

NECZA 2011 PROGRAM

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**The 15th Meeting of the
North-East Corridor Zeolite Association**

Friday, December 9, 2011

**Lynch Seminar Room,
Department of Chemistry
University of Pennsylvania**

NECZA Organizing Committee

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Acknowledgments

The organizing committee is grateful for the following contributions that help make this meeting possible



The Lynch Seminar Room and Facilities



Refreshments



Lunch Venue



Program Publication

Program

8:00 – 8:50	Registration, Refreshment, Poster set-up
8:50 – 9:00	Meeting opening and Introduction
9:00 – 9:40	<u>Jack Mc Williams</u> (Mobil Oil, retired) <i>Mobil Zeolite Catalyst Development –The Early Years</i>
9:40 – 10:10	<u>Wolfgang Hölderich</u> (Aachen University) <i>New Non-Zeolitic Mesoporous Nb-based Catalysts for the Gas Phase Beckmann Rearrangement</i>
10:10 – 10:40	Break, Posters
10:40 – 11:20	<u>Debra Rolison</u> (Naval Research Laboratory) <i>Ultraporous 3D nanoarchitectures en route to energy- and size-scalable power</i>
11:20 – 12:00	<u>Yushan Yan</u> (University of Delaware) <i>Zeolite Thin Films: From Computer Chips to Space Station</i>
12:00 – 1:20	Lunch, Posters
1:20 – 2:00	<u>Guang Cao</u> (Exxon Mobil) <i>Synthesis of Molecular Sieves with Chabazite Structure Type</i>
2:00 – 2:40	<u>Scott Babitiz</u> (Rive Technology, Inc.) <i>Controlled Introduction of Zeolite Mesoporosity for Step Out FCC Catalyst Performance</i>
2:40 – 3:05	Break, Posters
3:05 – 3:20	Business Meeting
3:20 – 3:35	Selected poster presentation 1
3:35 – 3:50	Selected poster presentation 2
3:50 – 4:20	<u>Tim Golden</u> (Air Products and Chemicals) <i>Xe Recovery and Purification using Ag-exchanged Zeolites</i>
4:20 – 5:00	<u>Hai-Ying Chen</u> (Johnson Matthey) <i>Application of Molecular Sieves for Diesel NO_x Emission Control</i>
5:00	Close of meeting

Zeolite Catalysis at Mobil – the early years

Jack McWilliams

Consultant, 155 Erica Ct, Swedesboro, NJ 08085

Many are aware of Mobil's incredible successes in zeolite catalysis, especially notable in the 1970's through the 1980's with a steady string of new zeolites and other molecular sieves, and associated processes that came to dominate in their fields. One dramatic example is the development and commercialization of the world's first Gas to Gasoline facility in New Zealand in 1985.

In this narrative we look back at the beginnings of Mobil's interest in catalysis and its applications to the business of refining and petrochemical manufacture. We see that from the earliest days, Mobil was driven to extract more yield or better quality of gasoline and other refined products, and was disposed to do this through improved processes and use of better catalytic materials. In hindsight we can see that some strategic decisions along the way were critical, especially creating the ability to self-manufacture catalysts and catalytic materials. Success in catalytic cracking led to a concerted effort to look into further application of zeolites and to the possibility of expanding beyond the then known stable of natural and synthetic materials. This in turn led ultimately to discovery and development of ZSM-5 and other high silica zeolites and novel crystalline materials.

A talent laden staff located in three laboratories that were physically separated – but not too far to inhibit collaboration, helped create an environment that promoted novel synthesis, modification methods and application of new materials to existing and new processes.

Speaker Biography

J.P. "Jack" McWilliams received his BS in Chemical Engineering from New Jersey Institute of Technology, and MS and PhD degrees also in Chemical Engineering from the University of Pennsylvania, working under A. Norman Hixson. He joined Mobil Research and Development Corp. at Paulsboro, NJ in 1972. Initially assigned to Frank Dwyer's group, he quickly got involved with zeolite synthesis and processing and was a member of the team that converted a Mobil Chemical semiworks facility from demonstration status to full production capability for a wide variety of proprietary zeolite based catalyst types, most notably those utilizing ZSM-5. In addition to continuing work in the synthesis and catalyst formulation areas, he played a major role in the development of several zeolite based chemical processes such as xylene isomerization, toluene disproportionation, alkylation to ethylbenzene, p-ethyltoluene and others.

He continued his association with zeolite catalyst technology transfer from lab to plant by serving as technical liaison to and later a Director of Mobil Catalyst Corporation of Japan for nearly 15 years. He also spearheaded Mobil's effort in environmental applications of zeolite catalyst technology for control of SOx and NOx emissions from stationary and vehicle sources.

Jack has 55 US patents, including one that earned the 2004 Thomas Alva Edison Patent Award from the Research and Development Council of New Jersey – US 4,992,606, “Process for Preparing Short Chain Alkyl Aromatic Compounds”.

Notes

New Non-Zeolitic Mesoporous Nb Based Catalysts for the Gas Phase Beckman Rearrangement

Wolfgang F. Hoelderich* and Mettu Anilkumar

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The precursor for nylon-6 fibres and engineering plastics is ϵ -caprolactam and for the polyamide Nylon-12 ω -laurolactam. The disadvantages of the classical processes for these two important intermediates are the use of fuming sulphuric acid and the formation of $(\text{NH}_4)_2\text{SO}_4$ due to neutralisation of the reaction mixture with ammonia in the oximation of the ketones as well as the Beckmann rearrangement of the oximes to the lactams in the liquid phase. Therefore there is a strong interest in „clean up“ the classical process, succeeding the production of cyclohexanol via hydration of e.g. cyclohexene over HZSM-5 catalyst and for the ammoximation of cyclohexanone to cyclohexanone oxime using NH_3 and H_2O_2 in the presence of TS-1, and finally for a „clean“ Beckmann rearrangement over a heterogeneous catalyst.

At our institute a specially modified [B]-MFI catalyst was developed for the Beckmann rearrangement in the gas phase [1,2]. The characterisation of such a catalyst produced evidence that structural defects with a mixture of extremely weakly acidic vicinal silanol groups and silanol nests are the active sites for this rearrangement. Sumitomo Chemicals Co has carried out a lot of gas phase investigations in the presence of silicalite zeolites [3,4] Currently, they have commercialized such a process and are producing 60,000 t/a of CL by this method [2,4].

