

NorthEast Corridor Zeolite Association
10th Annual Meeting*
December 7, 2007
Lynch Seminar Room, Department of Chemistry
University of Pennsylvania

www.necza.org

1. Program
2. Abstracts: Oral Presentations
3. Abstracts: Poster presentations

*The morning session is dedicated to the career of our friend, colleague and local host, Dr. David Olson.

Program Chair: Christopher Cahill (GWU)
Program Co-Chair: Haiming Liu (Arkema)

Program- NECZA 2007
December 7, 2007
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8:30-9:30	Registration/Posters (Coffee and Donuts)
9:30 - 9:35	Meeting opening/intro by Chair, Tribute session intro by Co-chair
9:35 -10:00	Tom Degnan: David. H. Olson: An Exemplary Zeolite Scientist and Scientific Mentor
10:00 - 10:10	Ray Gorte : Contributions of David Olson to Separation of Small Hydrocarbons by Adsorption
10:10 - 10:30	Haiming Liu: Measuring the n-Hexane Cracking Activity of Fe- and Al-based Acid Sites in H-ZSM-5
10:30 – 10:50	Break
10:50 - 11:30	Jing Li “Microporous Metal Organic Frameworks: A New Type of Adsorbent Materials for Gas Storage and Separation
11:30 - 12:00	David Olson: Metal Organic Frameworks Showing Hydrocarbon Adsorption Properties Commensurate With Their Pore Structure
12:00 - 1:00	Lunch
1:00-1:30	Posters
1:30-2:00	Travis Holman: Metal organometallic frameworks incorporating metallocyclopentadienes.
2:00-2:30	Wolfgang Hoeldrich : A New Process for ω -Lauro lactam via Beckmann-Rearrangement of Cyclododecanone Oxime in the Gas Phase
2:30-2:45	Break
2:45-3:00	Executive Meeting
3:00-3:30	Selected presentations from Posters
3:30-4:00	Michael Smith: The fractal character of pore surface in block-copolymer templated mesoporous silicates.
4:00	Adjourn and/or more poster visits.

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Oral Abstracts

David. H. Olson: An Exemplary Zeolite Scientist and Scientific Mentor

Thomas. F. Degnan¹

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Among the many contributions of David Olson to the field of zeolite science are his forays into structure-property relationships of large and medium pore zeolites, his early structural characterization of ZSM-5, a significant role in the development of several new aromatics processes and his seminal work on the mechanism of formation of MCM-41. This presentation traces the evolution of David Olson's work during his 33-year industrial career at Mobil's Paulsboro and Princeton Laboratories. David contributions were very important to the progress of zeolite science during a period of significant advances in the discovery of new materials and in understanding the catalytic chemistry behind how these materials functioned.

Contributions of David Olson to Separation of Small Hydrocarbons by Adsorption

Raymond J. Gorte
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Among the many contributions David Olson made to zeolite science is the separation of small hydrocarbons by selective adsorption. This talk will briefly review some of that work performed at the University of Pennsylvania.

Measuring the n-Hexane Cracking Activity of Fe- and Al-based Acid Sites in H-ZSM-5

Haiming Liu, Guenter Kuehl, Istvan Halasz, and David Olson*

The relative n-hexane cracking activity of Brønsted acid sites in H-[Al]-ZSM-5, H-[Fe]-ZSM-5, and H-[Al,Fe]-ZSM-5 zeolites has been investigated as a function of temperature, Cs-exchange level, and aging. Similar to H-[Al]-ZSM-5, acid sites in H-[Fe]-ZSM-5 are homogeneous. The Brønsted acid site reaction rate constant over H-[Fe]-ZSM-5 was found to be 15% of that of H-[Al]-ZSM-5. The acid sites in H-[Fe,Al]-ZSM-5 show inhomogeneity as expected for the coexistence of strong Al-based acid sites and weaker Fe-based acid sites. In Cs-exchanged materials, an equilibrium relationship has been found for the distribution of Cs between the two different Brønsted acid sites. Using equilibrium constants 6.6 and 75, the activity-decreasing effect of replacing protons with Cs⁺ ions can be described both for H-[Fe,Al]-ZSM-5 and for mildly steamed H-[Al]-ZSM-5, respectively. FTIR results also indicated preferred Cs poisoning on the more active acidic sites. The peaks representing the stronger and weaker acid sites in H-[Fe,Al]-ZSM-5 are not resolved in either FTIR or temperature programmed ammonia desorption. The aging of H-Fe sites appears to influence that of H-Al sites in H-[Fe,Al]-ZSM-5.

