New Silica-pillared Material prepared from the Layered Silicic Acid of Ilerite

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A new siliceous porous material of high BET surface area is derived from an intercalation of octylamine and tetraethylorthosilicate into the layered silicic acid of ilerite; the resultant pillared material has a BET surface area of over 1000 m^2 g^{-1} at 600 °C and 580 m^2 g^{-1} even at 900 °C.

Pillaring of layered inorganic materials by silica compounds is an attractive method of obtaining porous materials of high thermal stability for use as molecular sieves, catalysts and other applications, since the size of the pores is thought to be easily controlled by the height of the pillars between layers.[1-3]

Layered silicic acids, which are easily derived from layered silicates[4] such as ilerite (Na$_2$Si$_8$O$_{17}$·nH$_2$O),[5,6] magadiite (Na$_2$Si$_{14}$O$_{29}$·nH$_2$O), kenyaite (Na$_2$Si$_{22}$O$_{45}$·nH$_2$O) and kanemite (NaHSi$_2$O$_5$·3H$_2$O) by proton exchange, are found to be very useful hosts in the formation of pillared materials because of the presence of reactive silanol groups on their interlayer surfaces.[6-8] Silanol groups, which are acidic enough to allow proton transfer to an amine group,[9] are oriented in a crystallographically regular manner on the interlayer surface.[7] Consequently, such groups will easily provide a porous material with a high degree of uniformity during pillar formation.[10,11] Yanagisawa et al.[12] reported high surface area mesoporous silicas using kanemite by ion exchange of the interlayer ions with alkyltrimethylammonium ions. Inagaki et al.[13] improved the synthetic method and prepared highly ordered mesoporous materials and proposed a 'folded sheets' formation mechanism. Landis et al.[10] have used interlayer hydrolysis of tetraethylorthosilicate (TEOS) upon primary-organoammonium-exchanged forms to prepare silica-pillared materials of a wide variety of layered metal oxides including layered silicic acids of magadiite and kenyaite. An appropriate combination of host and guest compounds is important to achieve a successful result.

In the present work, we report a new siliceous porous pillared material with high BET surface area and high thermal stability by using H-ilerite (layered silicic acid of ilerite) as a host. Ilerite, which is also commonly known as octosilicate,[6] was synthesized at 105 °C over 9 days from a suspension of silica gel and NaOH solution using a molar ratio of SiO$_2$: NaOH : H$_2$O = 1 : 0.5 : 7. H-ilerite was then prepared at room temp. over 6 h by treatment of ilerite with 0.2 mol dm^{-3} HCl. At the preswelling step, using organic compounds in the conventional procedure, a host compound is usually intercalated with an aqueous solution of an organoammonium salt or amine,[10] and the resultant composite is obtained as a gel.[11] By contrast, we used neat octylamine as solvent in the absence of water and suspended the host compound in the liquid amine throughout the reaction. Thus silicic acid (1 g) was dispersed in octylamine (8 ml) at room temp. for 24 h; octylamine (20 ml) and TEOS (50 ml) were added to the mixture and allowed to react at room temp. for 24 h with stirring. The resultant product was centrifuged and air-dried at room temp. for 48 h. The final white silica-pillared product was obtained by calcination in air above 600 °C for 1 h.

Fig. 1 shows the X-ray diffraction (XRD) patterns of intercalated material of H-ilerite with octylamine and TEOS, and of the calcined products, together with the XRD patterns of ilerite and H-ilerite. The XRD pattern of H-ilerite is dramatically changed upon intercalation, as shown in Fig. 1(a) (ii) and (iii). The broad peak at 2θ ≈ 15–30° of (iii) suggests a decrease of crystallinity of the product due to layer displacement along the a and b axes. The calcined products exhibit reflections corresponding to basal spacings of ca. 3.3 nm (2θ 2.55°) in the temperature range 600–900 °C. Since the layer thickness of H-ilerite is approximately 0.74 nm,[4-6] the gallery height of the products can be calculated as 2.56 nm. Further evidence for the

expansion of the basal spacing by the silica-pillared product comes from direct examination of the lattice fringe image spacing by transmission electron microscopy. Scanning electron micrographs revealed no morphological change upon calcination at < 800 °C, and showed the same thin square platey crystals as that of original ilerite. However, at 900 °C large parts of the crystals did not retain their shape and their surfaces lost the smoothness of the original platey morphology. From the disappearance of the basal reflection [Fig. 1 (vii)], calcination at 1000 °C led to the destruction of the porous framework.

