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Spectroscopic Signatures of Nitrogen-Substituted Zeolites

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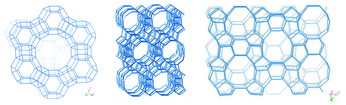
Abstract

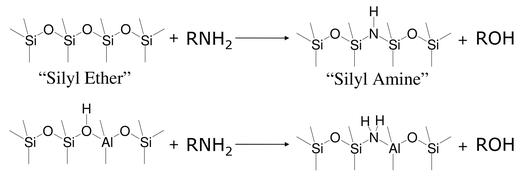
- **Zeolites are crystalline microporous materials**
  - Zeolites are typically acids
  - Treating zeolites with amines at high temperatures has been shown to produce basic (alkaline) catalysts in which nitrogen is substituted for oxygen
  - Goal: Find a way to characterize nitrogen substituted zeolites
- **Methods**
  - Experiment: nuclear magnetic resonance spectroscopy, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, physical adsorption
  - Calculations: cluster models. Reaction energies, chemical shielding/chemical shifts (NMR), quadrupolar NMR, vibrational spectra (infrared/Raman).
- **Materials of interest**
  - Y zeolite (FAU structure)
  - Beta zeolite (BEA structure)
  - ZSM-5 (MFI structure)



- **We find compelling evidence from experiments and simulations that nitrogen incorporates into zeolite frameworks. Questions remain of the stability of these materials.**

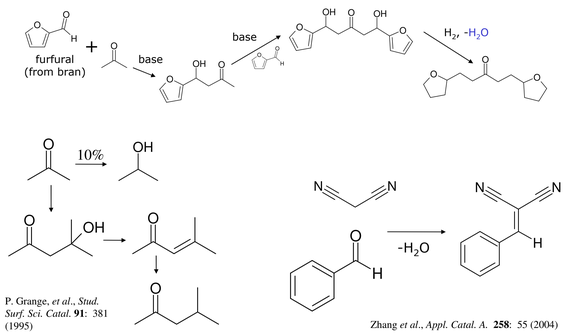
Zeolites as Acid/Base Catalysts

- Zeolites are usually strongly acidic
  - Low-aluminum zeolites are stronger acids
  - High-aluminum zeolites are weak(er) acids
- The alkaline or alkaline-earth forms are weakly basic: NaY, CsX, K-ZSM-5
  - Low-aluminum zeolites (e.g. K-ZSM-5) are *very* weak bases
  - High-aluminum zeolites (e.g. CsX) are merely weak bases
- **IDEA**: Replace some oxygen in the zeolite with nitrogen to produce a stronger base



Examples of Uses for Zeolitic Base Catalysts

Condensation reactions



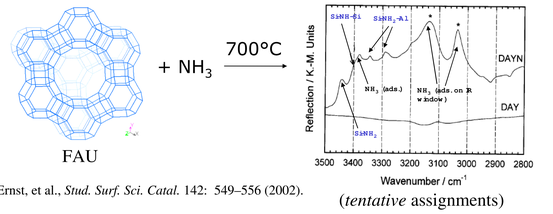
P. Grange, *et al.*, *Stud. Surf. Sci. Catal.* **91**: 381 (1995)

Zhang *et al.*, *Appl. Catal. A.* **258**: 55 (2004)

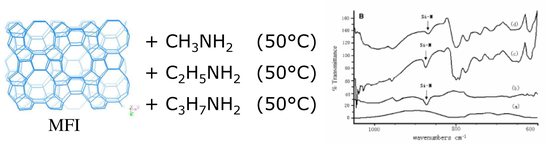
How to Make Zeolites into Bases

- Step 1: Heat
  - Removes water
  - Removes some hydroxides on surface
- Step 2: Expose to a nitrogen source:
  - Ammonia (NH_3)
  - Alkylamines (CH_3NH_2, $C_2H_5NH_2$, etc.)
  - Others: Polysilazane (SiCl4+NH3 deposited and pyrolized), Silicon nitride (Si3N4), Azides (NaN3, etc.), Nitrogen gas (N2)

Experimental Characterization: Infrared

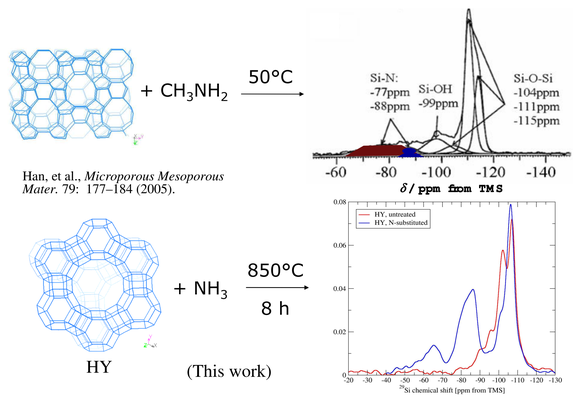


Ernst, et al., *Stud. Surf. Sci. Catal.* 142: 549–556 (2002).