This knowledge was transferred to the Beckmann rearrangement of cyclododecanone oxime to ω -laurolactam. surprisingly, also success-fully managed in the gas phase over [Al,B]-BEA zeolite with a mixture of extremely weakly acidic vicinal silanol groups and silanol nests as active sites [5]. Up to date, only zeolitic materials have been playing a pivotal role in the gas phase Beckmann rearrangement.

Surprisingly, we found non zeolitic catalysts showing extremely good catalytic performance. First attempts have been carried out over mesoporous materials such as MCM-41 etc. Al MCM-41 did not show any activity in contrast to materials modified with Nb. Such catalysts (Si/Nb-16, 32, 64 and 128) have been synthesized by hydrothermal method and well characterized by various physical techniques. E.g. catalyst acidity was measured by NH_3 -TPD and pyridine FT-IR techniques indicating weakly acidic silanol groups. The catalytic tests in a fixed bed reactor show an optimum at 300 °C resulting in 100% conversion and 95 %. The effect of Si/Nb ratio, temperature, space velocity, etc., on catalyst activity, product selectivity and catalyst stability will be discussed. The regeneration study was conducted in air or in non-oxidative gas such as N_2 for five or even more cycles.

Even more surprising, against all predictions and completely unexpected is that just Nb doped silica results in similar catalytic performance as the zeolitic catalysts. Such a simple catalyst is much cheaper than the commercially used zeolitic catalysts as well as the Nb MCM-41 systems. This non-zeolitic material $\text{Nb}_2\text{O}_5/\text{SiO}_2$ is very active and selective for the gas phase Beckmann rearrangements in a fixed bed reactor. The acidity of 3 wt% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ was measured by ammonia TPD and pyridine FT-IR spectroscopy methods. The main reason for the excellent performance of the $\text{Nb}_2\text{O}_5/\text{SiO}_2$ sample is due to weakly acidic vicinal silanol groups and nest silanols with negligible Brønsted acid sites. At 300-325 °C in ethanol as solvent, high yields of caprolactam and lower deactivation rates are achieved with selectivity

up to 98.4%. Successful catalyst regeneration is possible in air as well as non oxidative medium such as N₂. In this presentation more details of these interesting findings will be given and explored.

References

1. G. Dahlhoff and W.F.Hölderich, Chemical Innovation, ACS, 2 (2001) 29-40
2. G. Dahlhoff and W.F. Hölderich, Catal. Rev.-Sci. Eng.,43,4 (2001) 381-441
3. H. Ichihashi, M. Kitamura, Cat. Today 73 (2002) 23.
4. Y. Izumi et al. Bull. Chem. Soc. Jpn 80 (2007) 1280.
5. W. Eickelberg and W.F. Hölderich, 14th ICC, 2008 Seoul, Korea, p. 108

Speaker Biography

Wolfgang received his doctorate degree from Institute for Inorganic Chemistry of the University of Karlsruhe in 1975. After a postdoctoral experience, Wolfgang joined BASF AG. During his industrial career he had charge of several leading positions in research of heterogeneous catalysis. He was a member and representative of research in the 4 person steering committee of the BASF catalyst business profit center. Since 1992 Wolfgang has been a University professor and Director of the Department of Chemical Technology and Heterogeneous Catalysis at the University of Technology RWTH-Aachen. Wolfgang's main research areas include: heterogeneously catalysed synthesis of fine and intermediate chemicals such as caprolactam etc. as well as the use of renewable feeds as starting material. Acid / base catalysis, in particular zeolites as catalysts as well as oxidation catalysis are fields of interest.

He has been awarded more than 230 patents and has published over 300 papers on heterogeneous catalysis; co-editor of 4 books as well as two special issues on industrial catalysis for Applied Catalysis. He is a member of several editorial boards and international advisory boards. He has received many awards and recognitions; among them the E.V. Murphree Award of the American Chemical Society for Industrial Chemistry and Chemical Engineering sponsored by ExxonMobil 2007.

Notes

Ultraporous 3D nanoarchitectures en route to energy- and size-scalable power

Debra R. Rolison, J. W. Long, M. B. Sassin, C. N. Chervin, and NRL's
Nanoarchitectural Firm

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When multifunction and molecular transport paths are critical, as they are in rate-critical applications such as catalysis, energy storage and conversion, sensing, and fabrication, the challenge is to move beyond the creation of a functional nanoscale object or feature. High performance and large-scale construction require architectural design [1,2,3]. We currently rely on carbon aerogel-like nanofoam papers as our core scaffold because such desirable properties as high specific surface area, electronic conductivity, and through-connected pore structure make them ideal—and practical—plug-and-play electrode substrates for high-rate electrochemical energy storage devices thereby bringing architectural design on the nanoscale to the macroscale [4]. Achieving this blend of desirable properties requires an optimal balance of critical architectural features: (1) open, three-dimensionally interconnected macropores sized at 100–300-nm, which is a difficult-to-obtain size range in porous carbons, and (2) pore walls of a size that reduce dead weight and volume (preferably ~20-nm wall thickness when the void is sized at 100–300 nm), while retaining mechanical strength and flexibility without compromising electronic conductivity (preferably greater than 20 S cm⁻¹). Our work with carbon nanofoam papers revisits what was known about fabric- and paper-supported aerogels to create a new, low-cost, and scalable nanocomposite that exists within this “Goldilocks zone” of desirable properties. These carbon nanofoams have catalyzed breakthroughs in our work with asymmetric electrochemical capacitors, air cathodes for metal–air batteries, 3-D batteries, and semifuel cells. We can “paint” the walls of a conductive nanoarchitecture with conformal nanoscopic coatings of redox-active polymers or oxides in order to produce high performance electrochemical capacitors [5–7], air cathodes, or lithium-ion insertion electrodes. An architectural viewpoint provides a powerful metaphor to guide the chemist and materials scientist in the design of aerogel-like nanoarchitectures and in their physical and chemical transformation into multifunctional objects that yield high performance.

