Synthesis of Porous Catalysts by Condensation Reaction of Silanol-modified Cage Siloxanes with Metal Species

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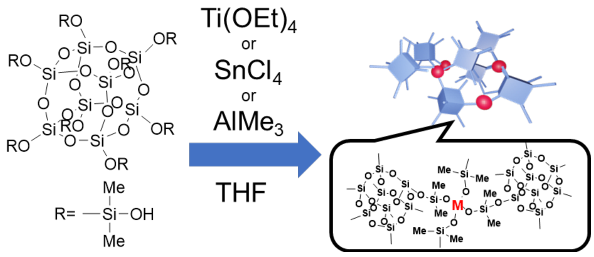
Silica-based porous catalysts, represented by zeolites, play a crucial role in various industrial applications.[1] Understanding their catalytic functions by controlling the environments of the active sites is an important issue. However, it is difficult to control the active sites by conventional synthesis methods including hydrothermal and aqueous sol–gel methods. We have focused on the condensation reaction between silanol groups and metal sources under non-aqueous conditions. In this study, siloxane-based porous catalysts were synthesized by the condensation reaction of silanol-modified cage siloxanes with metal species (Ti, Sn, and Al), and their catalytic activities were investigated.

Cage siloxane with dimethylsilanol groups was reacted with each of the three different metal species at the stoichiometric ratio in anhydrous THF solvent (Scheme 1). The first one is titanium ethoxide to form Si–O–Ti bonds.[2] The formation of the Si–O–Ti bonds and the isolation of TiO_4 units were confirmed by FT-IR and XAFS analysis. The second one is tin tetrachloride to form Si–O–Sn bonds. Because the Sn–Cl groups partially remained, the obtained compounds were treated with water or phosphate buffer to hydrolyze the Sn–Cl groups into Sn–OH groups. The use of phosphate buffer was effective to avoid the formation of SnO_2 and UV–Vis spectra showed that the Sn environment was isolated, although the Sn content in the sample significantly decreased. The third one is trimethylaluminum to form Si–O–Al bonds in the presence of triethylamine. ^{27}Al MAS NMR analysis confirmed that the aluminum was four-coordinated. N_2 adsorption/desorption analysis showed that all the samples had both micropores and mesopores. The catalytic reaction was investigated using the Ti-containing catalyst. The cyclohexene epoxidation reaction proceeded with a high selectivity. Thus, the reactions between silanol-modified cage siloxanes and metal precursors in the non-aqueous solvent resulted in the formation of porous networks via the Si–O–M bonds. Additionally, the isolation of the metal sites in the frameworks was achieved. This simple building block approach to preparing porous materials will contribute to the production of metalosiloxane-based catalysts with controlled metal environments.



Scheme 1 Synthesis of the metalosiloxane catalyst

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