The N$_2$ adsorption–desorption isotherms at −196 °C on the products and the corresponding t curves are shown in Fig. 2. The micropore parameters such as micropore surface area (S_{int}), mean pore diameter ($2t$) and pore volume (V), evaluated from adsorption isotherms by the t-plot method[14,15] are summarized in Table 1, with BET surface area (S_{BET}). S_{BET} for the product calcined at 600 °C is 1152 m^2 g^{-1}, and decreases with increasing calcination temperature. Since H-ilerite has a S_{BET} of
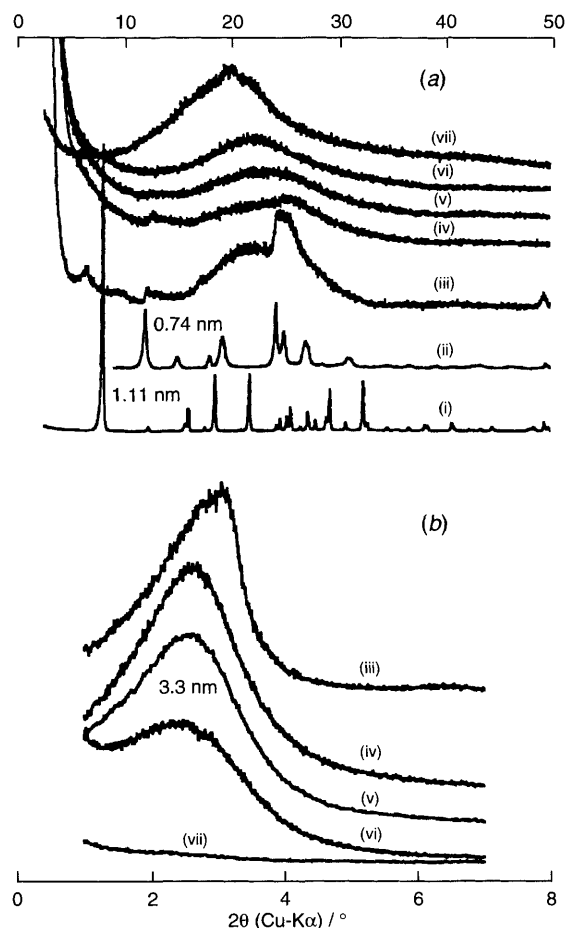

Fig. 1 (a) X-Ray powder diffraction patterns of (i) ilerite, (ii) H-ilerite, (iii) intercalated material of H-ilerite with octylamine and TEOS, and (iii) calcined at (iv) 600, (v) 700, (vi) 900 and (vii) 1000 °C. (b) Expansion of 2θ = 0–8° region. These patterns were recorded on a Rigaku RU300 diffractometer with Cu-Kα radiation. Numerical data indicate basal spacings.