References

- [1] D. R. Rolison, *Science* **299** (2003) 1698–1701.
- [2] D. R. Rolison, J. W. Long, *Acct. Chem. Res.* **40** (2007) 854–862.
- [3] D. R. Rolison, J. W. Long, J. C. Lytle, A. E. Fischer, C. P. Rhodes, T. M. McEvoy, M. E. Bourg, and A. M. Lubers, *Chem. Soc. Rev.* **38** (2009) 226–252.
- [4] J. C. Lytle, J. M. Wallace, M. B. Sassin, A. J. Barrow, J. W. Long, J. L. Dysart, C. H. Renninger, M. P. Saunders, N. L. Brandell, D. R. Rolison, *Energy Environ. Sci.* **4** (2011) 1913–1925.
- [5] J. W. Long, B. M. Dening, T. M. McEvoy, D. R. Rolison, *J. Non-Cryst. Solids.* **350** (2004) 97–106.
- [6] A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud, J. W. Long, *Nano Lett.* **7** (2007) 281–286.
- [7] M. B. Sassin, A. N. Mansour, K. A. Pettigrew, D. R. Rolison, J. W. Long, *ACS Nano* **4** (2010) 4505–4514.

Speaker Biography

Debra R. Rolison heads the Advanced Electrochemical Materials section at the NRL (also known as the U.S. Navy's nanoarchitectural firm), where her research focuses on multifunctional nanoarchitectures for rate-critical applications, such as catalysis, energy storage and conversion, and sensors. She received a Ph.D. in Chemistry (UNC-CH, 1980) and is a Fellow of the American Association for the Advancement of Science, the Association for Women in Science, the Materials Research Society (inaugural class), and the American Chemical Society. Rolison received the 2011 ACS Award in the Chemistry of Materials and the 2012 C. N. Reilley Award of the Society for Electroanalytical Chemistry. She is also an Adjunct Professor of Chemistry at the University of Utah (2000–present). When not otherwise bringing the importance of order and disorder to materials chemistry, Rolison writes and lectures widely on issues affecting women in science, including proposing Title IX assessments of science and engineering departments. She is the author of over 200 articles and holds 24 patents.

Notes

Zeolite Thin Films: From Computer Chips to Space Station

Yushan Yan

*Distinguished Engineering Professor
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Zeolites are a class of inorganic crystalline materials with uniform and molecular-sized pores. Thus far, zeolite materials have been commercially used as shape-selective catalysts and molecular-sieving gas separation/purification media, and for both applications, they are used in powder composite forms such as pellets and granules. Zeolite thin films have been researched for the past twenty years primarily driven by their potential use as separation membranes and membrane reactors. In this talk, I will discuss our effort on the design and synthesis of zeolite thin films and coatings for a number of technologically and economically significant applications that have not been considered before, including low dielectric constant (low-k) films for future generation computer chips, corrosion and wear resistant coatings for aerospace alloys, and hydrophilic and antimicrobial coatings for water separation in space station. Our work of using zeolite as wear resistant coatings will also be discussed.

Speaker Biography

Professor Yushan Yan received his B. S. in Chemical Physics from the University of Science and Technology of China in 1988, and his Ph.D. in Chemical Engineering from the California Institute of Technology in 1997. He studied heterogeneous catalysis at the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences from 1988 to 1992. He worked for AlliedSignal Inc. as Senior Staff Engineer and Project Leader from 1996 to 1998 before joining the University of California at Riverside (UCR) as Assistant Professor. He was promoted to Associate Professor in 2002 and Professor in 2005. In 2006, he was selected as one of the five inaugural University Scholars at UCR. He was appointed Department Chair in 2008 and given the title of Presidential Chair in 2010. He moved to the University of Delaware in September 2011. His research focuses on zeolite thin films for semiconductors and aerospace applications and new materials for fuel cells, energy storage and solar hydrogen generation. He received the Donald Breck Award in 2010 from the International Zeolite Association for his zeolite thin film research, and was awarded one of the 37 inaugural-round ARPA-E projects in 2009 from the Department of Energy for his hydroxide exchange membrane work. He is a Fellow of the American Association for the Advancement of Science. He has been an inventor of a large number of issued or pending patents. Several of his patents were licensed to form startup companies, e.g., NanoH₂O, Full Cycle Energy, Zeolite Solution Materials (ZSM), and OH-Energy. His research work has been widely cited in the scientific community (h-index = 41 and average citation/paper = 40 and also extensively covered by technical magazines and media including *New Scientist*, *Business Week*, *C&EN News*, *Materials Today*, *China Press* (newspaper) and *Chinese Daily News* (newspaper), CNBC, CNN.com, KABC, VOA, and many other print, video and radio media.

Notes

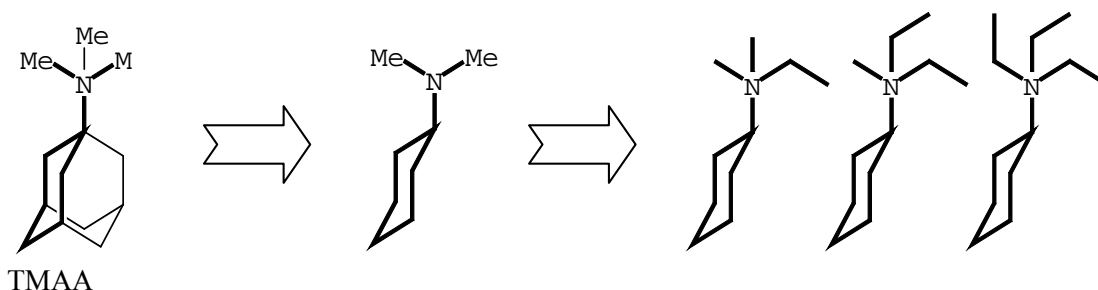
Synthesis of Molecular Sieves with Chabazite Structure Type

Guang Cao

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Zeolitic and zeotype materials having the chabazite framework type (CHA) have recently received much commercial interest. In addition to the commercialization of methanol to olefins (MTO) technology in China last year, for which the active catalyst is the SAPO-CHA (short for silicoaluminophosphate having the CHA framework), Cu modified chabazite has also been found to show superb performance for NO_x abatement. , , ,

We have developed synthesis methods for the preparation of both SAPO-CHA (including AlPO₄-CHA) and chabazite (aluminosilicate) materials with or without using fluoride. We designed a series of organic templates based on selective preservation of the molecular moieties of the well-known organic template for the CHA structure, trimethyladamantammonium (TMAA). The organic templates we derived are not only effective but also low cost. Rationales for the template design will be detailed and examples for the synthesis of SAPO-CHA, AlPO₄-CHA, and chabazite having a wide range of Si/Al ratios will be provided.



