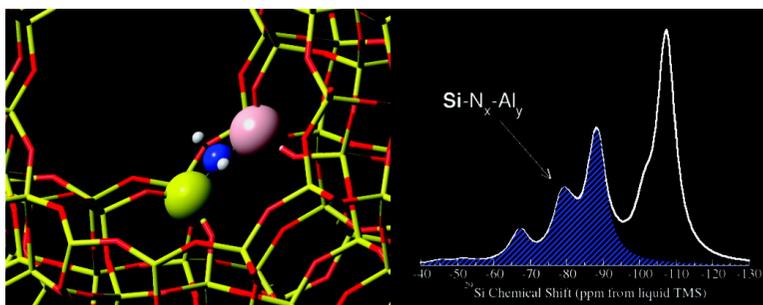## Communication

Spectroscopic Signatures of Nitrogen-Substituted Zeolites

Karl D. Hammond, Fulya Dogan, Geoffrey A. Tompsett, Vishal Agarwal, W. Curtis Conner Jr., Clare P. Grey, and Scott M. Auerbach

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Spectroscopic Signatures of Nitrogen-Substituted Zeolites

Karl D. Hammond,[†] Fulya Dogan,[§] Geoffrey A. Tompsett,[†] Vishal Agarwal,[†] W. Curtis Conner, Jr.,[†]
Clare P. Grey,[§] and Scott M. Auerbach*,[†,‡]

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and Department of Chemistry, State University of New York, Stony Brook, New York 11794

Received June 24, 2008; E-mail: auerbach@chem.umass.edu

Nanoporous acid catalysts such as zeolites form the backbone of catalytic technologies for refining petroleum.[1] With the promise of a biomass economy, new catalyst systems will have to be discovered, making shape-selective base catalysts especially important because of the high oxygen content in biomass-derived feedstocks. Strongly basic zeolites are attractive candidates, but such materials are notoriously difficult to make due to the strong inherent acidity of aluminosilicates. Several research groups have endeavored to produce strongly basic zeolites by treating zeolites with amines,[2-5] but to date there is little compelling evidence that nitrogen is incorporated into zeolite frameworks. Here, we detail synthesis, NMR spectroscopy, and calculations showing that nitrogen adds to both surface and interior oxygen while preserving the zeolite framework. This finding is crucial for the rational design of new biomass-refinement catalysts, allowing 50 years of zeolite science to be brought to bear on the catalytic synthesis of biofuels.

In a hypothetical amine-substituted zeolite, oxygen is replaced by nitrogen to form a stronger base; these materials have been predicted to be nearly twice as strong as traditional zeolite bases.[6] However, the nature of active sites in the actual materials—in particular, whether nitrogen replaces oxygen primarily in the zeolite framework or on the surface—is difficult to characterize experimentally. What is needed is compelling evidence that nitrogen has substituted into the zeolite framework. To pursue such evidence, we compare quantum calculations on amine-substituted HY (FAU structure[7]) zeolite clusters with ^{29}Si NMR spectra of corresponding materials to explain new peaks in the spectra.

Amine-substituted zeolites were fabricated by exposing Y zeolite (Si/Al = 6.1) to dry ammonia at 850 °C for 8 h in a flow-through furnace. Powder XRD (Supporting Information, SI) confirms that the material maintains an FAU structure with a high degree of crystallinity. Solid state (MAS) ^{29}Si NMR spectra were measured using an 8.47 T spectrometer. The presence of nitrogen in ammonia-treated samples was confirmed by elemental analysis and energy dispersive X-ray (EDX) analysis (see SI). We measured IR spectra of treated and untreated samples (SI); broad bands in the 800–1000 cm^{-1} range obscure unambiguous assignments of Si–N vibrations.

