Seed-assisted Synthesis of Nanosized Al-rich MFI in the Presence of Zeolite Nanosheet Seeds for Bulky Molecule Catalysis

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1. Introduction

Crystalline microporous aluminosilicate zeolites are widely applied in catalysis due to their inherent microporosity and strong acidity. Downsizing the crystal size overcomes mass-transfer constraints and enhances accessibility into the internal active sites of the zeolite.[1)] Here, we showed organic structure directing agent-free synthesis of nanosized Al-rich MFI zeolites via hydrothermal conversion of FAU zeolite in the presence of self-pillared pentasil (SPP) nanosheet as a seed crystal.[2)] The structural properties of MFI zeolite synthesized using different starting materials were systematically examined and correlated with catalytic performance in the conversion of 1,3,5-triisopropylbenzene (TiPBz). We also investigated the crystallization behaviour of the obtained MFI zeolites.[3)]

2. Experimental

A typical nanosized MFI zeolite, denoted as TPA(Amor.), was synthesized hydrothermally using colloidal silica (HS-40) and sodium aluminate in the presence of 5 wt% of MFI zeolite synthesized with tetrapropylammonium hydroxide. The SPP(FAU) was obtained via hydrothermal conversion of dealuminated FAU zeolite (Si/Al = 22) in the presence of 5 wt% of prepared SPP zeolite nanosheets. A commercial MFI (Tosoh, HSZ-820NAA, Si/Al = 11.15) also served as a reference. TiPBz cracking of protonated zeolites was evaluated using a fixed-bed pulse reactor, and the catalyst stability was tested over 20 injections at 350 °C.

3. Results and Discussion

The synthesis parameters, including Si/Al, H_2O/Si, and NaOH/Si were optimized to achieve a pure MFI zeolite phase with high yield. TPA(Amor.) yielded pure MFI zeolite at a Na/Si ratio of only 0.3, while the SPP(FAU) facilitated MFI zeolite formation across a wider range of alkalinity, from 0.35 to 0.5.

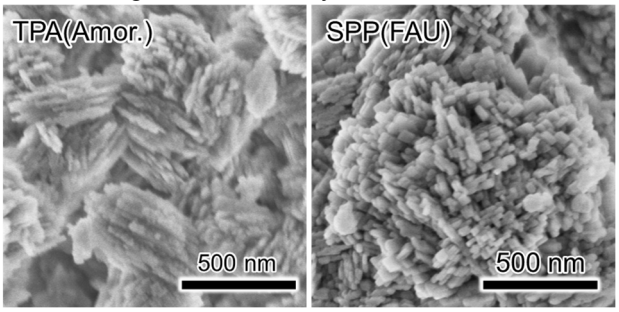

Fig. 1 SEM images of the obtained zeolites.

SEM images (Fig. 1) highlight clear morphological differences among the samples. SPP(FAU), TPA(Amor.), and commercial sample exhibit external surface areas of 68, 50, and 19 $m^2\ g^{-1}$, respectively. Notably, the SPP(FAU) showed the highest TiPBz conversion among the samples. During 20 pulse injections, SPP(FAU) also exhibited the highest stability, as the TiPBz conversion of SPP(FAU) decreased only from 89% to 72%, compared to a sharper decline for TPA(Amor.) (87% to 49%) and commercial sample (80% to 28%).

The formation pathway of zeolites was also investigated by varying the hydrothermal treatment time from 0 to 48 hours. Based on XRD, the relative crystallinity of TPA(Amor.) gradually increased with hydrothermal treatment time from 6 to 48 h, whereas SPP(FAU) showed a rapid increase in crystallinity from 40 to 48 h.

Fig. 2 shows that SPP(FAU) maintains higher solid yields (65.6–77.5%) than TPA(Amor.) (36.8–49.3%) despite of a higher alkalinity in the synthesis. This is due to the formation of stable intermediates in SPP(FAU) synthesis, which promotes abundant nucleation and rapid crystal growth. This unique crystallization on SPP(FAU) has an important role in creating its large intercrystalline voids and extended external surface area, giving the promoted catalytic cracking of TiPBz.

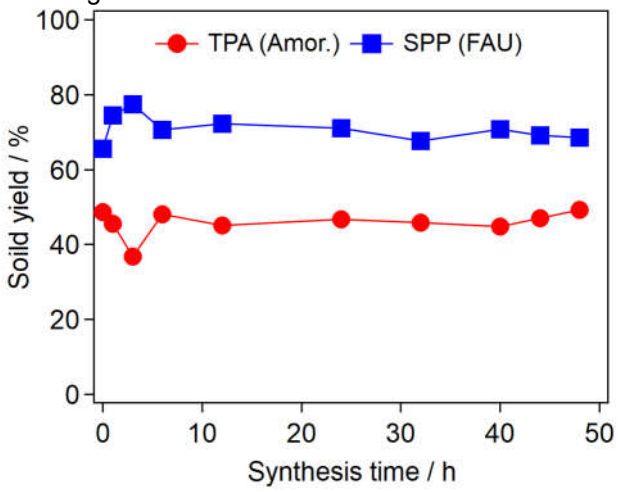

Fig. 2 Solid yields of zeolites obtained at different hydrothermal treatment times.

1) Li C. et al. *Angew. Chem. Int. Ed.*, **57**, 47, 15330, 2018.
2) Zhang X. et al. *Science,* **336,** 6089, 1684, 2012.
3) Amen T. et al. *Dalton Trans.*, **55**, 784, 2026.