¹ WO/2008/132452 A2, 2008

¹ U.S. Patent 7,601,662, 2009

¹ R. Lobo, et al., *J. Phys. Chem. C*, 2010, 114 (3), pp 1633–1640

¹ C. H. F. Peden, et al., *J. Catal.*, 2010, 275, 187-190

Speaker Biography

Guang Cao received his BS degree in chemistry from Jilin University in Changchun, China, and his PhD degree in chemistry from the University of Texas at Austin. He has been with Exxon (now ExxonMobil) Research and Engineering Company since 1992. He is currently the Section Head of the Catalytic Systems Section at the Corporate Strategic Research Labs of ExxonMobil in Annandale, New

Jersey. He is a member of the US National Committee for the IUPAC. He is also a member of the International Activities Committee of the American Chemical Society and a member of the ACS's Diversity and Inclusion Advisory Board. He has about 40 issued US patents.

Notes

Controlled Introduction of Zeolite Mesoporosity for Step-Out FCC Catalyst Performance

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A new surfactant-based technique has been developed that allows for the controlled introduction of mesoporosity into zeolite crystals, while maintaining the chemical and physical properties of the zeolite (microporosity, crystallinity, and acidity). Of particular interest is that the mesoporosity created with this technique: 1) does not result in poor zeolite stability, and 2) survives hydrothermal deactivation of the zeolite. While this technique has been successfully applied to several different zeolite structures (FAU, MFI, MOR) of varying Si/Al ratios, our immediate interest is in applying this technology to make mesoporous Y zeolite for FCC catalysts. Mesoporous Y zeolite can be used to make FCC catalysts that will enable refiners to increase throughput and profitability without capital investment. During the presentation, how Rive™ zeolite technology improves FCC catalyst performance and the results from our first refinery trial will be discussed.

Rive™ zeolite technology was invented at MIT in the early 2000's by Garcia-Martinez and Ying. It modifies the zeolite structure by creating a network of controllable/tuneable sized (2 - 6 nm.) mesoporous "Molecular Highways" throughout the zeolite crystals. These "Molecular Highways" admit and pre-crack even the largest feed molecules, while also channeling product gasoline and diesel molecules safely out of the zeolite. Further development of this technology has improved the hydrothermal stability of these Rived mesopores. This provides a unique opportunity to apply this technology to FCC where catalysts are subjected to very harsh hydrothermal conditions.

Pilot-scale ACE and MAT tests to evaluate the performance of Rived zeolites "neat" and in FCC catalysts for cracking oil feeds have demonstrated both improved selectivities to transportation fuels (gasoline, diesel) and a reduction of undesirable reaction products (bottoms and coke). Lump kinetic modeling of these performance results corroborate that Rived mesopores improve the diffusion of transportation fuels out of the zeolite pore structure before they are able to undergo undesirable secondary cracking.

The first refinery scale trial using Rived zeolites in a commercial FCC catalyst was recently completed. These results have demonstrated: the ability to scale up Rive zeolite manufacturing, the viability of FCC catalysts containing Rive zeolites as a drop in replacement for conventional FCC catalysts, and confirmation that this technology can deliver improved FCC unit performance in refineries.

Ying, Jackie Y and Garcia-Martinez, Javier, US Patent 7,589,041, Sept. 15, 2009

Speaker Biography

Scott Babitz is Manager of Research and Development with Rive Technologies in Monmouth Junction, NJ. Scott received his PhD in Chemical Engineering under the guidance of Harold Kung at Northwestern University, where he investigated enhanced catalytic cracking in steam de-aluminated zeolites. After completing his PhD in 1998, he joined Akzo-Nobel / Albermarle Catalysts, Pasadena TX, where he worked on manufacturing process development and technology transfer for FCC and zeolite catalysts. Scott left Texas in 2008 to join start-up Rive Technologies new R&D facility and pilot plant in the heart of New Jersey's Einstein's Alley in Monmouth Junction.

Notes

Xe Recovery and Purification using Ag-exchanged Zeolites

T.C Golden, T.S. Farris, and J.M. Occhialini

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Krypton and xenon are produced by concentration from air. Since their concentrations in air are so small (krypton 1.14 ppmv and xenon 0.086 ppmv) large volumes of air must be processed to produce reasonable quantities of krypton and xenon. Once the rare gases are initially captured and purified, reuse of the gases in its various applications is also of interest. For instance, the recycling of xenon from the air of operating rooms, where it has been used as an anesthetic, may provide a method to reduce the amount of new xenon needed from large air separation plants.

In practice, krypton and xenon are reclaimed from the liquid oxygen portion of a cryogenic air distillation process. Since the volatilities of krypton and xenon are lower than that of oxygen, krypton and xenon concentrate in the liquid oxygen sump in a conventional air separation unit. This concentrated stream of krypton and xenon can be further concentrated by stripping some oxygen in a distillation column to produce “raw” krypton and xenon. However, this “raw” stream contains other air impurities less volatile than oxygen, which have to be removed before pure krypton or xenon can be produced. In particular, the “raw” stream contains carbon dioxide and nitrous oxide, both of which have low solubility in liquid oxygen and tend to freeze out during the concentration of krypton and xenon, resulting in operational problems. In addition, various hydrocarbons (C₁ to C₃) present in the liquid oxygen can concentrate during the stripping of oxygen to produce a liquid oxygen stream with dangerously high levels of hydrocarbons.

