

Synthesis of Highly Ordered Mesoporous Materials from a Layered Polysilicate

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The ion exchange reaction of interlayer Na⁺ ions of a layered polysilicate kanemite with alkyltrimethylammonium ions, followed by calcination, gives highly ordered mesoporous materials with a hexagonal array of uniform channels.

The preparation of micro- and meso-porous materials from layered substances has attracted increasing attention because of their possible use as catalysts, molecular sieves and hosts for inclusion compounds, since they can be designed to have larger pore sizes than zeolites. The synthetic method used most frequently is the so-called pillaring method which means the insertion of robust inorganic species as pillars between layers.¹

One of the authors has proposed a quite different strategy from pillaring for the preparation of porous materials from layered silicates.² The method consists of interlayer cross-linking of a layered silicate in the ion exchange reaction with organic cations. During the ion exchange (typically with alkyltrimethylammonium ions), the silicate layers of the single-layered polysilicate (kanemite,³ NaHSi₂O₅·3H₂O) are condensed to form three-dimensional silicate networks, which is confirmed by ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) and transmission electron microscopy (TEM). By calcination, the silicate-organic complexes were converted to micro- and meso-porous materials with uniform pore-size distributions. The specific surface areas of the calcined products are 900 m² g⁻¹ and the pore size can be altered by the variation of the alkyl chain length of the alkyltrimethylammonium ions used. Recently, Kresge *et al.*⁴ have reported the synthesis of ordered mesoporous molecular sieves (MCM-41) by the calcination of aluminosilicate gels in a concentrated solution of alkyltrimethylammonium ions. A hexagonal array of uniform channels has been identified by TEM and diffraction methods. They have proposed a liquid-

crystal 'templating' mechanism for the formation of ordered mesoporous materials.

The synthesis of highly ordered mesoporous materials from layered materials has its own advantages based on the molecular design of nanoscale modifications of layered host materials. One of the authors has already proved the applicability of trimethylsilylation for the kanemite-organic complexes to control the pore-size distribution more precisely.⁵ In addition, we have succeeded in giving acidity to the mesoporous materials by incorporation of Al³⁺ in the SiO₂ framework.⁶

Here, we report the successful formation of highly ordered mesoporous materials derived from layered polysilicate kanemite by optimizing the reaction conditions of the ion exchange reaction described previously.²

The starting material for kanemite was slightly changed from that reported previously.² A hydrated sodium silicate glass was used in this study, the ratio of SiO₂/Na₂O being adjusted to 2.00. Then the hydrated glass was calcined at 700 °C and immersed in water. The conditions for the ion exchange reaction were also modified. 50 g of kanemite was dispersed in an aqueous solution of hexadecyltrimethylammonium chloride (1000 ml, 0.1 mol dm⁻³) and the mixture was heated at 70 °C for 3 h with stirring. After cooling to room temperature, the pH of the suspension was adjusted to 8.5 with 2 mol dm⁻³ HCl. The resulting product was filtered, washed with water repeatedly, and air-dried to yield a silicate-organic complex. The product was calcined in air at 700 or 1000 °C for 6 h to remove the organic fraction.

The characteristic powder X-ray diffraction (XRD) peaks due to kanemite disappeared in the patterns of the silicate-organic complex and the calcined products (Fig. 1). However, for the silicate-organic complex and the calcined products, several peaks in the low angle region were observed (Fig. 2), which were not clearly detected in the previous report.² These peaks could be indexed as a hexagonal cell with $a = 44.1, 43.5$ and 39.8 \AA ($2d_{100}/\sqrt{3}$) for the organic complex and the calcined products at 700 and 1000 °C, respectively.

