Synthesis of Sn-containing siloxane-based porous materials using cage siloxane as a building block

([1]*Graduate School of Advanced Science and Engineering, Waseda University,* [2]*Kagami Memorial Research Institute for Materials Science and Technology, Waseda University*)
○Takuya Hikino,[1] Koki Fujino,[1] Kazuyuki Kuroda,[1,2] Atsushi Shimojima[1,2]
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Introduction Double four-membered ring siloxanes (cage siloxanes) have attracted much attention as building blocks for silica-based nanomaterials because they can be modified with a variety of functional groups. [1)] Crosslinking these molecules with metal atoms can generate porous catalysts with isolated metal sites. Recently, we reported the synthesis of porous materials with isolated titanium (Ti) sites, which are active in epoxidation reactions, by the reaction of cage siloxane and titanium ethoxide.[2)] Tin (Sn) is also interesting as an active site because Sn-containing zeolites are useful in sugar isomerization, reduction of ketone and aldehyde.[3)] In this study, we synthesized Sn-containing porous materials by cross-linking cage siloxane with Sn species.

Experimental Cage siloxane with dimethylsilanol groups was reacted with tin tetrachloride in a THF solvent at a molar ratio of Si/Sn = 8 under nitrogen atmosphere. Immediately after the addition of tin tetrachloride to a solution of cage siloxane, a clear gel-like precipitate was formed. The gel was stirred at 40 °C under vacuum condition to evaporate the solvent to obtain a powder. (**Sn-D4R**) The powder was treated with water at room temperature for 1 d to hydrolyze the unreacted chloride groups. (**Sn-D4R-water**)

Results and Discussion The FT-IR spectrum of **Sn-D4R** showed the disappearance of the Si–OH groups (888 cm^{-1}), suggesting that Si–OH groups of cage siloxane reacted with $SnCl_4$. The XRD pattern of **Sn-D4R** showed a broad peak (d = 1 nm) and some sharp peaks, and the sharp peaks disappeared after the water treatment. The XPS spectrum of **Sn-D4R** suggested that a part of chloride groups remained in the material. The ^{119}Sn MAS NMR spectrum of **Sn-D4R** showed the signals at −605 and −620 ppm, suggesting that the Sn species were in a six coordinated state. The nitrogen adsorption–desorption isotherms showed the BET area increased from 387 m^2/g to 613 m^2/g by the water treatment.

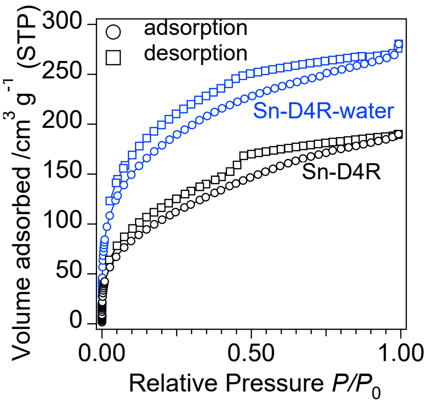

Fig. 1 N_2 adsorption-desorption isotherms of **Sn-D4R** and **Sn-D4R-water**

References 1) A. Shimojima, K. Kuroda, *Molecules* **2020**, *25*, 524. 2) T. Hikino *et al.*, *Chem. Lett.* **2021**, *50*, 1643. 3) J. Přech *et al.*, *Chem. Soc. Rev.*, **2018**, *47*, 8263.