A new xenon recovery process has been developed, enabled by a proprietary adsorbent innovation. The AgLiLSX adsorbent, originally developed for high-purity oxygen production, significantly surpasses the best-quoted literature capacity for xenon adsorption. This performance has helped eliminate 75% of the unit operations found in current commercial xenon processes. The process has been successfully scaled up from a small-scale lab unit to a commercial unit capable of producing in excess of 300,000 liters per year of xenon. Due to its inherent simplicity this new process sets a new, worldwide benchmark as the low-cost system for producing xenon.

Speaker's Biography

Tim Golden is a Principal Research Associate at Air Products and Chemicals, Inc. After gaining a B.S. degree in Chemistry at Wilkes College in 1978, he enrolled in the Fuel Science program at Penn State and earned his Ph.D in 1981. After a stint as a post-doc, Tim joined Air Products and Chemicals, Inc. in 1983. Since that time, Tim has worked in R&D in the area of adsorptive separation and purification of gases. He has worked on the development of various adsorption-based separation processes including landfill gas purification, non-cryogenic O₂, N₂ and CO production, pressure swing adsorption for the production of hydrogen, improved air pre-purification technologies for cryogenic air and syn gas separation, Xe recovery and recycle systems, recovery of monomers from polyolefin plants and purification of NF₃.

Tim is a co-inventor on 65 US patents and author of 42 papers and book chapters. He previously served on the editorial boards of the Journal of Porous Materials and Industrial & Engineering Chemistry Research. Tim is married with two children and enjoys playing soccer, traveling and pubs.

Notes

Application of molecular sieves for diesel NO_x emission control

Hai-Ying Chen

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Diesel engines utilize fuel more efficiently than gasoline engines, which allow a significant reduction of CO₂ emission from diesel engine powered vehicles. The reduction of NO_x emission in diesel exhaust, however, has been a major challenge since it requires to selectively convert low concentration of NO_x pollutants (~100ppm) in the presence of large excess of O₂ (~10%). Many technologies have been investigated and several of them have been commercialized. The selective catalytic reduction (SCR) of NO_x with NH₃ is now considered as one prime path. Molecular sieve supported transition metal catalysts are of particular interest for mobile-source applications because of their high intrinsic activity and their capability of withstanding periodic high temperature excursions.

One type of the traditional catalysts are Cu exchanged medium pore molecular sieves (10-ring, such as ZSM-5) or large pore molecular sieves (12-ring, such as beta). Long-term thermal stability evaluation of this type of catalysts revealed that the catalysts severely deactivated because of the loss of acidity of the molecular sieves and the negative interaction between the exchanged Cu ions and the molecular sieve framework structure. In addition, those catalysts suffered from hydrocarbon poisoning when constantly operated at low temperatures. A series of small pore molecular sieve (8-ring) supported Cu catalysts were recently developed. These newly developed Cu SCR catalysts exhibit significantly improved hydrothermal stability and hydrocarbon tolerance and have been successfully commercialized.

Speaker's Biography

Dr. Hai-Ying Chen is a Product Development Manger at Johnson Matthey Inc., Emission Control Technologies, in Wayne, Pennsylvania. He received his Ph. D. degree in Chemistry from Fudan University (Shanghai, China) in 1994, and conducted postdoctoral research work at Northwestern University (Evanston, IL, USA) from 1996 to 2000. Since he joined Johnson Matthey in 2000, Chen has been working extensively in the development of advanced catalysts for exhaust emission control. Chen has published more than 40 papers in various catalysis journals and co-author many patents and patent applications. He was one of the recipients of the American Chemical Society Award for Team Innovation in 2009.

Notes

Poster Abstracts

Synthesis of Large-Pore Periodic Mesoporous Silica with Crystalline Channel Walls and High Hydrothermal Stability

Paritosh Mohanty,¹ Berenika Kokoszka,¹ Cong Liu,¹ Manuel Weinberger,¹ Manik Mandal,¹
Vincenzo Stagno,² Yingwei Fei,² and Kai Landskron^{1*}

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We developed a route to synthesize periodic mesoporous silica with crystalline channel walls starting from ordered mesoporous silica through high-pressure technique. These materials preserve the mesostructure ordering after such treatment, while the channel walls become completely crystalline. The obtained material has high BET surface area of $\sim 250 \text{ m}^2 \text{ g}^{-1}$, pore volume of $0.70 \text{ cm}^3 \text{ g}^{-1}$, and pore size of $\sim 15.0 \text{ nm}$. The synthesized material is steam stable at least up to $800 \text{ }^\circ\text{C}$ for several hours and shows great potential to be applicable in petroleum cracking. The present method of synthesizing crystalline silica shows promise to make these material available through industrial scale-up because pressures as low as 1-2 GPa can be applied.

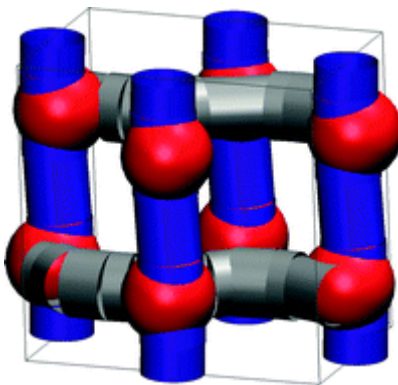
A Computational Method for the Three-dimensional Characterization of Zeolite Porous Networks

Eric L. First, Chrysanthos E. Gounaris, James Wei and Christodoulos A. Floudas
Department of Chemical and Biological Engineering, Princeton University, A325 Engineering Quad, Princeton, NJ 08544

Zeolites are crystalline materials used for shape-selective separations and catalysis due to their regular microporous structure. While there are nearly 200 known natural and synthetic zeolite frameworks,¹ as well as millions of theoretically plausible zeolite-like structures,^{2,3} the difficulty of comprehensive empirical study has limited their industrial adoption to only a few framework types.

We have developed a new computational approach based on optimization, geometry, and graph algorithms to automatically characterize the three-dimensional porous structure of zeolites.⁴⁻⁷ The method identifies all void spaces that can potentially accommodate a guest molecule and classifies them into interconnected channels and cages. The results of our characterization approach are used to calculate quantities of interest, including pore size distribution, accessible volume, surface area, largest cavity and pore limiting diameters, and probability of pore occupancy.