**Microporous Metal Organic Frameworks:
A New Type of Adsorbent Materials for Gas Storage and Separation**

JeongYong Lee, Kunhao Li, Long Pan, David H. Olson, Jing Li
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Microporous metal organic frameworks (MMOFs) are a subgroup of metal coordination polymers that have received intensive attention over the past several years. These materials contain micropores (pore diameter less than 20Å) and represent a new type of adsorbents. They exhibit a physisorption mechanism similar to other porous materials but possess numerous advantageous features. For example, the MMOFs incorporate a variety of different metals and ligands that can be functionalized, and thus, are likely to interact with adsorbed gas molecules more strongly than other types of adsorbents; The MMOFs contain perfectly ordered pores that allow gas adsorbates to access the interior space more effectively; The crystal structures and pore properties of the MMOFs can be systematically and deliberately tuned to achieve selectivity of gas adsorption. The pore characteristics and gas adsorption-desorption properties of selected MMOFs will be discussed, and their capacity and potential for applications in gas separation/storage will be assessed.

**Metal Organic Frameworks Showing Hydrocarbon Adsorption Properties
Commensurate with Their Pore Structure**

David Olson, Kunhao Li and Jing Li

Department of Chemistry and Chemical Biology,
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Piscataway, NJ 08854, USA

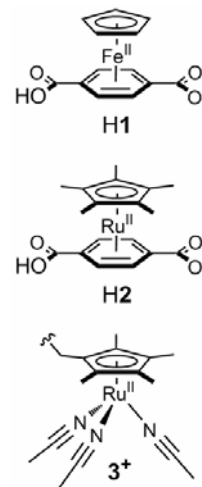
For zeolites, the observation of hydrocarbon adsorption commensurate with the adsorbents pore structure is relatively rare. p-Xylene adsorption in ZSM-5 is one of the early examples. Commensurate adsorption phenomena in metal organic framework materials is more common. Several examples will be discussed.

Metal organometallic frameworks incorporating metallocyclopentadienes.

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The use of organometallic ligands for the construction of framework materials remains relatively unexplored, but appropriately chosen organometallics have the obvious potential to impart useful functional properties (*e.g.* catalytic, sensory, magnetic, *etc.*) to this burgeoning class of materials. The synthesis and characterization of a series of metal-organometallic framework (MOMF) materials that incorporate metallocyclopentadiene based ligands will be presented. In particular, a variety of framework materials derived from ligands **1** and **2**, facially metalated $[(\eta^5\text{-Cp})\text{Fe}]^+$ and $[(\eta^5\text{-Cp}^*)\text{Ru}]^+$ derivatives of the popular terephthalate ligand, will be discussed. Appendage of the metallocyclopentadiene moieties to the terephthalate ligand effectively differentiates the two arene faces and gives rise to a series of polymorphic MOMFs with inclusion properties that are influenced by the channel structure. Some of the MOMFs derived from **1** and **2** exhibit permanent porosity and preliminary gas sorption properties of these materials will be discussed. Frameworks derived from **1** and **2** are first generation MOMFs with the ultimate aim being the construction of porous materials incorporating catalytically active $[(\eta^5\text{-Cp}^*)\text{Ru}(\text{CH}_3\text{CN})_3]^+$ (**3**⁺) moieties. Strategies and progress concerning these efforts will also be outlined.



A New Process for ω -Lauro lactam via Beckmann-Rearrangement of Cyclododecanone Oxime in the Gas Phase

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The polyamide Nylon-12 is prepared from ω -lauro lactam, which in turn is industrially produced by Beckmann rearrangement of cyclododecanone oxime in the liquid phase. This reaction is homogeneously catalysed, using fuming sulphuric acid as catalyst. Neutralisation of the reaction mixture with ammonia leads to the formation of large amounts of ammonium sulphate.

We present a new process for the rearrangement reaction. Various solid acid catalysts were investigated for their activity in the gas phase rearrangement reaction at temperatures ranging from 200 to 350 °C. Vapour phase behaviour of reactant, product and side product were investigated in detail to confirm that the reaction was heterogeneously catalysed at the chosen reaction conditions.

At a temperature of 320 °C, reduced pressure and a WHSV of 0.3 h⁻¹, acid treated [Al,B]-BEA zeolite led to nearly complete conversion and ω -lauro lactam selectivities of up to 98 %. After 8 h TOS a coke accumulation of 5 wt.% on the catalyst was observed. The catalyst was regenerated eight times at oxidative and non-oxidative conditions without any measurable loss of activity. In comparison to the conventional process, this reaction features a strongly decreased amount of side and by-products.

