Synthetic Methods to Incorporate Boron Heteroatoms in B-Al-MFI Zeolites to Independently Vary Crystallite Size and Al Distribution

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Introduction

The catalytic properties of zeolites depend on Brønsted acid site number and density, Brønsted acid strength, and confining micropore structure, and the location and distribution of Al atoms in MFI zeolite frameworks have been recognized to influence catalytic reactivity and selectivity [1]. The proximity of Al sites in paired (Al-O-(Si-O)$_{x=1,2}$-Al) or isolated (Al-O-(Si-O)$_{n>2}$-Al) configurations in MFI zeolites [2] has been linked to changes in rate and selectivity for a variety of reactions, including propene oligomerization [3]. The crystallite sizes and proton site density within MFI zeolites influence the rate, selectivity, and deactivation for propene oligomerization because longer diffusion paths and higher active site densities preferentially increase intracrystalline residence times of larger products [4]. These structural properties are typically correlated variables among zeolites prepared by hydrothermal crystallization, but can be independently varied through alternative synthesis methods [5]. We discuss such methods here, focusing on the addition of B heteroatoms into synthesis solutions containing ethylenediamine (EDA) and tetra-n-propylammonium (TPA$^+$) as organic structure directing agents (SDA).

Materials and Methods

In this study, two synthetic methods were used to influence the crystallite size and Al distribution (paired and isolated) in B-Al-MFI (Si/Al = 50) samples. One series (B-Al-MFI-TPA) was synthesized at varying Si/B ratio, using TPA$^+$ as the sole SDA (448 K, 4 d) [6]. A second series (B-Al-MFI-EDA) was synthesized at varying Si/B ratio, using TPA$^+$ and EDA as co-SDAs (443 K, 7 d). Temperature programmed desorption (TPD) of ammonia of B-Al-MFI after liquid-phase NH_4^+-exchange quantified all framework B and Al heteroatoms, but TPD performed after NH_4-form MFI were purged in flowing He (433 K), or after gas-phase NH_3 adsorption (433 K) onto H-form MFI, quantify only protons at framework Al atoms (H^+_{Al}) [5]. The quantification of paired Al sites in the framework of B-Al-MFI samples was performed using saturation Co^{2+} ion-exchange procedures (353 K). Characterization of carbon, nitrogen, and hydrogen (CNH) content was used to estimate EDA/TPA$^+$ ratios within as-made B-Al-MFI samples.

Results and Discussion

Temperature-programmed desorption (TPD) of ammonia following aqueous-phase NH_4^+-ion exchange quantifies both framework Al and B species in B-Al-MFI. The number of ammonia evolved after liquid-phase NH_4NO_3 saturation and subsequent purging in dry helium at 433 K agreed quantitatively with the amount of total Al measured by atomic absorption spectroscopy (H^+/Al = 0.75-1.06) on a series of B-Al-MFI samples (Fig. 1a). Among B-Al-MFI samples with varying Si/B ratio, B-Al-MFI-EDA samples contain >95% of their framework Al present as isolated sites. In contrast, B-Al-MFI-TPA samples in the same composition range contain 20-40% Al present in paired configurations (Fig. 1b). Previous studies have reported that the Al arrangement in the framework of zeolites can be influenced by using different organic SDAs in synthesis media [7] and through the addition of inorganic SDAs (Na^+) [8].

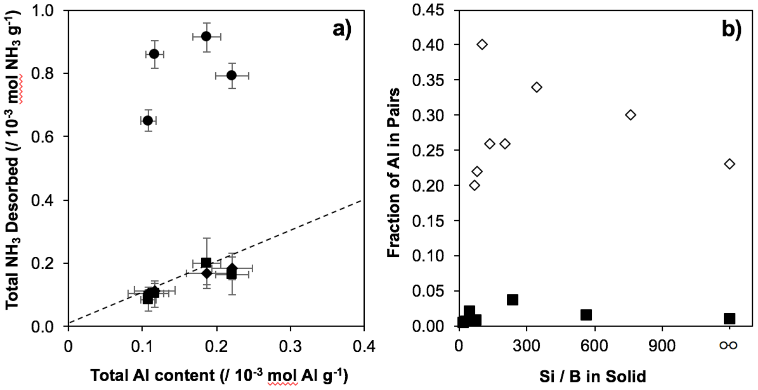

Figure 1. (a) NH_3 desorbed during TPD from B-Al-MFI samples after aqueous-phase NH_4NO_3 saturation (●) without He purge, (■) with He purge at 433 K, and (◆) gas-phase NH_3 saturation at 433 K. Dashed line represents parity. **(b)** The fraction of paired Al as a function of Si/B ratio in B-Al-MFI-TPA (open) and B-Al-MFI-EDA (closed)).

CNH elemental analysis was performed to determine the ratio of EDA/TPA$^+$ occluded within as-made B-Al-MFI samples, considering that the theoretical C/N ratios of TPA$^+$ and EDA are 12 and 1, respectively. The molar ratio of occluded EDA to TPA$^+$ is 4.15 in B-Al-MFI-EDA samples, while it is 12.04 in B-MFI-TPA samples. Thus, we surmise that EDA acts as an SDA that biases incorporation of Al in isolated positions within B-Al-MFI, and that the EDA / TPA$^+$ ratio occluded within as-made B-Al-MFI can serve as a predictor of framework Al distribution.

Significance

We propose that framework Al proximity and crystallite size can be varied independently by the choice of SDAs used and non-catalytic B heteroatoms incorporated during MFI zeolite synthesis. The ability to independently vary Al distribution and crystallite size in zeolites can expand the catalytic diversity of such materials used in acid-catalyzed reactions, and in particular for alkene oligomerization to heavier molecular weight compounds useful as chemicals and fuels.

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