21 m² g⁻¹ which is due exclusively to adsorption on *nonmicroporous* external surfaces, the silica-pillared products exhibit markedly larger S_{BET}, most of which is due to the presence of micropores < 2 nm in diameter. The MP plots[15] for the calcined products indicated a narrow micropore size distribution around the mean pore diameter of *ca.* 1 nm and only a slight decrease of diameter with increasing calcination temperature. Based on the gallery height of *ca.* 2.6 nm as
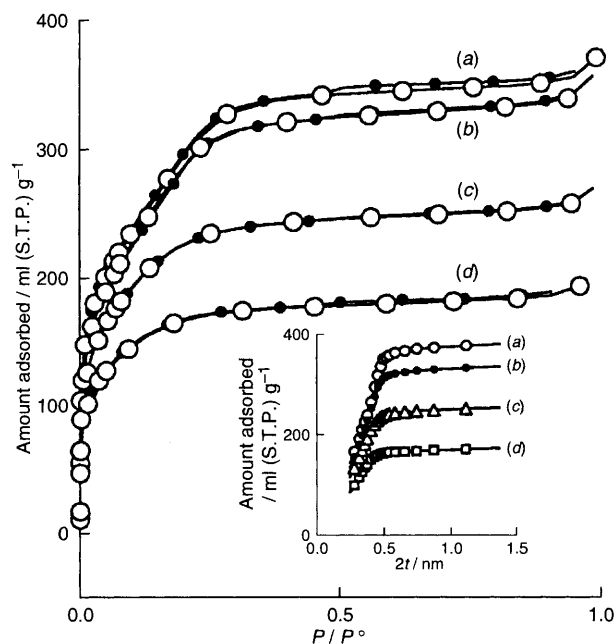

Fig. 2 N_2 adsorption (○)–desorption (●) isotherms at −196 °C for product calcined at (*a*) 600, (*b*) 700, (*c*) 800 and (*d*) 900 °C. The inset shows the corresponding *t* curves. After calcined samples were outgassed at 110 °C for 2 h, these isotherms were obtained using BELSORP28.

Table 1 Micropore parameters of silica-pillared products at various temperatures

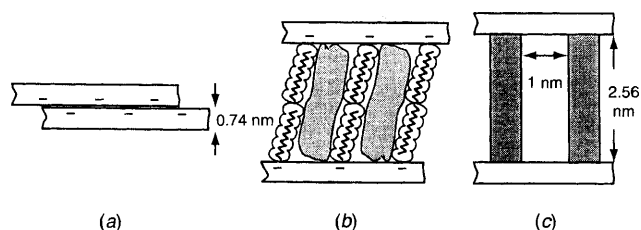|	600 °C	700 °C	800 °C	900 °C
S_{BET}/m² g⁻¹	1152	1011	828	586
S_{int}/m² g⁻¹	1133	992	814	573
V/ml g⁻¹	0.56	0.50	0.38	0.25
$2t$/nm	1.14	1.13	0.99	0.88

Fig. 3 Schematic formation process of silica-pillared porous material using the pillaring procedure of H-ilerite with octylamine and TEOS

determined from XRD analysis and TEM observation, the mean pore diameter of around 1 nm obtained from the N_2 adsorption isotherm corresponds to the distance between the pillars. The amount of C_6H_6 adsorbed for the products calcined at 600 °C and 800 °C were three times and twice as large, respectively, as that of a commercial faujasite-type zeolite with 1 nm micropore size calcined at 600 °C while the pores of this zeolite were found to completely collapse upon calcination at 800 °C.

A possible model for the formation process of the silica-pillared porous material is shown in Fig. 3. H-ilerite is thought to contain closely packed silicate sheets due to overlapping of two adjacent layers [Fig. 3(*a*)], on the basis of the reflections corresponding to the basal spacing and the width of the silicate sheet.[4–7] In order to induce pillaring of silica, octylamine is intercalated into the silicic acid sites in the first stage, leading to an increase of the basal spacing due to the formation of an octylamine–octylammonium bilayer.[9] Some of the octylamine is then replaced by TEOS in the organic–pillar precursor [Fig. 3(*b*)]. Calcination of the remaining organic substances and by-products from hydrolysis of TEOS leads to the formation of pores between the layers [Fig. 3(*c*)].

In conclusion, new siliceous porous materials with high BET surface area, 1152 m² g⁻¹ upon calcination at 600 °C and 586 m² g⁻¹ even at 900 °C, were obtained by intercalation of octylamine and TEOS into H-ilerite. These silica-pillared products, with *ca.* 1 nm distance between the pillars and 2.6 nm gallery height, may have the best thermal stability and the highest adsorption volume of all silica-pillared compounds prepared from other layered materials by pillaring. This porous material could be find use as a new functional material for cases where zeolites are not effective in a catalysis or as molecular sieves.

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