The fractal character of pore surface in block-copolymer templated mesoporous silicates

Michael A. Smith^{1,2} and Raul Lobo²

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2. Department of Chemical Engineering, University of Delaware

Traditional nitrogen physisorption analysis interprets the pore structure of triblock copolymer mesoporous silicates as a bimodal distribution of mesopores and smaller micropores. Samples of SBA-15, SBA-16 and SBA-11 were prepared and calcined between 300 and 900. Our analysis using a fractal FHH approach reveals an alternative interpretation: that the micropores are a manifestation of the fractal character silica PEO polymer interface. Calcination at higher temperatures is effectively an annealing process that smoothes the mesopore surface, such that by 900° C the surface dimension is ~ 2 . The fractal dimension provides a quantitative measure of micropore structure, an improvement of the traditional description of "micropore corona".

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Poster Abstracts

1. Nanoparticle Precursors and Phase Selectivity in Hydrothermal Synthesis of Zeolite

Beta

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A thorough understanding of the formation of crystalline materials from solution is crucial to predicting the final structure and properties of the resulting solids such as zeolites. One system that is particularly interesting is an aqueous solution containing tetraethyl orthosilicate (TEOS), tetraethylammonium hydroxide (TEAOH), aluminate, and boric acid that under hydrothermal conditions yields zeolite beta, a material with many industrial applications due to its unique microporous structure. In this system there is a critical aggregation concentration (cac) for silica above which the silicate species in solution aggregate into nanoparticles. This cac is sensitive to the concentration of boric acid in the solution due to its dissociation to form $B(OH)_4^-$. We investigated the intra and inter-particle structure of the nanoparticles in solution and found that aluminum has a major impact on these precursor species and that aluminum-containing nanoparticles aggregate into zeolite beta crystals (> 200 nm). The morphology, size, and crystallinity of zeolite beta evolves over time by a combination of Oswald ripening and aggregation of nanoparticles.

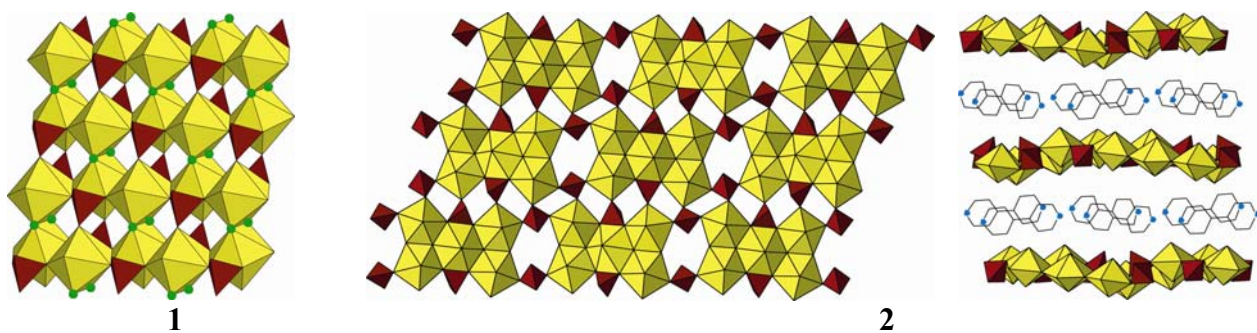
2. Hydrolysis of PF_6^- as a Route to Uranium Phosphates

