frameworks constructed from various metal cations and organic ligands of different functionalities.

For example, $\text{Zn}_4(\text{H}_2\text{O})_2(\text{C}_2\text{H}_2\text{N}_3)_4(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 14\text{H}_2\text{O}$, synthesized using 1,2,4-triazole and 1,4-benzenedicarboxylic acid as organic linkers, possesses a structure based on the sheets containing 8-membered rings of Zn polyhedra and triazole molecules along the (001) direction. The sheets are pillared by benzenedicarboxylates through Zn – O – C links to produce channels which are occupied by water molecules. Its thermal behavior has also been characterized by thermogravimetric analysis. It is stable up to 380°C before the organic molecules start to decompose, leading to the framework collapse.

Silica Self Assembly: From Nanoparticles to Ordered Mesoporous Solids

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ABSTRACT:

The link between M41S mesoporous and microporous silica materials during the initial stages of synthesis is analyzed with small-angle scattering and conductivity experiments. The phase behavior of silica in aqueous solutions is studied for a family of quaternary ammonium hydroxides from tetramethylammonium to dodecyltrimethylammonium. All solutions exhibit a critical aggregation concentration at a 1:1 $\text{SiO}_2:[\text{OH}]_{\text{initial}}$ with solutions containing short chain compounds forming optically transparent nanoparticle suspensions and solutions of long chain compounds phase separating into a solid and a liquid phase. The solid phase is analyzed with x-ray diffraction and thermogravimetric analysis and is found to have a hexagonal structure similar to MCM-41. Mid-sized chain length compounds form solutions containing both the phase separated solid and nanoparticles. In addition to studying phase behavior, the role of attractive hydrophobic interactions is studied through water/ethanol mixed solvent experiments. In ethanolic solutions, the entire family of quaternary ammonium compounds are found to form stable nanoparticle suspensions.

Gas Sorption and Separation of Hydrocarbons In Microporous Metal Organic Framework Materials

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A number of porous metal organic framework (MOF's) materials have been reported since 1990. Some of them have exhibited promising applications in gas storage and separation. Here we give an overview of their hydrocarbon and H₂ adsorption properties, followed by detailed data analysis of several examples synthesized by us. Recyclable Porous Materials (RPM-1 to 3), composed of a metal, biphenyldicarboxylic acid and exopyridine analogs have shown hydrocarbon sorption capacities of 5-15 wt% and H₂ uptake up to ~2.0 wt% at 77K (at 1 atm). Microporous metal organic material (MMOM-1), [Cu(hfipbb)(H₂hfipbb)_{0.5}] [H₂hfipbb = 4,4'-(hexafluoroisopropylidene)bis(benzoic acid)] has a unique channels system containing bottle like cavities that exhibits interesting and subtle separation properties. It adsorbs propene/propane rapidly but excludes butane or higher normal or branched hydrocarbons. It also shows 1.1% H₂ uptake at room temperature (48 atm). Moreover, MMOM-2, Zntbip (H₂tbip= 5-*tert*-butyl isophthalic acid) is capable of separating of methanol from water and methanol from dimethylether. At 77K, it adsorbs ~0.8% H₂. Interestingly, another metal organic framework, Y₂(Sdba)(H₂O)·EtOH·H₂O (H₂Sdba=4,4-sulfonydibenzoic acid), occlude cavities in its 3D framework. As synthesized, the cavities enrapture EtOH or MeOH; however, narrow entrances to the cavities exclude sorption of hydrocarbons after removal of solvent molecules.

Selective Hydrogenation on Zeolite-supported Bimetallic Catalysts

Wei Huang, R. F. Lobo, J. G. Chen

Abstract

We seek to develop novel bimetallic catalysts to achieve the selective hydrogenation of acetylene in the presence of excess ethylene at low temperature. Low-temperature hydrogenation offers the opportunity of using competitive adsorption to achieve the preferential hydrogenation of acetylene. Our group has found that bimetallic catalysts favor the low temperature hydrogenation. Results from many other groups have also shown that Pd is a good catalyst for the selective hydrogenation of alkynes in excess ethylene. Therefore we will modify Pd and embed bimetallic particles in an environment that is highly selective for acetylene hydrogenation.

Cation- π interaction offers the potential for selective adsorption of acetylene. We will use the ion-exchanged zeolite for the support of the bimetallic catalysts. The zeolite structure should have multiple dimensions and contain large pores, such as β -type zeolites.

Reactor studies and FTIR evaluation have been utilized to investigate the hydrogenation activities of the Pd, Pd-Ni and Pd-Ag catalysts. It is found that the Pd-Ag bimetallic catalyst has the highest selectivity of acetylene hydrogenation in excess of ethylene, but the reaction rate is the lowest. Pd-Ni bimetallic catalyst has relatively high selectivity and activity. The Pd catalyst has the lowest selectivity but highest activity. It is also found that the zeolite supported monometallic catalyst shows superior activity for the low temperature hydrogenation of acetylene than γ -Al₂O₃ supported monometallic catalyst. Modeling of reactions in FTIR shows differences in the rate constant, equilibrium constant, as well as the selectivity of the γ -Al₂O₃ supported monometallic catalysts and bimetallic catalysts. Currently, chemisorption and EXAFS experiments are underway to further characterize the monometallic and bimetallic catalysts.