The ^{29}Si MAS NMR spectrum of kanemite showed a sharp peak at $\delta -97.3$ due to a Q^3 unit [$\text{OSi}(\text{OSi})_3$], indicating the single layered structure.[†] The spectrum of the silicate-organic complex showed two peaks due to a Q^3 unit ($\delta -99.9$) and a Q^4 unit [$\text{Si}(\text{OSi})_4$, $\delta -109.1$]. The appearance of the strong Q^4 peak clearly indicates the formation of a 3D SiO_2 network from layered kanemite. The ^{29}Si MAS NMR spectrum of the calcined product (700 °C) exhibited a definite Q^3 peak at $\delta -100.0$ with an overlapped Q^4 peak at $\delta -108.5$. These findings based on NMR are quite consistent with the previous paper² and the resolution between Q^3 and Q^4 in the spectrum of the calcined product becomes clearer in this case.

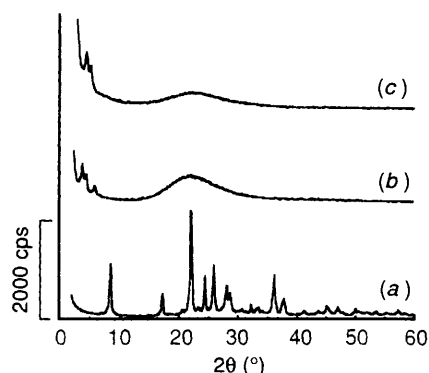


Fig. 1 X-Ray powder diffraction patterns of (a) kanemite, (b) silicate-organic complex and (c) calcined product at 1000 °C. These spectra were recorded on a Rigaku RAD-B diffractometer with $\text{Cu-K}\alpha$ radiation.

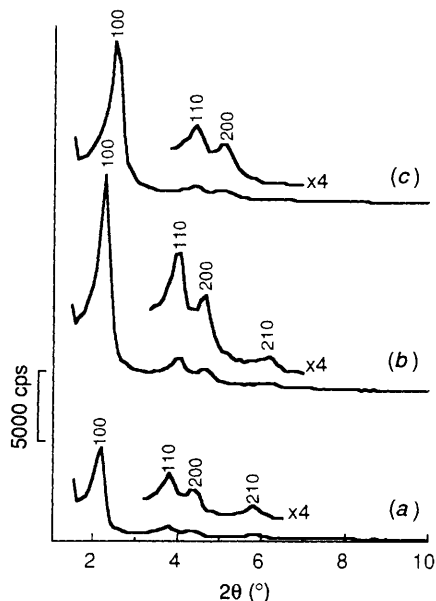


Fig. 2 X-Ray powder diffraction patterns in low angle region of (a) silicate-organic complex, (b) calcined products at 700 °C and (c) 1000 °C. These spectra were also recorded on a Rigaku RAD-B diffractometer with $\text{Cu-K}\alpha$ radiation.

[†] For Q^n , Q represents a silicon atom bonded to four oxygen atoms forming a tetrahedron and n indicates connectivity *i.e.* the number of other Q units attached to the SiO_4 tetrahedron.

Thermogravimetric analysis of the silicate-organic complex showed that the organic content was 53.3wt%, indicating that 0.24 mol of hexadecyltrimethylammonium ions per 1 mol of SiO_2 were occluded in the complex. The organic content is much larger than that in the previous paper.²

The transmission electron micrographs (Fig. 3) of the silicate-organic complex clearly showed the regular array of channels. The diameter of the channels is 3 nm. This TEM observation and the XRD results for the present materials are quite similar to those of MCM-41.⁴ However, the scanning electron micrograph (SEM) (Fig. 4) indicates that the morphology of the original kanemite is preserved for the silicate-organic complex. The morphology of the present materials is quite different from that of MCM-41 which shows a hexagonal prism.

The adsorption isotherms of the calcined products for N_2 adsorption at -196 °C showed type IV isotherms, suggesting the presence of mesopores. The mean pore diameters were 2.8 and 2.2 nm for the calcined products at 700 and 1000 °C, respectively. The Brunauer-Emmett-Teller (BET) surface areas were 1100 and 1070 $\text{m}^2 \text{ g}^{-1}$ for the calcined products at 700 and 1000 °C, respectively, indicating an excellent thermal stability of the calcined products in air. The optimization of the reaction conditions in the present system resulted in a further increase in the specific surface areas.