Nicholas Deifel¹, Christopher L. Cahill¹, and K. Travis Holman²

¹ The George Washington University, Department of Chemistry, Washington, DC

² Georgetown University, Department of Chemistry, Washington, DC

Metal phosphates are an important class of framework materials due to their rich structural diversity which lends them to potential applications such as ion exchange and catalysis. These materials are traditionally synthesized via hydrothermal routes wherein phosphate anions are introduced via preformed alkali metal phosphates, phosphoric acid or as a complex oxide such as P_2O_5 . Alternatively, we herein report the hydrolysis of the hexafluorophosphate anion (PF_6^-) to yield phosphate bearing phases. We demonstrate this phenomena in the hydrothermal UO_2^{2+} system which is of interest due to potential applications such as soil remediation and reactive barrier systems for nuclear waste. The formation of framework structures in uranium systems generally involves non-uranyl polyhedra that facilitate linking in the third dimension owing to the nature of the uranyl ion. Using the aforementioned *in situ* formation of phosphate anions over the course of a synthesis (vs. the use of a pre-formed building unit) has resulted in several uranium phosphate phases and, notably, a new uranium phosphate fluoride (**1**) and a new uranium phosphate anionic sheet (**2**) with a novel pentameric secondary building unit. Efforts to produce these materials with traditional phosphate sources have been unsuccessful, suggesting a new mechanism to introduce PO_4^{3-} building units as well as capture phases otherwise unobtainable. The phosphate fluoride, UFPO_4 , was made by combining uranium(VI) oxynitrate with tetraethylammonium PF_6^- under hydrothermal conditions. The resulting crystal structure [FW= 2824.1, orthorhombic, *Cmca*, $a=6.9954(5)$ Å $b=9.0241(7)$ Å $c=12.4785(9)$ Å, $V= 787.73(1)$ Å³, $Z=1$] is densely packed and consists of eight coordinate U^{4+} cations linked through corner and edge sharing phosphate tetrahedra and bridging fluorine atoms. The pentamer, $[(\text{UO}_2)_5(\text{PO}_4)_4(\text{OH})_4] (\text{H}_{10}\text{C}_{10}\text{N}_2)_3$, was made by combining uranium(VI) oxynitrate with tetrabutylammonium PF_6^- and 4,4' dipyridyl under hydrothermal conditions. The resulting crystal structure [FW = 4306.86, triclinic, *P-1*, $a=13.203(8)$ Å $b=14.097(7)$ Å $c=14.341(6)$ Å, $\alpha=94.49(7)$ $\beta=99.23(8)$ $\gamma=114.12(3)$ $V= 2415.3(64)$ Å³, $Z=1$] is a layered uranium phosphate sheet with protonated 4,4' dipyridyl in the interlayer.



3. Direct In Situ Determination of the Polarization Dependence of Adsorption on Ferroelectric Surfaces

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The ability to manipulate the orientation of the dipoles in ferroelectric ceramics holds promise as a method to tailor the surface reactivity of these materials for specific applications. Since ferroelectric domains can be patterned at the nanoscale, ferroelectric domain specific surface chemistries may also provide a new method for fabrication of nano-scale devices. While studies over the last 50 years have suggested that the orientation of ferroelectric domains may affect the energetics of adsorption on ferroelectric oxides, definitive evidence is still lacking. The first unambiguous observations of differences in the energetics of adsorption on ferroelectric domains are presented here for adsorption of methanol, ethanol and carbon dioxide on barium titanate surfaces. Domain-dependent sticking coefficients are observed using temperature-programmed desorption and scanning surface potential microscopy indicating that the ferroelectric orientation alters the depth of the precursor physisorption well and surface chemical reactivity.

4. Microporous Metal Formates for Hydrogen Storage and Hydrocarbon Separations.

Kunhao Li, David H. Olson, JeongYong Lee, Wenhua Bi, Ke Wu, Jing Li*

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[M₃(HCOO)₆]·DMF (M = Mn, Co, Ni) were synthesized by solvothermal reactions of formic acid and the corresponding metal nitrates in *N,N*-dimethylformamide (DMF). Crystal structures of [Co₃(HCOO)₆]·DMF and [Mn₃(HCOO)₆]·DMF were determined by single-crystal X-ray diffraction methods. The metal connectivity leads to a diamondoid topology. The structure contains zigzag channels of effective pore size of ~5-6Å along the *b* axis where guest dimethylformamide molecules reside. The channels were further connected by small apertures (~1.4Å × 5.3Å) along [101] directions.

The materials were confirmed by TGA-PXRD analysis to be thermally stable after removal of the DMF guest molecules. Based on nitrogen adsorption data, the surface area of [Co₃(HCOO)₆] were calculated to be 354 m²/g (Langmuir) and 304 m²/g (Bruner-Emmet-Teller), respectively. The estimated pore size is ~5.0 Å from H-K pore size distribution. [Co₃(HCOO)₆] takes up 0.75 wt% hydrogen at 77K and 1 atm (0.65 wt% for 87K, 1 atm). At elevated pressure and temperature, the hydrogen uptake is significantly lower with a maximum hydrogen uptake of 0.25 wt% at 70 bar and room temperature.

Equilibrium hydrocarbon adsorption measurements also revealed that [Co₃(HCOO)₆] has the potential of separating hydrocarbons via processes such as Pressure Swing Adsorption (PSA). In this presentation, supercritical CO₂ extraction of the DMF guest molecules as a more gentle activation process will also be discussed.