By applying our method over a database of framework types, we gain insights about zeolite selectivity, answering the questions: *For which molecules are zeolites most selective?* and *To what degree are zeolites selective?* ZEOMICS, an online database of structure characterizations, is freely available to the scientific community (<http://helios.princeton.edu/zeomics/>). Our web tool provides three-dimensional visualization of pore structures and enables users to submit additional structures of interest to be automatically processed by our algorithms.



References

- [1] C. Baerlocher; L. B. McCusker, Database of Zeolite Structures (2010) <http://www.iza-structure.org/databases/>.
- [2] M. W. Deem; R. Pophale; P. A. Cheeseman; D. J. Earl, *J. Phys. Chem. C*, **113** (2009) 21353-21360.
- [3] R. Pophale; P. A. Cheeseman; M. W. Deem, *Phys. Chem. Chem. Phys.*, **13** (2011) 12407-12412.
- [4] C. E. Gounaris; C. A. Floudas; J. Wei, *Chem. Eng. Sci.*, **61** (2006) 7933-7948.
- [5] C. E. Gounaris; J. Wei; C. A. Floudas, *Chem. Eng. Sci.*, **61** (2006) 7949-7962.
- [6] C. E. Gounaris; J. Wei; C. A. Floudas; R. Ranjan; M. Tsapatsis, *AIChE J.*, **56** (2009) 611-632.
- [7] E. L. First; C. E. Gounaris; J. Wei; C. A. Floudas, *Phys. Chem. Chem. Phys.*, **13** (2011) 17339-17358.

Mesostructured Y Zeolite for FCC Catalysis

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A technique that can introduce controlled mesoporosity (mesostructure) directly into crystalline zeolites would be highly desirable and will have great impact to catalytic processes, such as fluid catalytic cracking.¹ JGM made the discovery in 2004 of a new surfactant-templating approach to allow for precisely controlled mesoporosity to be introduced into zeolite crystals (i.e. mesostructuring), while maintaining the chemical and physical properties of the zeolites (i.e. microporosity, crystallinity, acidity, etc.).² Rive Technology is currently developing and commercializing the mesoporous zeolite technology in FCC catalysis, as well as in other applications.

This presentation describes the preparation, characterization and testing of the mesostructured Y zeolite and FCC catalyst. Figure 1 below shows the typical features of a mesostructured Y zeolite: a) well-controlled intracrystalline mesoporosity; b) good microporosity/mesoporosity combination and high hydrothermal stability; c) good crystallinity and strong acidity. FCC catalysts made from mesostructured Y zeolite, after proper laboratory deactivation (e.g. at 788 °C under 100% steam for 8 hours), were tested on a fixed fluidized bed ACE testing unit with different feedstocks, which produced significantly more gasoline and light cycle oil (transportation fuels), and less bottoms and coke. The much improved product selectivity could be attributed to the mesostructure introduced into the zeolites that eased the diffusion limitation in the conventional zeolites.

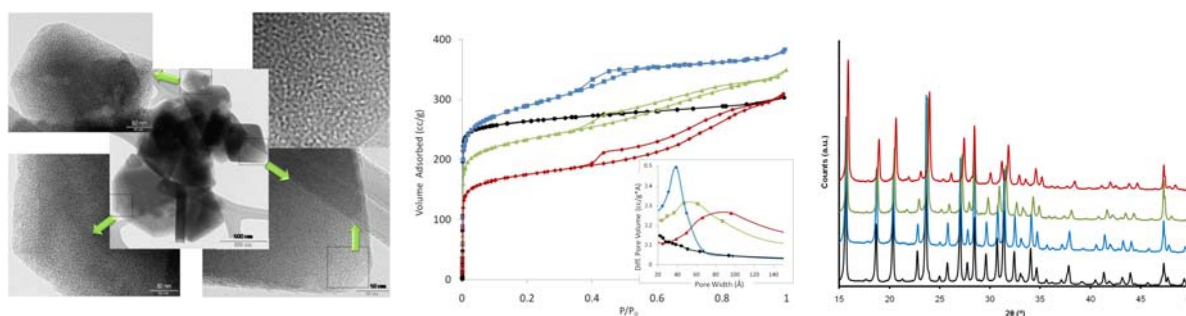


Figure 1. a) TEM micrographs of mesostructured Y zeolite showing intracrystalline mesoporosity and b) Ar adsorption isotherms and c) X-ray diffraction patterns of NH₄Y (black), mesostructured Y (blue), and mesostructured USY before (green) and after (red) deactivation at 788 °C in 100% steam for 4 hours.

References

- [1] a) J. Weitkamp, L. Puppe, in *Catalysis and Zeolites: Fundamentals and Applications*, Springer, Berlin, Germany, **1999**, b) A. Corma, *Chem. Rev.* **1997**, 97, 2373–241, c) J. Čejka, A. Corma, S. I. Zones, in *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Wiley-VCH, Weinheim, Germany, **2010**.
- [2] a) J. Y. Ying, J. García-Martínez, US Patent 7,589,041 B2, **2009**; b) J. García-Martínez, M. Johnson, US 20080138274, **2008**; c) J. García-Martínez, M. Johnson, US 20100021321, **2010**; d) L. Dight, J. García-Martínez, J. Valla, M. Johnson, US 20100190632, **2010**.

Characterisation of Zeolites by Dynamic Vapor Sorption Methods

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Aluminosilicates as well as other inorganic solids are of great importance due to their high adsorption capacity and surface reactivity and are used for various applications. Dynamic vapor sorption methods have been a useful tool for the characterization of these properties using organic vapors at process relevant temperatures. The most common dynamic techniques are gravimetric and inverse gas chromatography methods. Isotherm measurements allow the determination of surface area and pore size distribution as well as diffusion and the activation energy of diffusion. Chemisorption effects are measured by titration methods or thermal desorption. A combination of finite concentration IGC and thermal desorption provides the possibility to separate micropore adsorption from surface and mesopore adsorption. In this study, water and organic vapor isotherm measurements under vacuum and atmospheric conditions on a series of zeolites A5, A3, 13X, NH4-Beta and Co-Beta have been used to demonstrate the applications of Dynamic Vapor Sorption (DVS Vacuum) and Surface Energy Analyzer (SEA – IGC) for the characterization of inorganic porous materials.

