Synthesis of porous materials through titanium-crosslinking of cage siloxane

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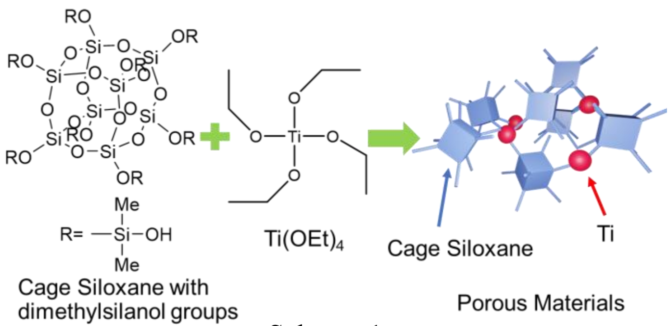
Introduction Siloxane-based nanoporous materials have a wide range of applications.[1)] Cage siloxanes have attracted much attention as building blocks to provide new design that has not been achieved in conventional silica-based porous materials such as zeolites.[2)] In this study, we synthesized microporous titanosiloxane materials with controlled Ti environments by the cross-linking reaction between cage-type siloxane molecules modified with dimethyl silanol groups and titanium tetraethoxide (Scheme 1).

Experimental Cage siloxane with dimethylsilanol groups was reacted with titanium tetraethoxide in a THF solvent at a molar ratio of Si/Ti = 4 under nitrogen atmosphere. Immediately after the addition of titanium ethoxide to a solution of cage siloxane, the mixture gelled. The gel was stirred at 40 °C to evaporate the solvent, and a white powder was obtained. The obtained powder was heat-treated at 250 °C for 1 d in air.



Scheme 1

Results and Discussion The powder X-ray diffraction pattern of the product showed a broad peak (d = ca. 1.2 nm). The FT-IR spectrum showed the band assigned to Si–O–Ti vibration at 920 cm^{-1}, indicating the formation of Si–O–Ti bonds by the reaction of SiOH groups and TiOEt groups. Solid-state ^{29}Si MAS NMR analysis confirmed that the signal arising from dimethylsilanol groups (–10 ppm) disappeared and a new signal appeared at –17 ppm. The retention of the cage siloxane unit (–109 ppm) was also confirmed. The ^{13}C CP/MS NMR spectrum showed no signals due to unreacted ethoxy groups (at 18 ppm and 59 ppm) after the heat treatment. Nitrogen adsorption-desorption isotherms showed that the BET area increased from 46 m^2/g to 370 m^2/g by the heat treatment, indicating the development of porosity. These results indicate the formation of a novel nanoporous material by cross-linking of cage siloxanes with titanium species.

1) J. Liang *et al*., *Adv. Mater.* **2017**, *29*, 30.
2) A. Shimojima, K. Kuroda, *Molecules* **2020**, *25*, 524.