The influence of the addition of aromatic ligands on the U-pimelate system

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Uranium oxide crystal chemistry is of interest due to its implications in photocatalysis as well as radiological waste treatment. Also of note is the unique nature of the uranium(VI) coordination environment. Uranium(VI) exists as a linear tri-atomic moiety, UO_2^{2+} , allowing for further coordination to occur only in the equatorial plane which gives rise to square, pentagonal, or hexagonal bipyramid geometries. Under certain conditions (pH, amount and type of solvent, etc.), the bipyramids can polymerize into higher order building units giving rise to dimers, trimers, tetramers, etc. In our lab we have been attempting to crystallize higher dimensional U-organic coordination polymers using a combination of aliphatic and aromatic ligands under hydrothermal conditions. While maintaining a constant U to water molar ratio, and presumably the UO_2^{2+} species in solution, a new family of structures has been synthesized exhibiting the influence of the size and shape of the organic ligand on the structure. Presented will be the synthesis and structural systematics of four novel Uranium containing compounds, **1** $\text{UO}_2(\text{C}_7\text{H}_{10}\text{O}_4)$, **2** $(\text{UO}_2)_4(\text{O})_2(\text{H}_2\text{O})_2(\text{C}_7\text{H}_{10}\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2) \cdot (\text{H}_2\text{O})$, **3** $\text{UO}_2(\text{C}_7\text{H}_{10}\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)$, **4** $(\text{UO}_2)_2(\text{C}_7\text{H}_{10}\text{O}_4)_3 \cdot (\text{C}_{12}\text{H}_{14}\text{N}_2)$.

The effects of Vanadium on the Photocatalytic properties of ETS-10

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ETS-10 is a microporous titanasilicate discovered by Kuzniky (US Pat. 4853202) and is composed of octahedral chains of TiO_6 connected to tetrahedral SiO_4 . These chains then stack perpendicular to each other to form a 7.5 Å, three-dimensional channel structure with a stoichiometry of $(\text{Na}, \text{K})_2\text{TiSi}_5\text{O}_{13}$. These TiO_6 chains, which are insulated by the SiO_4 groups, form a “quantum wire” for the electron-hole pairs which are formed upon irradiation with UV photons.

Electron-hole pairs are created when the photons from UV light excite an electron from the valence band to the conduction band, with this difference in energy being the band gap. These electron-hole pairs are then free to travel down the chain to the ends or to exposed titanium where they can react with gaseous molecules adsorbed on the surface.

The band gap of ETS-10 is 4.03 eV which sits in the far-UV region and thus has a very low quantum efficiency (reactions/photons absorbed) with solar light, in which only approximately 10% of the solar spectrum is within this energy range. Substitution of the titaniums with various transition metals has shown the ability to lower the band gap of ETS-10 to the near visible region. Transition metals such as iron, chromium, and niobium have all been isomorphously substituted for titanium up to molar ratios of approximately 0.5 (metal/Ti), with all metals showing a decrease in band gap. Vanadium, however, is unique in that not only does it lower the band gap but it can completely substitute for the titanium to form a new structure called AM-6, which is identical to ETS-10 only with vanadium instead of titanium.

Detail studies have been performed on various samples ranging from 0 to 100% vanadium using an in-situ DRIFTS cell, UV-vis, XRD, N_2 adsorption, Raman, NEXAFS, and EPR, to determine the effects of vanadium on its photocatalytic properties. These studies have shown photocatalytic reactivity for the oxidation of ethylene up to the 500nm range along with interesting structural features which are presently being determined to explain this increase in photoreactivity.

Serendipitous Synthesis of Neodymium Oxalates

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Owing to the wealth of molybdenum oxide clusters and their potential to form inorganic frameworks with lanthanides, we have begun an investigation into these systems. Reactions of neodymium nitrate, molybdenum trioxide, and 1,4-diazabicyclo[2.2.2]octane (DABCO) under hydrothermal conditions were conducted in an attempt to synthesize templated lanthanide molybdates. Although no templated lanthanide molybdates have been synthesized as of yet, we herein report the unintended synthesis of neodymium oxalates through the reductive coupling of adventitious CO₂. An example of these neodymium oxalates is the 3 dimensional structure of compound **1** Nd₂(OH)₄(C₂O₄) in which the Nd³⁺ is 9 coordinate. The structure contains 2 dimensional Nd-O sheets connected through oxalate linkages to form the 3 dimensional structure. Nd₂(OH)₄(C₂O₄) crystallizes in a monoclinic space group P21/c with a=7.5392(8), b=7.2597(8), c=6.5038(7), β=97.311(2).

"Hydrogen sorption in nanoporous materials"

Paul M. Forster, Juergen Eckert, Jong-San Chang, Anthony K. Cheetham, and John Parise

The safe and efficient storage of hydrogen is often cited as the major obstacle to be overcome in developing hydrogen as a fuel for mobile applications. Physisorption of molecular hydrogen in nanoporous materials offers an attractive, although relatively undeveloped, method for storage. We have investigated hydrogen uptake in purely inorganic nickel phosphates (VSB-1 and VSB-5) as well as a new hybrid material, sodium nickel 5-sulfoisophthalate. Coordinatively unsaturated Ni(II) sites accessible within the pores are shown to be responsible for increasing the sorptive capacity and improving the temperature range at which sorption occurs. These materials demonstrate the importance of combining high overall surface areas with surfaces chemically active for H₂ uptake.