Synthesis, Characterization and Luminescence Studies of Lanthanide-2,5-Thiophenedicarboxylate Frameworks

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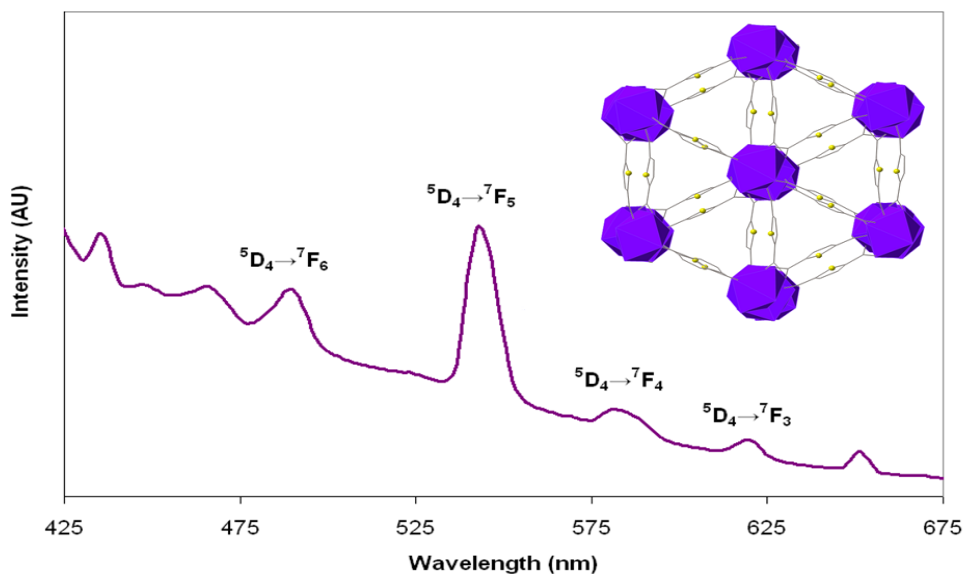
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By varying the solvents under solvothermal conditions, a series of lanthanide-thiophenedicarboxylate based 3-D networks of general formula $M_2(\text{TDC})_3$ [$M = \text{Tb}$ [1], Dy [2], Nd [3], $\text{TDC} = 2,5\text{-thiophenedicarboxylate}$] were synthesized using solvothermal conditions and characterized by single crystal diffraction techniques. Herein, we describe the Crystal structure of the networks and their luminescent properties. The Terbium based network shows the most intense emission among the three networks.



References

- [1] Kuppler, R. J.; Timmons, D. J.; Fang, Q. R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H. C.; *Coordination Chem.*, 253 (2009), 3042-3066.
- [2] Turner, D. R.; Hatton, J. S.; Batten, S. R.; *Allg. Chem*, 635(2009), 439-444.

Hydrocarbon Reactions over H-ZSM-5 by High Temperature Pre-treatments

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Zeolites are crystalline materials that are widely used in industry as solid acid catalysts¹. Brønsted acid sites (BAS) – hydroxyl groups bridged between Al and Si (Al-OH-Si) tetrahedra – are responsible for catalytic abilities of zeolites. The OH group in the BAS decomposes at high temperatures above 873 K² in a process called dehydroxylation. This temperature is often exceeded in the regenerator of a fluidized catalytic cracking (FCC) unit, and the zeolite catalyst will undergo some degree of dehydroxylation during normal FCC operation. The dehydroxylation can proceed via a dehydration mechanism of the acid sites³, however, production of hydrogen is also reported during the dehydroxylation process⁴. The production of hydrogen indicates that BAS are decomposed to form electron deficient redox sites. The activation of small alkanes over acid sites has been investigated extensively because of its relevance to technologically important processes such as FCC in petroleum refineries, but also because C-H and C-C bond activation is of fundamental scientific interest⁵. In this work, we investigate the reactivity and selectivity of sites generated by dehydroxylation using the monomolecular reaction of propane and isobutane.

ZSM-5 (MFI) is used to study the sample reactivity before and after thermal dehydroxylation. The samples are treated in an inert atmosphere at two temperatures: activation at relatively low temperature (below 873K) to simulate the pristine zeolite and 1098K to generate dehydroxylated sites. The reaction is limited to two monomolecular pathways: cracking and dehydrogenation. High temperature activation has dramatic effects on selectivity: for the monomolecular reaction of propane, dehydrogenation is enhanced in the samples after dehydroxylation while cracking is favored in the acid catalysts⁶. On the other hand, for the monomolecular isobutane reaction, the cracking-to-dehydrogenation ratio increases by a factor of ~2 after dehydroxylation. The measured activation energies for the dehydroxylated samples are different from the ones calculated for the sample before dehydroxylation. We further investigate if the presence of redox sites results in radical cation chemistry instead of protolytic chemistry in the samples after dehydroxylation.

References

- [1] Auerbach, S. M.; Carrado, K. A.; Dutta, P. K., *Handbook of Zeolite Science and Technology*, Marcel Dekker, New York, 2003
- [2] Szanyi, J.; Paffett, M. T., *Microporous Mater.*, 7 (4), 1996, 201-218
- [3] Stamires, D. N.; Turkevich, J., *J. Am. Chem. Soc.*, 86 (5), 1964, 749
- [4] Nash, M. J.; Shough, A. M.; Fickel, D. W.; Doren, D. J.; Lobo, R. F., *J. Am. Chem. Soc.*, 130 (8), 2008, 2460-2462
- [5] Gounder, R.; Iglesia E., *J. Am. Chem. Soc.*, 131 (5), 2009, 1958-1971
- [6] Al-majnouni, K.A.; Yun, J.H.; Lobo, R.F., *ChemCatChem*, 3 (8), 2011, 1333-1341

Realizing three-dimensionally ordered, hydrothermally stable mesoporous catalysts via assembly and nanotemplating strategies

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Realization of high-selectivity catalytic conversions under the hydrothermal conditions of the biorefinery demands the development of next-generation, hydrothermally stable heterogeneous catalysts bearing three-dimensionally ordered mesoporous (3DOM) and hierarchical (i.e., macro-meso-microporous) pore structure that can accommodate bulky sugar molecules and their derivatives. The enhanced hydrothermal stability and reducible structure of titania establishes its promise as a robust substrate for liquid phase biofuel catalysis. Through a hierarchical nanotemplating strategy involving the infiltration of assembled, size-tunable silica nanoparticles with titanate solutions, we have successfully fabricated three-dimensionally ordered mesoporous titania structures with tunable pore size ranging from nanometers to tens of nanometers. The mesopore structure during high-temperature calcination, treatment intended for titania polymorph interconversion and enhanced crystallinity, is bolstered by the presence of the hard silica template. The resulting nanoparticulate walls and ordered mesostructure lead to BET surface areas as high as 289 m²/g. The confinement imparted by the sacrificial template enables fundamental insight into titania polymorphism as it relates to its sensitivity to the degree of confinement and surface chemistry imparted by the template.

