Synthesis of Thermally Stable Silica-Pillared Layered Manganese Oxide by an Intercalation/Solvothermal Reaction

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Silica-pillared layered manganese oxide with high surface area and high thermal stability was first synthesized from birnessite(H)-type manganese oxide by intercalation of octylamine followed by tetraethyl orthosilicate (TEOS) molecules and then by solvothermal treatment in TEOS liquid. Layered phases of manganese oxide with basal spacings of 2.01 and 2.43 nm, respectively, were obtained for each intercalation reaction. The Si/Mn molar ratio increased from 0.63 to 0.84 by the solvothermal treatment, but the basal spacing (2.44 nm) of the layer barely increased. The increase of silica content stabilized the pillared structure against thermal treatment. Porous layered manganese oxides were obtained by heating the silica-pillared material at appropriate temperatures. The manganese oxide sample obtained at 400 °C had a BET surface area of 260 m^2/g with a gallery height of about 1.6 nm between layers.

Introduction

It is well-known that porous oxides with pore radii larger than 0.3 nm can be obtained by a pillared reaction, using layered metal oxides. The oxide pillars prevent the interlayer spaces from collapsing and result in stable microporous structures with high surface areas.[1−3] There are a number of transition metal oxides and their oxysalts that are interesting candidates for host layers, which are used to synthesize porous pillared materials with different pore structures and properties. The pillared compounds of titanates,[4,5] zirconium oxide and phosphates,[6−9] niobium oxide,[10] and bismuth molybdic acid[11] with layered structures have been studied extensively in terms of synthesis methods, properties, and their applications. TEOS is one of the commonly used silica sources; it has been used for pillaring other layered hosts such as magadiite and zirconium phosphate.[2,10,12,13] Other sources of silica have also been used as pillar precursors.[14,15] The obtained silica-pillared materials have high surface area and thermal stability.

Layered manganese oxides exhibit excellent cation exchange and molecule adsorptive properties; they can be used as molecular sieves, battery materials, catalysts for the oxidation−reduction process, and precursors to synthesize many porous manganese oxides with tunnel structures.[16−20] However, there have been relatively few studies on the pillaring reaction of layered manganese oxides or manganese-related oxides.[21−24] Pillared man-

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ganese oxides with Keggin ions or organic molecules as guest molecules have been reported, but they have relatively small surface areas and low thermal stability. Furthermore, some of the results reported do not show clear evidence for the formation of a pillared structure. The difficulty in forming a pillared structure is caused by the high surface charge density of the interlayer and/or by the thin layer characteristic of manganese oxide sheets.[25] The high charge density causes a strong attractive force between the interlayers, making it difficult for guest ions to intercalate. Layered manganese oxides consist of a layer of MnO_6 octahedra, in contrast to the three-layered structure of montmorillonite; therefore, the manganese oxide sheet is more flexible and less stable against heat treatment.

The expansion of the interlayer space by preintercalation of large organic molecules is an effective method to enable the smooth intercalation of pillared materials, preserving the layered structure.[3,6] By the two-step intercalation of octylamine followed by TEOS into a birnessite(H)-type manganese oxide, we have prepared porous manganese oxides pillared with silica.[26] The obtained material calcined at 200 °C had a large BET surface area, but its thermal stability was not so good; the porous structure was destroyed if heated above 300 °C. Its applications to adsorbents and catalysts are limited. However, we have found that solvothermal treatment can be used for material synthesis to produce good porosity and thermal stability. The present paper describes the synthesis of thermally stable silica-pillared manganese oxide by solvothermal treatment in TEOS liquid after the intercalation reaction. The solvothermal treatment resulted in the increase of silica amounts in the interlayer. Subsequent heat treatment gave microporous manganese oxide with good porosity and thermal stability.

