

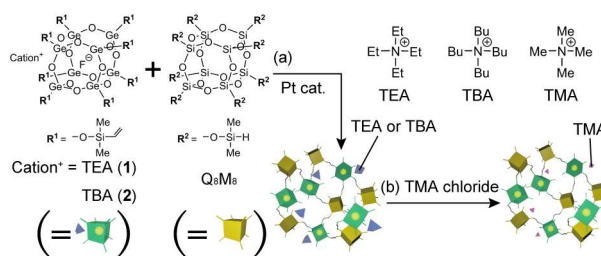
Preparation of ion-exchangeable porous materials via cross-linking of cage germanoxanes encapsulating fluoride ions

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【Introduction】 Inorganic cage compounds are useful as nano-building blocks for porous materials because they are rigid and can be modified with various functional groups at the corners.¹⁾ For further functionalization, the use of the cavity in the cage structure is of interest. It is known that double 4-ring (D4R) cage siloxanes²⁾ and germanoxanes³⁾ can encapsulate fluoride anions inside the cages. The exchange of counter cations with various cations is expected to be useful in controlling the nanostructures of the porous materials constructed with cage compounds and their applications. Here, we report on the exchange of cations not only in the as-prepared discrete cage germanoxane but also in the cross-linked porous materials. Furthermore, the difference in the porous structures due to the different cations in the porous materials was examined.

【Experimental】 A dimethylvinylsilylated cage germanoxane containing a fluoride anion inside the cage and a tetraethylammonium (TEA) cation outside (**1**) was synthesized according to our previous report.⁴⁾ **1** and tetrabutylammonium (TBA) bromide were stirred in toluene, forming a cage germanoxane with a TBA cation (**2**). **1** and **2** were cross-linked with dimethylsilyl-modified cage siloxane (Q₈M₈) by a hydrosilylation reaction (Scheme 1a). The products were added to an ethanol solution of tetramethylammonium (TMA) chloride to exchange the cations (TEA or TBA) with TMA cation (Scheme 1b).



Scheme 1. Preparation of porous materials from cage germanoxanes and their cation exchange.

【Results and discussion】 Synthesis of **1** and **2** and the formation of their cross-linked networks with Q₈M₈ were confirmed by FT-IR and NMR spectra. The N₂ adsorption–desorption isotherms indicated that the cross-linked networks were micro and mesoporous. ¹³C MAS NMR analyses confirmed that these porous solids underwent almost complete cation exchange with TMA chloride. The N₂ adsorption–desorption measurement showed the increase in the Brunauer–Emmett–Teller (BET) area and pore volume upon cation exchange with TMA cations. These results suggest that the exchange of the counter cations of the porous materials prepared from the cage germanoxanes is effective to tune the pore characteristics.

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