Quantum calculations were performed with a GAUSSIAN program[8] on clusters containing 14 tetrahedral (Si, Al) atoms. Such clusters contain at least three "layers" of atoms around the central atoms in the cluster, which is sufficient to converge the shielding constants (σ) and chemical shifts (δ) with respect to system size.[9] Each cluster is terminated by OH groups, and all terminal OH groups and any atoms bound to two or more OH groups were frozen at their crystallographic coordinates. Terminal hydrogens were placed along O–Si* bonds pointing to missing Si* atoms, 0.86 Å

from the oxygen. All calculations were performed with the B3LYP hybrid exchange-correlation functional.[10] Geometries were optimized using the 6-311G(d,p) basis set;[11] magnetic shielding constants were then computed with gauge-including atomic orbitals (GIAO)[12] using the cc-pVTZ basis set.[13] The chemical shift was determined by subtracting the shielding constants from those of silane and then applying the experimental chemical shift of −104.34 ppm for silane relative to neat liquid tetramethylsilane (TMS).[14]

The ^{29}Si chemical shifts of each cluster and the energy changes due to the addition of ammonia and loss of water are presented in Table 1. The reaction energies listed are changes in the electronic energy only; no correction for zero-point energy, thermal energy, or entropy has been applied. These corrections are likely small compared to the reaction energies considered. Adding nitrogen to a siliceous site is endoergic by ca. 100 kJ/mol. This value is consistent with Corma's value of 118 kJ/mol for the reaction of disilylether to form disilylamine.[15] Using the same theory and basis set used herein, the energy change of this reaction is 98 kJ/mol. Substituting nitrogen adjacent to an aluminum atom, however, only requires 35 kJ/mol. The reaction at the cluster surface, where terminal OH is replaced by NH$_2$, leads to a reaction energy of 30 kJ/mol. Aluminum, therefore, significantly facilitates amine substitution, being comparable in energy to surface replacement.

The chemical shifts in Table 1 for a silicon atom that is second-neighbor to one, two, and three aluminum atoms are quantitatively

Table 1. Electronic Energy Differences (ΔV) Between FAU Clusters and ^{29}Si Chemical Shifts (δ) of Each Cluster[a]

species	ΔV [kJ/mol]	$\delta_{TMS}(^{29}\text{Si})$ [ppm] calcd	expt[b]
siliceous sites			
≡Si−O−**Si**≡	0	−107.4	−106
≡Si−NH−**Si**≡	99.5	−84.6	N/O[c]
≡Si−NH−**Si**−NH−Si≡	210.0	−64.6	N/O
sites on the surface			
≡**Si**−OH	0	−94.6	−95
≡**Si**−NH$_2$	30.1	−78.7	−80
sites with a single aluminum atom nearby			
≡Al−OH−**Si**≡	0	−101.3	−101
≡Al−NH$_2$−**Si**≡	32.3	−88.2	−86
≡Al−NH$_2$−**Si**−NH−Si≡	140.4	−67.7	N/O
sites with two aluminum atoms nearby			
≡Al−OH−**Si**−OH−Al≡	0	−93.7	−94
≡Al−NH$_2$−**Si**−OH−Al≡	35.7	−81.5	−80
≡Al−NH$_2$−**Si**−NH$_2$−Al≡	70.5	−67.1	−68
sites with three aluminum atoms nearby			
(≡Al−OH−)$_3$**Si**−	0	−85.5	−89
(≡Al−OH−)$_2$**Si**−NH$_2$−Al≡	34.8	−67.1	−68
≡Al−OH−**Si**(−NH$_2$−Al≡)$_2$	65.1	−51.7	
(≡Al−NH$_2$−)$_3$**Si**−	104.0	−45.5	

[a] Energies include ammonia and water as reactants and products, respectively. Bonds without explicit termination are part of a siliceous framework. [b] Assignments based on Figure 1; overlapping peaks are assigned multiple times [c] Presumably not observed due to high energy.