Experimental Section

Preparation Method. The starting material, layered manganese oxide (birnessite), was prepared by the method reported in the literature.[27] A mixed solution of 0.6 M NaOH and 2 M H_2O_2 was poured quickly into a 0.3 M $Mn(NO_3)_2$ solution and stirred for 25 min. The precipitate was then subjected to hydrothermal treatment at 150 °C for 16 h in a 2 M NaOH solution. The precipitate obtained had a chemical formula of $Na_{3.7}Mn_{12}O_{25}\cdot 9H_2O$. It was treated with a 0.1 M HCl solution at room temperature for 3 days to produce a protonated sample with the chemical composition of $Na_{0.21}H_{3.49}Mn_{12}O_{23}\cdot 9.5H_2O$, and it is abbreviated as BirMO(H).

Sample BirMO(H) (2 g) was mixed with a 1.5 M octylamine solution and stirred at room temperature for a week. The solution was separated by centrifugation, and the precipitate was washed with ethanol (40 cm^3) three times and dried at room temperature. The octylamine-intercalated sample is hereafter abbreviated as OILMO. Sample OILMO (1.5 g) was added to 150 cm^3 of TEOS liquid (Wako Chemicals Co.) and stirred at 65 °C for a week. After the reaction, the solution was filtered and the precipitate was dried at room temperature for 2 days. The obtained material is abbreviated as SPLMO.

Sample SPLMO (1 g) was then soaked in 80 cm^3 of TEOS liquid in a Teflon-lined stainless steel vessel and autoclaved at 140 °C under autogenous pressure for 48 h. The obtained material was washed with ethanol and then dried for 2 days at room temperature. The silica-pillared layered manganese oxide after solvothermal treatment is hereafter abbreviated as SPLMOT. Sample SPLMOT was heat-treated in air at different temperatures for 2 h; the obtained materials are abbreviated as SPLMOT (200), etc., where the number in parentheses indicates the heating temperature.

Chemical Analyses. The Mn contents of the samples were determined by atomic absorption spectrometry after they were dissolved in a mixed solution of HCl and H_2O_2. The Si contents were determined using an inductively coupled plasma (ICP) spectrometer after they were melted in a mixture of Na_2CO_3 and H_3BO_3 (sample:Na_2CO_3:H_3BO_3 = 1:5:1) and subsequently dissolved in a 6 N HCl solution. Total carbon (TC) and total nitrogen (TN) contents of the samples were measured by gas chromatography with a SUMIGRAPH-type NCH-21 analyzer. Total nitrogen was assumed to be due to the presence of octylamine, and carbon in excess of the amount expected for octylamine was attributed to the presence of residual alkoxide associated with polymerized siloxane.

Physical Properties. An X-ray diffraction (XRD) analysis was carried out using a Rigaku-type RINT 1200 X-ray diffractometer with a graphite monochromator at room temperature. Infrared spectra were obtained by the KBr method on a Perkin−Elmer infrared spectrometer (1600 Series FTIR). TG-DTA curves were obtained on a MAC Science thermal analyzer (system 001, TG-DTA 2000) at a heating rate of 5 °C/min. SEM observation was carried out with a Hitachi-type S-2460N scanning electron microscope. Nitrogen adsorption−desorption at −196 °C was carried out on a Quantachrome-type 1-C apparatus for samples degassed for 4 h below 10^{-3} mmHg.

Results and Discussion

X-ray Diffraction Studies. The X-ray diffraction pattern of BirMO(H) is shown in Figure 1. The sample has a layered structure with a basal spacing of 0.73 nm along the *c* axis, with crystal water and exchangeable H^+ ions in the interlayer space.[27]

The X-ray diffraction pattern of the OILMO sample reveals that the layered structure remains, while the basal spacing increases to 2.01 nm (Figure 1), which is almost 3 times larger than that of BirMO(H). The presence of higher order diffraction peaks indicates a stacked structure of expanded manganese oxide sheets. The interlayer spacing is calculated as 1.6 nm, which is a little larger than the geometric length of octylamine (about 1.2 nm).

