

Synthesis, Characterization, and Simulation of Nitrogen-Substituted Y Zeolite Catalysts

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Introduction

Zeolites acting as acids form a class of extremely important catalysts that have replaced homogeneous catalysts in many chemical processes. The microporous nature of zeolites provides a unique, confined reaction environment for catalytic reactions, increasing selectivity. Extending the ability of zeolites to include base-catalyzed reactions has been an active area of research for over forty years, and is especially important in light of recent interest in biomass energy. Preparing zeolites that act as strong bases has proven to be difficult, however, and characterizing the resulting materials is a relatively new field. Most published spectral assignments rely on intuitive assignments of NMR or IR spectra, for example [1]. We seek to provide a definitive spectroscopic signature that corresponds to highly nitrogen-substituted zeolite Y, a material that should act as a strong base under appropriate conditions. We do this via a combination of synthetic techniques, physical adsorption, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, and ²⁹Si nuclear magnetic resonance.

Materials and Methods

Zeolites Y with an Si/Al ratio of 6 (Zeolyst CBV712) were treated under flowing ammonia in a fused quartz tube furnace. Ammonia (anhydrous, 99.9%, Merriam-Graves Corp.) was dried using a NaA/NaX mixture to remove all traces of water. Temperatures are measured and controlled by a thermocouple mounted in the center of the tube. The zeolite is degassed under flowing ultra-pure nitrogen at 110°C for two hours, then at 400°C for six hours. The gas flow is switched to ammonia, and the furnace is heated (1.5°C/min) to 750°C, which is held for 8h. The ammonia is again replaced with nitrogen, and the zeolite is cooled.

Calculations are performed with GAUSSIAN Development Version [2] on clusters containing 14 tetrahedral (Si/Al) atoms. Shielding constants are calculated using GIAO-B3LYP/cc-pVTZ [3]. Silicon NMR spectral integrals are computed by a quasi-random aluminum distribution according to Vega [12]. The nitrogens are distributed randomly among the Brønsted acid sites. Once those fill, the remaining nitrogens are distributed randomly amongst the remaining oxygen sites.

Results and Discussion

Silicon NMR calculations (Table 1) indicate peaks at -88, -67, and -45 ppm correspond to silicon nuclei near one, two, and three nitrogen atoms, respectively. Another

peak at -51 ppm corresponds to a silicon atom near three Al and two N atoms. These peaks align remarkably well with observed resonances in the measured spectra (Figure 1).

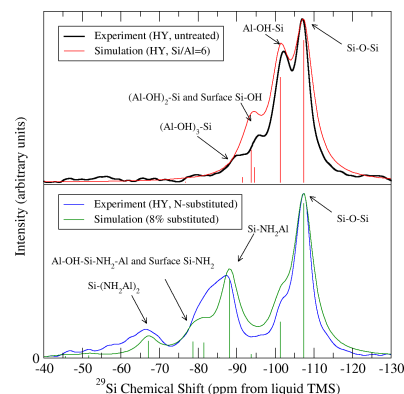


Figure 1. Measured and predicted NMR spectra of untreated HY zeolite (top) and HY zeolite treated for 8 h under ammonia (bottom). Sticks denote calculated chemical shift values.

The amount of substitution is consistent with elemental analysis: about 4% nitrogen by weight.

Significance

The results of these studies indicate that the treatment procedure produces nitrogen-substituted zeolites with very little loss in either crystallinity or microporosity. Screening of various methods suggests that silicon NMR is by far the most diagnostic method for nitrogen substitution. However, physical adsorption and/or X-ray are required as well, since the NMR spectrum can in select cases (not shown) resemble that of a substituted zeolite without maintaining high crystallinity and microporosity. The resulting materials are expected to be strong base catalysts.

References

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