† Department of Chemical Engineering, University of Massachusetts.
‡ Department of Chemistry, University of Massachusetts.
§ State University of New York.

consistent with the experimental spectrum (Figure 1, top) and published experimental assignments.[16] The trends in chemical shift as nitrogen is substituted into the framework are qualitatively consistent with new peaks that appear in NMR spectra of silicon oxynitride glasses, which appear at chemical shifts of ~ −90, −78, and −65 ppm.[17] Ammonia (a base) adsorbed in an acidic zeolite is known to give an NH_4^+ species, but our calculations of the Si resonances of a Brønsted acid site (−101.3 ppm) and a silicon atom close to NH_4^+ (−98.1 ppm) predict that adsorbed NH_4^+ cannot account for the new NMR signals.
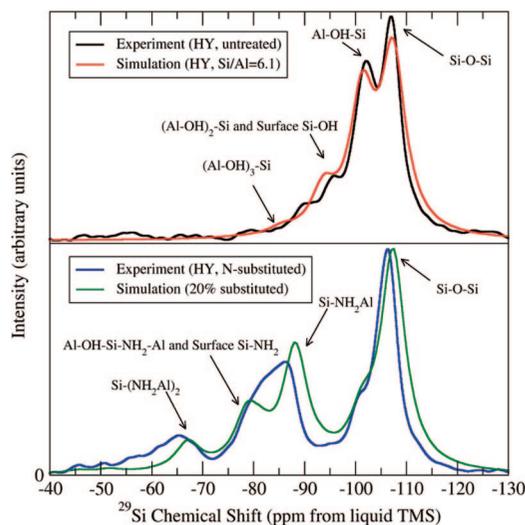

Figure 1. ^{29}Si NMR spectra of HY zeolite (Si/Al = 6.1) with 0% (top), 20% of oxygen substituted for NH groups.

The ultimate question we seek to answer is whether there is definitive spectroscopic evidence indicating substitution of oxygen for nitrogen in the zeolite framework. We therefore need to compare our calculated values to an experimental spectrum. We accomplish this by assuming each type of silicon nucleus from Table 1 generates a Lorentzian NMR line shape, with a weighting based on the presumed fraction of silicons of each type. The aluminum distribution is assumed to be quasi-random among the tetrahedral sites following the work of Vega.[18] The nitrogen distribution was assumed to obey the following restrictions: (1) no substitution between two silicon atoms due to the energy relative to that at aluminum-proximate sites; (2) surface substitution of Si−NH₂ for Si−OH, being lower in energy *and* more accessible, takes place before framework substitution; and (3) the probabilities of substitution(s) near a silicon that is second-neighbor to one, two, three, and four aluminum atoms are the same and random. We discounted the presence of intermediates where the structure is broken due to their high energies (data not shown). The resulting spectra for an Si/Al ratio of 6.1 are shown in Figure 1, overlaid with experimental spectra of HY zeolite with the same Si/Al ratio. The calculated spectrum of the substituted zeolite assumes 10% of silicon atoms are on the surface and that each peak has a half width at half maximum of 2.9 ppm, both of which are fitting parameters. For an FAU structure with 20% of its oxygen substituted for nitrogen, about 80% of the *total* nitrogen substitutions occur inside the framework using these assumptions.

The predicted spectra in Figure 1 agree well with experiment. For untreated HY (Figure 1 top), agreement is excellent except for the (Al−OH)₃−Si moiety (−90 ppm), whose chemical shift may be sensitive to proton siting; we will explore this in future work. For ammonia-treated HY (Figure 1 bottom), we assign the broad peaks in the −75 to −95 ppm range to surface **Si**−NH₂

(near −79 ppm), framework ≡Al−NH₂−**Si**−OH−Al≡ (−81 ppm), and framework ≡Al−NH₂−**Si**≡ (−88 ppm). The peak at −67 ppm is assigned to ≡Al−NH₂−**Si**−NH₂−Al≡ and (≡Al−OH−)₂**Si**−NH₂−Al≡. Silicon atoms with three or four Al neighbors are unlikely at this Si/Al ratio. The broadened line shape in the experimental spectrum for the treated zeolite in the −80 to −90 ppm range likely arises from a distribution of Si environments, various bond lengths and angles, that cannot be captured by the clusters explored in this work.