When the OILMO sample was treated with TEOS liquid, the basal spacing further increased to 2.43 nm (Figure 1), indicating that TEOS molecules intercalated into the interlayer space. High-order diffraction peaks were weakened by the TEOS treatment, suggesting that the stacked structure was weakened. When SPLMO was heated at 200 °C for 2 h, the layered structure was maintained, but the basal spacing decreased to 2.14 nm, owing to the decomposition of organic components. With further heating at 300 °C for 2 h, the layered structure was almost destroyed.

The solvothermal treatment of the SPLMO sample in TEOS liquid resulted in a slight increase of basal spacing to 2.44 nm (Figure 1). The obtained SPLMOT sample showed a higher thermal stability than the SPLMO sample. The layered structure was still maintained, even after heating at 500 °C for 2 h, though the peak intensity decreased considerably. The layered structure was destroyed by heating at 600 °C.

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Table 1. Chemical Analysis Results of Samples at Different Stages

sample	content (mmol·g^{-1}) TC	TN	Mn	Si	octylamine/Mn	ethoxide/Mn	Si/Mn
OILMO	13.2	1.84	7.75		0.24		
SPLMO	5.59	0.67	6.37	4.01	0.11	< 0.01	0.63
SPLMOT	5.83	0.38	6.00	5.03	0.06	0.03	0.84
SPLMOT (200)	3.89	0.30	6.44	5.33	0.04	0.01	0.83
SPLMOT (400)	<0.01	<0.02	7.56	6.37			0.84
SPLMOT (600)	<0.01	<0.02	7.29	6.11			0.84

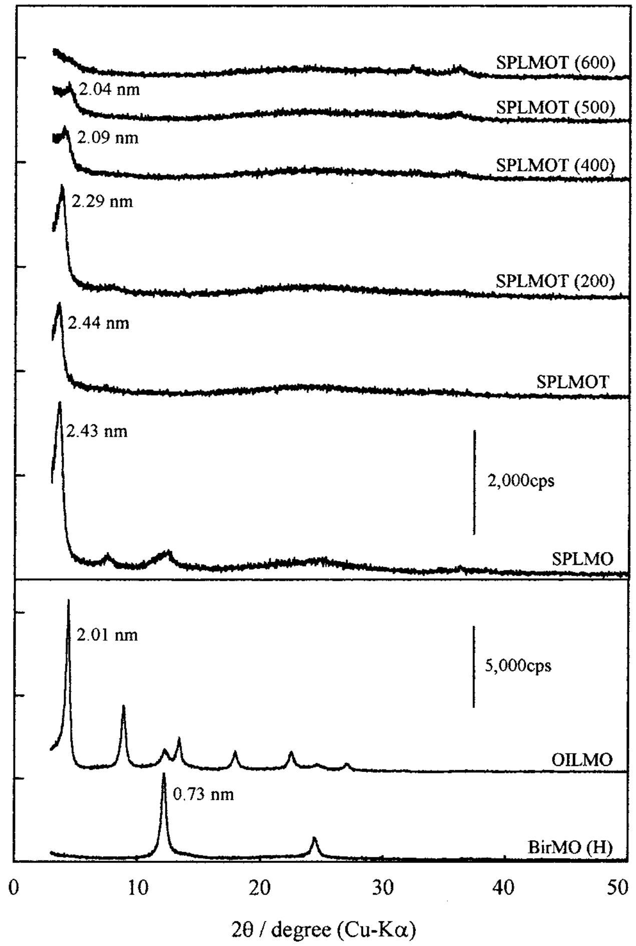

Figure 1. XRD patterns of samples at different stages.

