One-step Dual Template Synthesis of Meso-/Microporous Zeolites with Tunable Textural and Catalytic Properties

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Introduction
The hierarchical meso-/microporous zeolites couple the catalytic features of microporosity and the improved mass transport consequences of mesoporosity in a single material, possessing the capacity of overcoming the mass-transfer constraints and the resultant low catalyst utilization in processing of bulky molecules. The synthesis and catalytic behavior of meso-/microporous zeolites have become the subject of intense research. Facile methods for synthesis of meso-/microporous zeolites are highly desired because they are important to keep potential applications for a zeolite structure as broad as possible [1].

In this talk, we report the synthesis and catalytic characterizations of meso-/microporous lamellar MFI zeolite materials, with a focus on tailoring their textural properties and catalytic performances using a simple one-step dual template synthesis strategy. By tuning the molar ratio of dual templates in the synthesis, the textural properties of the lamellar zeolite materials can be systematically tailored. A correlation between the synthesis recipe, textural property, and the catalytic performance was developed to guide the designed synthesis of meso-/microporous zeolite catalysts for desired performances.

Materials and Methods
Tetrapropylammonium hydroxide (TPAOH), a molecular template for producing traditional microporous MFI [2], and an organic surfactant C22H45-N+(CH3)2-C6H12-N+(CH3)2-C6H13, (C22-6-6), a template for crystallization of multi-lamellar MFI [3], were employed for the dual template synthesis of meso-/microporous lamellar MFI. The hydrothermal synthesis with a composition of 30Na2O/1Al2O3/100SiO2/10C22-6-6/TPAOH/4000H2O/18H2SO4, in which (x) was tuned from 0 to 20, was conducted at 150°C for 5 days [4]. The textural and acidity properties of the resultant zeolite catalysts were systematically characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, nitrogen and argon isotherms, elemental analysis, Si and Al nuclear magnetic resonance, Fourier transform infrared spectra of adsorbed pyridine, and dimethyl ether titration. Ethanol dehydration reactions and catalytic conversion of benzyl alcohol in mesitylene were performed to examine the catalytic performance of the synthesized zeolite samples under rigorously kinetic controlled conditions and space-demanding catalytic reaction conditions, respectively.

Results and Discussion
The morphology of the as-obtained meso-/microporous MFI zeolites changed from intertwined to house-of-cards-like and then to dense packing plates by increasing the concentration of TPAOH in the synthesis recipe. Argon adsorption-desorption isotherm data (Figure 1(A)-(B)) indicated that mesopore sizes of the samples increased to reach a maximum and then decreased by increasing x in the synthesis recipe. Ethanol activation under kinetic controlled conditions indicated that all these catalysts had similar intrinsic catalytic properties, while the catalytic conversion of benzyl alcohol in mesitylene results (Figure 1(C)) showed that activity of the samples had a volcano-shape trend with increasing the TPAOH concentration, which is consistent with the variation of the morphology and mesoporosity of the zeolite samples upon varying x values. Based on these obtained results, a linear dependence of the catalytic activity in diffusion constrained reaction on the textural property of the catalyst was established (Figure 1(D)). The consistency in the variation of morphology, mesoporosity, and catalytic activity with varying x values in the synthesis suggests TPAOH can be used as a secondary template to tailor the textural and catalytic properties of meso-/microporous lamellar MFI catalysts that are primarily guided by C22-6-6/TPAOH template.

Figure 1. (A) Ar adsorption-desorption isotherms, (B) pore size distributions, and (C) rate constants of benzyl alcohol reaction in mesitylene are systematically changed upon tuning the dual template molar ratios in the synthesis of meso-/microporous MFI zeolites. (D) shows the linear dependence between the alkylation rate and relative mesoporosity of the catalysts.

Significance
The present study advances the systematic characterization of meso-/microporous zeolites that are prepared by soft-template methods. The study also suggests one-step dual template synthesis strategy can be a general simple approach toward designed synthesis of hierarchical meso-/microporous zeolites with tailored textural and catalytic performances.

References