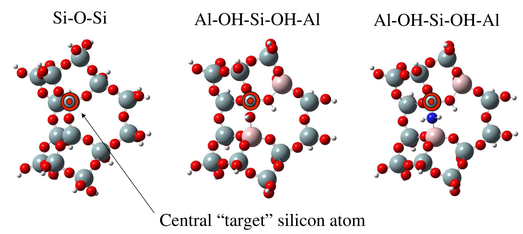


J. Guo, et al., *Microporous Mesoporous Mater.* 94: 607–613 (2006).

Experimental Characterization: NMR



Cluster Calculations



Things to vary from cluster to cluster:
- Aluminum atoms nearby
- Placement of hydrogen
- Number of nearby nitrogen vs. oxygen atoms

Chemical Shift Calculations

$$\Delta E = \hbar\gamma\Delta I(1-\sigma)B$$

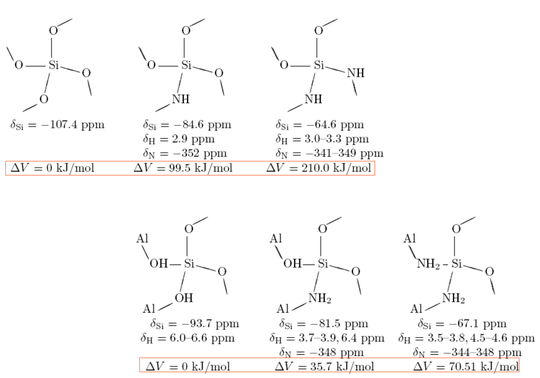
Change in magnetic moment (constant for each nucleus)

External magnetic field (constant)

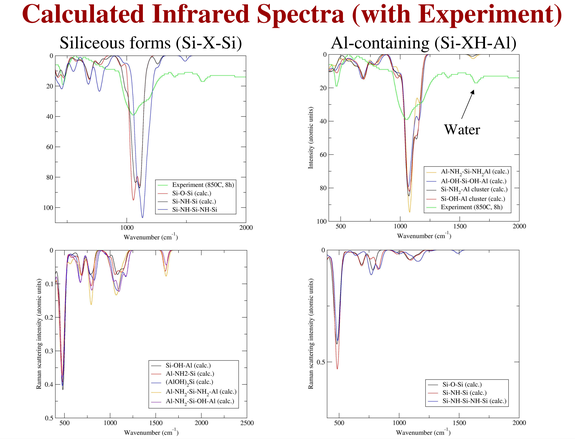
Shielding constant (function of electron density)

$$\delta = \frac{\Delta E - \Delta E_{\text{ref}}}{\Delta E_{\text{ref}}} = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} = \frac{\sigma_{\text{ref}} - \sigma}{1-\sigma_{\text{ref}}} \approx \sigma_{\text{ref}} - \sigma$$

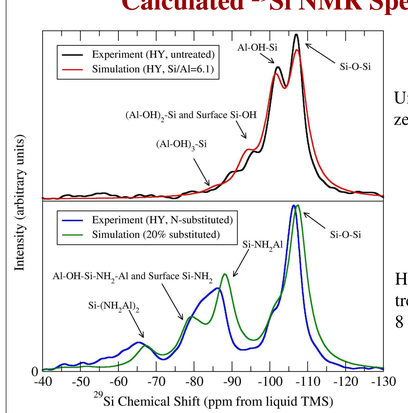
Calculated Energies of Amine Substitutions



Calculated Infrared Spectra (with Experiment)



Calculated ^{29}Si NMR Spectrum



Untreated HY zeolite (Si:Al = 6:1)

HY zeolite (Si:Al = 6:1), treated under NH_3 for 8 hours at ~800°C

Conclusions and Future Work

- Nitrogen prefers to substitute between Si and Al, not between Si and Si
- Approximately 20% of total oxygens are substituted for nitrogen after 8 hours of treatment. Of those, 87% take place inside the framework
- Current/Future Work:
  - High-resolution physical adsorption
  - Stability of treated zeolites
  - Extraframework aluminum simulations
  - Non-silicon NMR spectroscopy

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