Chemical Analysis. Mn, Si, TC, and TN contents of the manganese oxide samples at different stages are given in Table 1. We can calculate the octylamine and ethoxide contents from TN and TC contents because TN corresponds to the octylamine content and the octylamine molecule has a TC/TN ratio of 8. The octylamine content was 1.85 mmol/g for OILMO, corresponding to 83% of the ion exchange capacity (2.72 mmol/g) of BirMO(H). The SPLMO sample had an octylamine content of 0.67 mmol/g and a TC/TN molar ratio of 8. This shows that 64% of octylamine is deintercalated from the interlayer by the TEOS intercalation and the intercalated TEOS molecules are completely hydrolyzed to silicate. The Si/Mn ratio increased from 0.63 to 0.84 by the solvothermal treatment with a decrease of octylamine content to 0.38 mmol/g. The solvothermal treatment resulted in the additional intercalation of TEOS molecules with deintercalation of the interlayer octylamine molecules. The TC/TN molar ratio (15) shows that the hydrolysis of the intercalated TEOS is

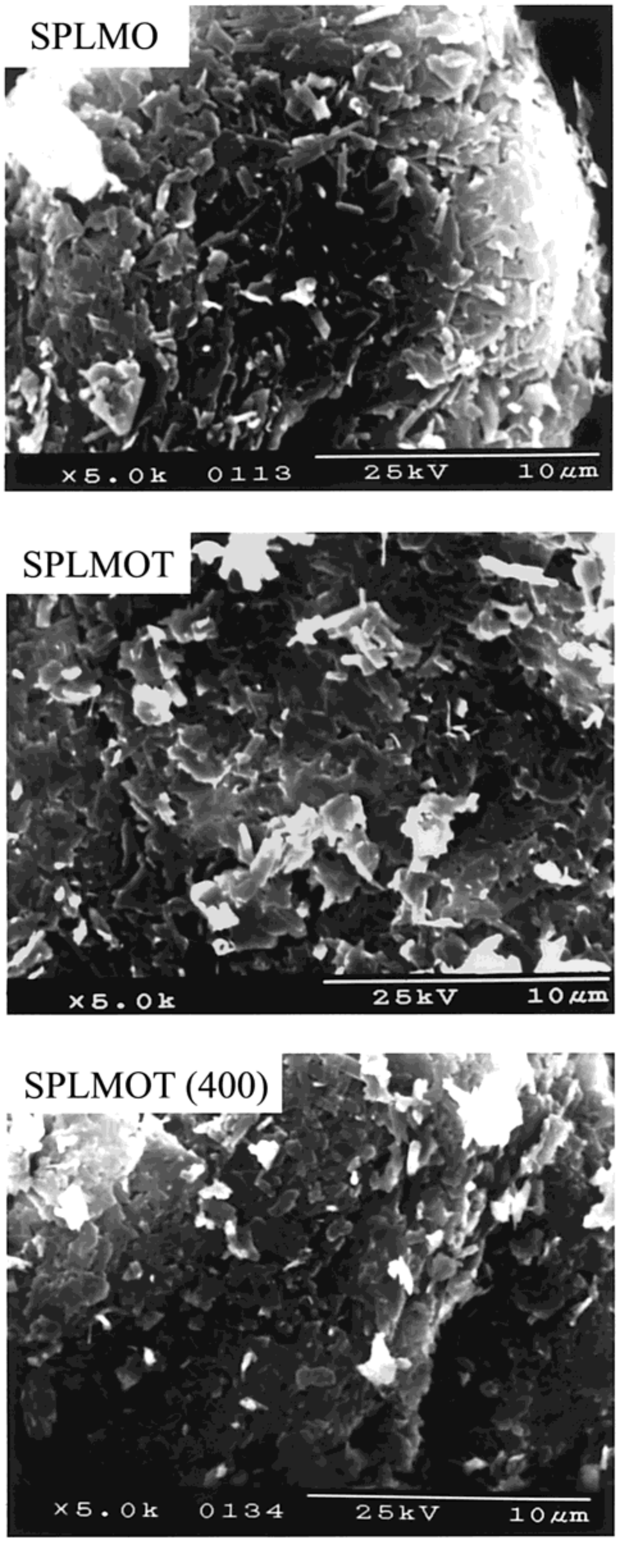

Figure 2. SEM photographs of samples SPLMO (above), SPLMOT (middle), and SPLMOT (400) (bottom).