5. Dehydrogenation of Brønsted Acid Sites and Hydroxyl Nest Groups in Zeolites

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The acidity and activity of zeolites as catalysts is due to the presence of Brønsted acid sites (Si-OH-Al) in the framework. The OH vibration associated with this acid site can be observed in the IR spectra of dehydrated samples in the 3630-3660 cm^{-1} region. Previously, it has been shown that upon heating to temperatures in excess of 873K, the intensity of these OH vibrations decreases gradually until it completely disappears. This phenomenon has been called dehydroxylation and has been thought to be the product of the dehydration of adjacent acid sites.

A hydroxyl nest is a common defect in zeolite frameworks where a tetrahedral atom (T=Si, Al, etc.) is missing from the structure. In the absence of the T-atom a cluster of four silanol groups are left forming medium-strength hydrogen bonds with each other. Hydroxyl nests can be formed in aluminosilicate or borosilicate zeolite materials by leaching or steaming at high temperatures. Silicalite-1 synthesized in basic media is well known for containing large numbers of silanol nests. These silanol groups in silicalite-1 have been characterized by infrared spectroscopy. The OH region of the spectra (3760-3300 cm^{-1}) shows two characteristic peaks that have been assigned to isolated silanol groups in the exterior and interior of the zeolite (3760-3720 cm^{-1}), and to hydrogen-bonded groups of silanol units that give a much broader signal centered at about 3400 cm^{-1} . Upon heating to temperatures exceeding 873K, these bands decrease in intensity, and a new triplet is formed in the 911-896 cm^{-1} region. Previously, the disappearance of these signals has been attributed to dehydration of the silanol groups. Using temperature-programmed-desorption (TPD), we show that the product of the thermally treated H-zeolites and the dehydroxylation of hydroxyl nests in silicalite-1 is hydrogen and not water.

6. Acid Site effects on the photocatalytic properties of ETS-10 & ETVS-10s toward the reduction of VOCs

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We have investigated ETS-10 and vanadium-incorporated ETS-10 as photocatalysts for the reduction of volatile organic components (VOCs) since their unique structure may help elucidate the material and surface properties needed to overcome some of the disadvantages of traditional semiconductors like anatase. ETS-10 is a microporous titanasilicate¹ composed of octahedral chains of TiO₆ embedded in a tetrahedral SiO₄ framework. These chains stack perpendicular to each other to form a 7.5 Å, three-dimensional channel structure with an ideal stoichiometry of (Na, K)₂TiSi₅O₁₃. Vanadium has been shown to substitute for the titanium along the chain forming (V/(V+Ti))ETVS-10s and can completely replace titanium forming an analogous structure to ETS-10, called AM-6.^{2,3} This incorporation of vanadium has also shown visible photocatalytic activity that has been explained experimentally and theoretically.^{4,5}

These chains of TiO₂ behave as 1D semi-conducting wires which are insulated by the SiO₂ framework. Therefore chain termination sites on the surface of the crystal or at defects along the chain play a crucial role in the electron-hole transfer from the chain to adsorbed organic molecules. Previous work has shown that ion exchange leads to an increase in chain termination for ETS-10 samples along with different photocatalytic properties.^{6,7} In this research we will determine the effects of acid site formation through NH₄ ion exchange in an attempt to maximize the photocatalytic reactivity of the ETVS-10 samples for VOCs decomposition.

Materials were characterized using X-ray diffraction (XRD), N₂ adsorption, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), UV/vis spectroscopy, and Raman spectroscopy. A Diffuse Reflectance Infrared Fourier Transform Spectrometer (DRIFTS) coupled with a UV-lamp has been implemented to investigate the formation of electron-hole pairs upon excitation of ETS-10 and ETVS-10s.

References

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7. Binding of NO₂ in BaY Faujasite Catalysts: *In situ* Time-resolved X-ray Diffraction Studies

Jonathan C Hanson¹, XianQin Wang², Ja Hun Kwak², Jose Rodriguez¹, Charles H.F. Peden², Janos Szanyi^{2*}

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²*Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA,*

Introduction

The reduction of harmful NO_x species emitted by internal combustion engines, factories and power plants has been a daunting task for controlling environmental pollution[1]. Zeolites possess unique features as gas adsorbents, gas separators, and catalysts[2]. BaY faujasite zeolites have been reported to be very promising catalysts for the non-thermal plasma-assisted catalytic reduction of NO_x species[3-5]. In order to understand these processes we have determined the structures of the NO_x species and the Barium cations in the zeolite under a wide range of conditions using *in situ* time-resolved X-ray diffraction.[6]

Materials and Methods

A BaY faujasite zeolite with a Si/Al ratio of ~2.6 was prepared from a NaY zeolite obtained from Zeolyst International (CBV 100) following procedures described elsewhere[3]. Time-resolved X-ray diffraction experiments on the dehydration and NO₂ adsorption/desorption on these samples were carried out at beamline X7B ($\lambda = 0.922 \text{ \AA}$), National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, with a MAR345 image plate detector.