The presence of the observed peaks in FAU zeolite, in particular, the peak near −86 ppm, provides *compelling evidence* that nitrogen substitution occurs inside the framework. Framework substitutions of the form ≡Al−NH₂−**Si**≡ make up over 25% of the total Si at this Si/Al ratio, assuming 20% of oxygen atoms are substituted for nitrogen (76 nitrogens per unit cell).

We conclude that high-temperature ammonia treatment of HY zeolite produces a mixture of surface and framework substitutions, the latter confined to reactions that replace Brønsted acid sites with NH₂ groups. The important consequence of this conclusion is that nitrogen substitution leaves the framework intact, paving the way for base-catalyzed reactions using strong amine-like bases, and allowing over five decades of zeolite science to be applied to the catalytic processing of biofuels.

Supporting Information Available: Complete ref 8 and experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds. *Handbook of Zeolite Science and Technology*; Marcel-Dekker: New York, 2003.
(2) Yamamoto, K.; Sakata, Y.; Nohara, Y; Takahashi, Y; Tatsumi, T. *Science* **2003**, *300*, 470.
(3) Kerr, G. T.; Shipman, G. F. *J. Phys. Chem.* **1968**, *72*, 3071.
(4) (a) Ernst, S.; Hartmann, M.; Sauerbeck, S.; Bongers, T. *Appl. Catal. A: Gen.* **2000**, *200*, 117. (b) Ernst, S.; Hartmann, M.; Hecht, T.; Jaen, P. C.; Sauerbeck, S. *Stud. Surf. Soc. Catal.* **2002**, *142*, 549.
(5) (a) Han, A.-J.; He, H.-Y.; Guo, J.; Yu, H.; Huang, Y.-F.; Long, Y.-C. *Microporous Mesoporous Mater.* **2005**, *79*, 177. (b) Guo, J.; Han, A.-J.; Yu, H.; Dong, J.-P.; He, H.; Long, Y.-C. *Microporous Mesoporous Mater.* **2006**, *94*, 166. (c) Han, A.-J.; Guo, J.; Yu, H.; Zeng, Y.; Huang, Y.-F.; He, H.-Y.; Long, Y.-C. *ChemPhysChem* **2006**, *7*, 607.
(6) Astala, R.; Auerbach, S. M. *J. Am. Chem. Soc.* **2004**, *126*, 1843.
(7) International Zeolite Association, Database of zeolite structures, http://www.iza-structure.org/databases.
(8) Frisch, M. J.; et al. *Gaussian Development Version*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.
(9) Bussemer, B.; Schröder, K. P.; Sauer, J. *Solid State Nucl. Magn. Reson.* **1997**, *9*, 155.
(10) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys* **1980**, *58*, 1200. (d) Stephens, J. P.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(11) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(12) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.
(13) (a) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358. (c) Davidson, E. R. *Chem. Phys. Lett.* **1996**, *260*, 514.
(14) Makulski, W.; Jackowski, K.; Antušek, A.; Jaszuński, M. *J. Phys. Chem. A* **2006**, *110*, 11462.
(15) Corma, A.; Viruela, P.; Fernández, L. *J. Mol. Catal. A: Chemical* **1998**, *133*, 241.
(16) Klinkowski, J.; Ramdas, S.; Thomas, J. M.; Fyfe, C. A.; Hartman, J. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1025.
(17) van Weeren, R.; Leone, E. A.; Curran, S.; Klein, L. C.; Danforth, S. C. *J. Am. Ceram. Soc.* **1994**, *77*, 2677.
(18) Vega, A. J. *J. Phys. Chem.* **1996**, *100*, 833.

JA8044844