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Spectroscopic Signatures of Nitrogen-Substituted Zeolites

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Abstract

Zeolites are crystalline microporous materials. They are typically acid catalysts, including those used in cracking processes. The strong acid sites are typically "aluminosilicate" sites, which can be denoted as Si-Al-(O-H-). The zeolite framework is composed of tetrahedral units of silica (SiO4) and alumina (AlO4) sharing oxygen atoms to form a three-dimensional network. The primary acid sites are Brønsted acid sites, which are protonic acid sites created by the presence of an Al-OH group. The Brønsted acid sites can be further characterized by their strength, which is often classified as strong, medium, or weak depending on the local environment of the Al-OH group. For example, Al-OH groups in zeolites are typically strong acids, whereas Al-OH groups in amorphous aluminosilicates are typically medium acids.

Zeolites as Acid/Base Catalysts

**Examples of Uses for Zeolitic Base Catalysts**

- **Condensation reactions**
  - **Step 1:** Heat
  - **Step 2:** Expose to a source

**How to Make Zeolites into Bases**

- **Step 1:** Heat
  - Removes water
  - Removes some hydroxides on surface
- **Step 2:** Expose to a nitrogen source:
  - Ammonia (NH3)
  - Alkylamines (CH3NH2, C2H5NH2, etc.)
  - Others: Polysilazane (SiG4N5H3 deposited and pyrolyzed), Silica-nitride (Si3N4), Ailsdes (Na3N3, etc.), Nitrogen gas (N2)

**Materials of interest**

- Aluminosilicate (Al-Si-O)
- Silica (Si-O)
- Alumina (Al-O)
- Nitrogen-substituted zeolites (N-O)
- Framework aluminum (Al-O)
- Framework silicon (Si-O)
- Framework oxygen (O-O)

**Methods**

- **Experiments:** Nuclear magnetic resonance spectroscopy, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, physical adsorption
- **Calculations:** Cluster models

**Experimental Characterization:** Infrared

- Untreated HY zeolite (Si:Al = 6:1)
  - High-resolution physical adsorption
  - Extraframework aluminum simulations

**Experimental Characterization:** NMR

- Si-O-Si
- Al-OH-Si-OH-Al
- Al-OH-Si-OH-Al

**Cluster Calculations**

- **Central “target” silicon atom**
- **Change in magnetic moment (constant for each nucleus)**
- **Shielding constant (function of electron density)**
- **Calculated Energies of Amine Substitutions**
- **Calculated Infrared Spectra (with Experiment)**
- **Calculated 29Si NMR Spectrum**

**Chemical Shift Calculations**

- **ΔE = hγ(1 − σ)B**
  - **External magnetic field (constant)**
  - **Shielding constant (function of electron density)**

- **ΔE = ΔE_ref**
  - **ν = ν_ref**
  - **σ = σ_ref**
  - **δ = ΔE = ΔE_ref**

- **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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