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

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Porous thin films scalable to tens of nanometers in thickness with tunable hierarchy in pore size and topology hold exciting technological implications spanning, among others, high-selectivity and high-flux membrane separations to rapid-response sensors selective for large and small target molecules. Owing to their inherent microporosity, inorganic materials such as zeolites, carbons, and some nanoparticle assemblies, hold specific promise in such applications where molecular selectivity is critical. Yet, control over porous film thickness has been a persistent challenge for films composed of such materials and supported on porous or non-porous substrates, leading in some cases to stress-induced crack formation and sluggish molecular flux. We address the challenge of controlling film thickness of porous inorganic films, and in some cases controlling underlying porosity of these films, through a hierarchical templating strategy rooted in convective deposition of tunable nanoparticles and subsequent replication and materials scaffolding techniques. Specifically, we will address three classes of porous thin films scalable to just tens of nanometers in thickness: convectively deposited nanoparticulate colloidal crystalline films, carbon replica films characterized by either ordered mesoporosity or asymmetric mesopore-supported ultra-thin microporous layers, and (sacrificial) carbon-scaffolded ultra-thin zeolite films (e.g., silicalite-1, SAPO-34) composed of extensive high-aspect-ratio single-crystal domains. We will describe stages in film formation, sensitivity of film properties to synthesis conditions, transition from non-porous to highly-porous substrates as film supports, and the role of pore topology in thin film scaffolding.

Surface and Pore Structure Assessment of Hierarchical Zeolites by Advanced Water and Argon Sorption Studies

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Hierarchical (mesoporous) zeolites can be prepared by direct synthesis or by post-synthetic treatment of microporous zeolites, for example by demetallation. Alkaline treatment is a widely applied post synthesis method for the preparation of hierarchical zeolites. The selective dissolution of framework Si leads to the creation of intra-crystalline mesopores, which have proven to be highly beneficial in improving the zeolite utilization efficiency for catalytic applications.. Due to its lower solubility, the framework Al remains undissolved in basic solution, leading to a decrease in the Si/Al ratio of the mesoporous zeolites and possible modification of the surface properties. Desilicated zeolites are known to have increased Lewis acidity, which may be largely removed by subsequent acid washing, which is thought to restore the acidic properties of the parent zeolite. Characterization methods which permit surface sensitivity will be advantageous in understanding the compositional alterations occurring in zeolites upon alkaline treatment.

Within this context we report in this paper results of a systematic experimental study of the adsorption- and phase behavior of simple fluids (nitrogen, argon) and water vapor in zeolites, novel mesoporous zeolites and mesoporous molecular sieves. Advanced pore size analysis is performed by applying dedicated NLDFT (Non-Local Density-Functional Theory) methods for argon 87 K adsorption in MFI zeolites. Combining argon and water adsorption allows one to provide further insight into the pore and surface structure and properties of hierarchical zeolites prepared by desilication. Argon adsorption clearly reveals the two different relative pressure regions of micro- and mesopore filling for mesoporous zeolites, whereas for water adsorption it is not possible to distinguish between micro and mesopore filling ranges. However, water adsorption allows one to obtain information with respect to the surface properties (e.g. hydrophobicity/hydrophilicity) which is found to be sensitive both to the Si/Al framework ratio and to the distribution of Al species present in the zeolite, as well as the presence of polar surface groups (on mesopore- and external surfaces). Our study clearly suggests that combining argon (87K) and water adsorption allows one to provide further insights into surface and structural properties of hierarchical zeolites prepared by desilication. In addition, our study raises the awareness of the influences of compositional effects arising from post-synthetic modification of zeolites by demetalation

Structure-Property Relationships between Fractal Description of Pore Structure and Catalyst Effectiveness in V-SBA-15

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The accurate description of a material's surface properties is necessary to describe molecular processes in catalysis. SBA-15 is a template-synthesized mesoporous silicate that has found extensive use as a model support for studies in supported catalysis. We investigate the effect of differences in underlying silica surface on supported metal oxide catalysis; in this study SBA-15 is used as the support for a vanadia catalyst in the partial oxidation of methanol. By increasing calcination temperature we are able to control the SBA-15 surface structure from one with high microporosity and significant surface roughness to one without microporosity and minimal surface roughness. We use surface fractal dimension obtained from nitrogen adsorption as our measure of surface roughness and microporosity. As the SBA support surface is changed from a highly porous (fractal dimension ~ 2.4) species to a more smooth (fractal dimension ~ 2.2) species there is an increase in the MeOH TOF for higher loading samples (0.25 V/nm^2). The opposite trend is observed for lower loading samples (0.125 V/nm^2). Possible explanations for this behavior are at higher loadings, vanadia are occluded in a highly fractal support and to a lesser degree in a less fractal support, resulting in decreasing TOF on a per mole vanadia basis as you move from a less fractal to higher fractal support. For a lower loading sample, there is less vanadia occlusion on the surface. It is postulated that for a smoother fractal dimension, the adsorption potential is less than for a rougher fractal dimension on the basis of pore volume. A less fractal surface will produce a lower local concentration of reactant species whereas a higher fractal surface will produce a higher local concentration of reactant species by pore volume, thus increasing the adsorption potential, resulting in increased TOF numbers in higher fractal surfaces. This may explain the increasing TOF trend from lesser fractal to higher fractal dimension support for lower loading samples.