Synthesis of hierarchical TS-1 zeolites from a hydrolysis resistant polymer and their excellent catalytic performance in bulky molecules oxidation

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The traditional TS-1 zeolite is a typical microporous material, the diffusion of bulky molecules in TS-1 is greatly affected.[1] Besides, because of the highly hydrolyzable titanium source, the preparation of TS-1 requires complex synthesis conditions. Moreover, the difference in hydrolysis rate between the silicon source and titanium source tends to increase the difficulty of titanium insertion into the framework, and it is easy to generate extraframework Ti species during the synthesis. We propose a method of synthesizing hierarchical TS-1 from highly hydrolysis-resistant polymers containing titanium and silicon (Fig. 1a). This method completely solves the above problems and can conveniently and stably synthesize high-quality TS-1 free of extraframework Ti species. The TS-1 zeolite synthesized from the polymers exhibits excellent reaction performance in the oxidation of n-hexane and cyclohexene.

SEM and TEM images of the TS-1 zeolites synthesized with the polymers are displayed in Fig. 1b. TS-1 zeolites synthesized from polymers is a kind of nano domain aggregated MFI with a mean size around 300 nm. We further investigated the characterizations of the low-temperature N_2 physical adsorption (Fig. 1c). It revealed that TS-1 synthesized from polymers has a higher external surface area (134 m^2g^{-1}) than the samples synthesized by conventional methods (48 m^2g^{-1}).

The catalytic performance of TS-1 synthesized from polymers was evaluated by the oxidation reactions of n-hexane and cyclohexene. The results in Fig. 1e shows that the catalytic activity of TS-1 synthesized from polymers (TS-1-P) was much higher than that of TS-1 synthesized by conventional processes (TS-1-C), regardless of the oxidation reaction of n-hexane or cyclohexene.

Cyclohexene has a molecular dimension of about 0.5 nm. Thus, in contrast to n-hexane, cyclohexene suffers from strong diffusion constraints when diffusing in the 10-ring pores. Contrary to linear alkenes, molecular diffusion is the rate-determining parameter for the first oxidation reaction. The superiority in oxidation performance of TS-1 synthesized from polymers is mainly attributed to the sample had a high external surface area and hierarchical structure, which leads to the reactant being easily accessible to the active sites, especially for cyclohexene, which is a relatively larger molecule compared with n-hexane.

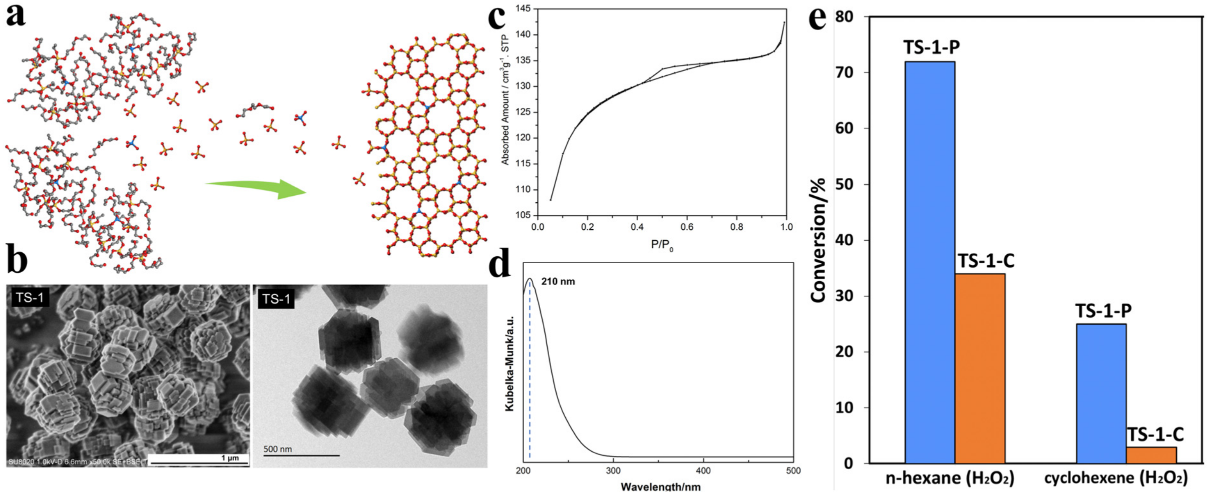

Figure 1: (a) Schematic illustration of synthesizing TS-1 zeolites. (b) SEM and TEM of TS-1-P. (c) N_2 adsorption-desorption isotherms of TS-1-P. (d) UV-Vis spectra of TS-1-P. (e) Oxidation of n-hexane and cyclohexene over TS-1-P. Reaction condition: cat., 50 mg; alkene and H_2O_2, 10mmol. CH_3OH, 10ml; 333K; 4h.

References

[1] W. B. Fan et al.: *Synthesis, crystallization mechanism, and catalytic properties of titanium-rich TS-1 free of extraframework titanium species.* J. Am. Chem. Soc. **130**, 10150-10164 (2008).

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