A schematic model for the formation of the mesoporous materials from kanemite is shown in Fig. 5. The silicate layers of kanemite can wind around the exchanged alkyltrimethylammonium ions. This causes the condensation of silanol groups on the adjacent silicate layers of kanemite, since the silicate layers have the flexibility to wind due to its single layered structure.

The preparative conditions employed in the present study are quite different from those for MCM-41. The most obvious difference is the concentration of the alkyltrimethylammonium ions employed. In order to prepare MCM-41, a 26wt% hexadecyltrimethylammonium chloride solution was used,



Fig. 3 Transmission electron micrograph of silicate-organic complex. This micrograph was obtained on a JEOL JEM-200CX at an accelerating voltage of 200 kV.

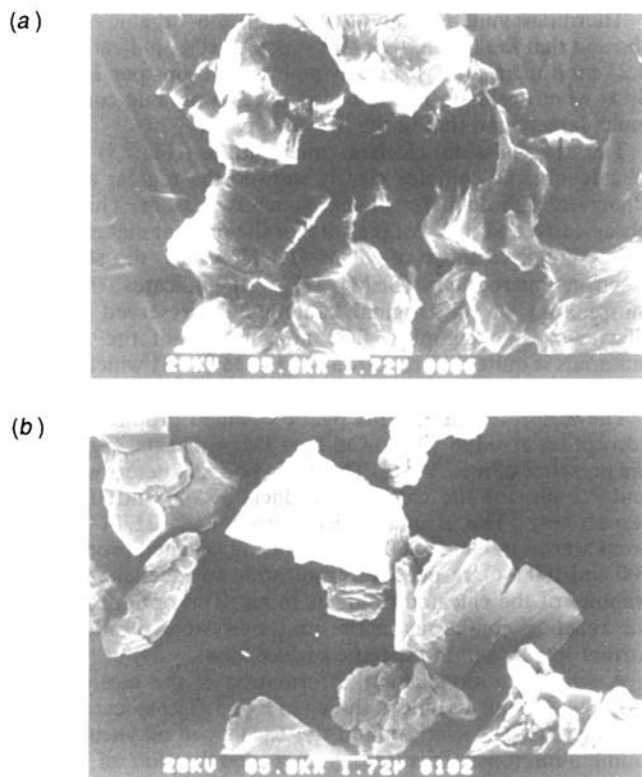


Fig. 4 Scanning electron micrographs of (a) kanemite and (b) silicate-organic complex. These micrographs were obtained on a Akashi SHIGMA-V.

whereas only a 3.2wt% aqueous solution was employed in this study. The highly concentrated surfactant solution is necessary for the formation of MCM-41 because an ordered micelle is essential for a proposed liquid-crystal 'templating' mechanism.

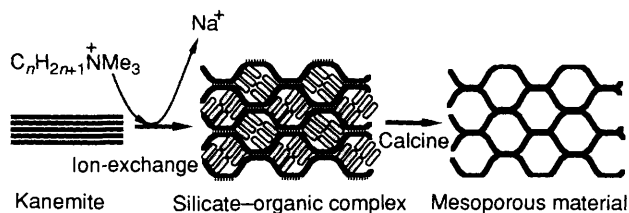


Fig. 5 Schematic model for the formation of the mesoporous material from kanemite

The present ion exchange reaction takes only 3 h at 70 °C. The reaction time is much shorter than in the previous report.² Although an autoclave is necessary for MCM-41, we can synthesize similar mesoporous materials in an open-vessel. The arrangement of mesopores reported previously may be somewhat disordered, which is attributable to an insufficient cation exchange of Na^+ for organic cations.

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