The structures were determined and refined with powder diffraction analysis tools.[7]

Results and Discussion

Figure 1 shows the series of powder diffraction patterns obtained during adsorption and desorption of NO₂. The strongest line(111) provides an indication of the contents of the zeolite supercage(Figure 2). High values are indicative of nearly empty while low values suggest nearly full cages.

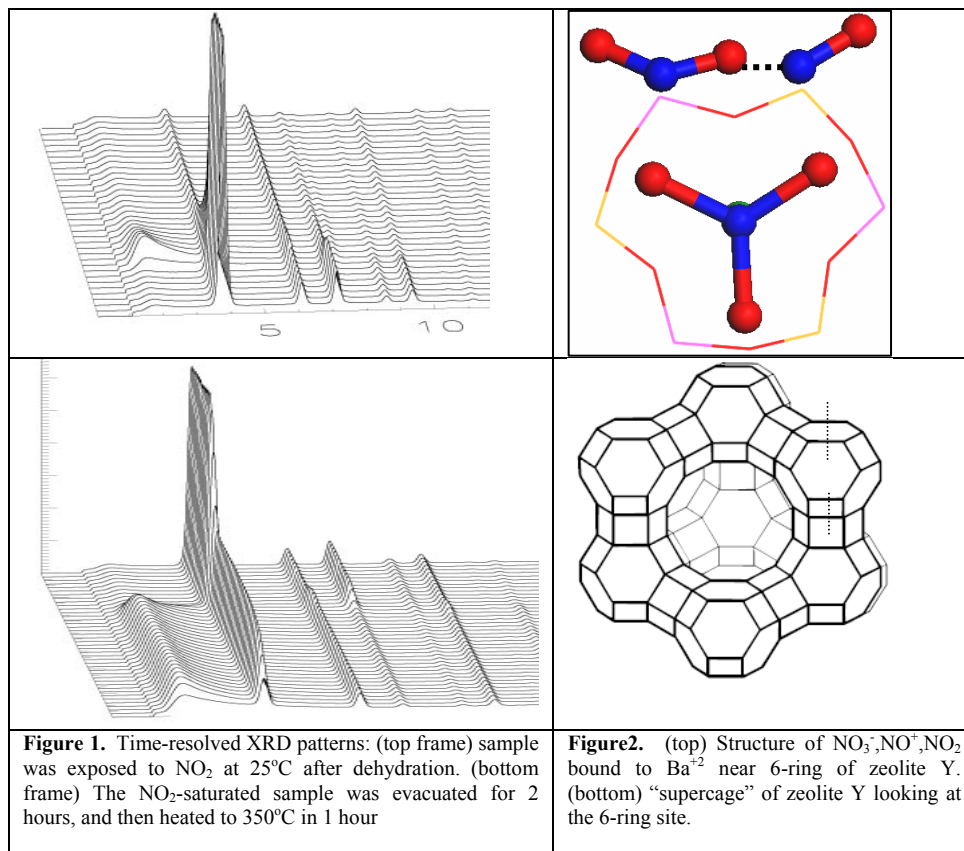
Consistent with the reported FT-IR results, three different ionic NO_x species (NO⁺, NO⁺-NO₂, and NO₃⁻) were observed in the NO₂-dosed, dehydrated BaY zeolite. The stabilities of the NO_x species are attributed to the strength of the interactions between the NO_x, the cations, and the framework.

Likewise, the population of Ba cations at different locations strongly depends on the amount of NO_x species; and Ba cations migrated between different locations as a consequence of NO₂ adsorption/desorption. Figure 2 shows the local geometry of the NO_x species in the vicinity of the Ba⁺² ions bound to the six membered rings in the supercage.

Significance

This work provided a direct observation of Ba cation migration to the different locations in the zeolite to accommodate the binding of the NO_x molecules. This unique feature plays a pivotal role in the catalytic performance of the BaY zeolite.

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