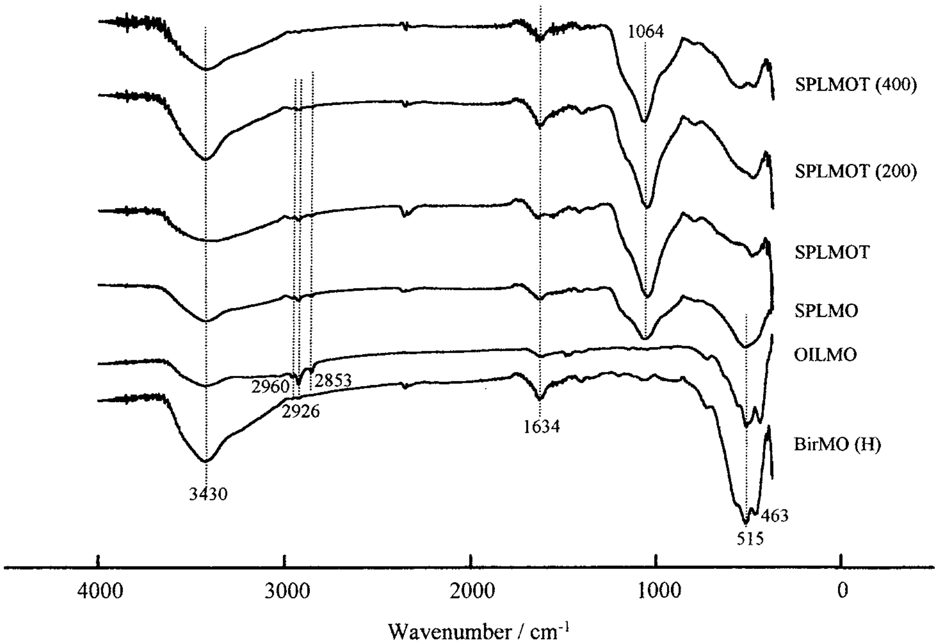

Figure 3. IR spectra of BirMO(H), OILMO, SPLMO, SPLMOT, SPLMOT (200), and SPLMOT (400).

incomplete and a small number of ethoxide molecules are present in the interlayer.

Scanning Electron Microscopy (SEM). SEM photographs of samples SPLMO, SPLMOT, and SPLMOT (400) are shown in Figure 2. They resemble each other and consist mainly of platelike particles corresponding to a layered structure. This shows that the platelike form of the starting BirMO(H) is maintained after the solvothermal treatment. Silica particles are not clearly observed in the samples, indicating that silica particles are rarely deposited on the external surface of the particles.

IR Spectra. The infrared spectra of samples SPLMO, SPLMOT, SPLMOT (200), and SPLMOT (400) are compared in Figure 3 with the spectra of BirMO(H) and OILMO. The spectra of the silica-pillared materials were different from those of BirMO(H) and OILMO. The bands around 3430 and 1634 cm^{-1} can be assigned to stretching and bending vibrations respectively of $-$OH groups of adsorbed water molecules. The bands around 515 and 463 cm^{-1} in the BirMO(H) spectrum can be assigned to the Mn$-$O stretching vibrations.[27] In OILMO, weak bands at 2853, 2926, and 2960 cm^{-1} corresponding to the C$-$H asymmetric and C$-$H symmetric stretching frequencies of the intercalated octylamine appeared.[28] A new band around 1064 cm^{-1} appeared for the SPLMO sample, which can be assigned to the stretching frequency of the O$-$Si$-$O bond.[28] After the solvothermal treatment, the bands around 1064 cm^{-1} changed sharply. This suggests that the crystallinity of the silica particles increased and the particles became more compact as a result of the solvothermal treatment. A similar spectrum was obtained for the SPLMOT (200) sample, although only the stretching intensity of the C$-$H group was further weakened. The octylamine in the interlayer decomposed completely by heating at 400 °C, so the stretching vibration of C$-$H bonds was not observed for SPLMOT (400).

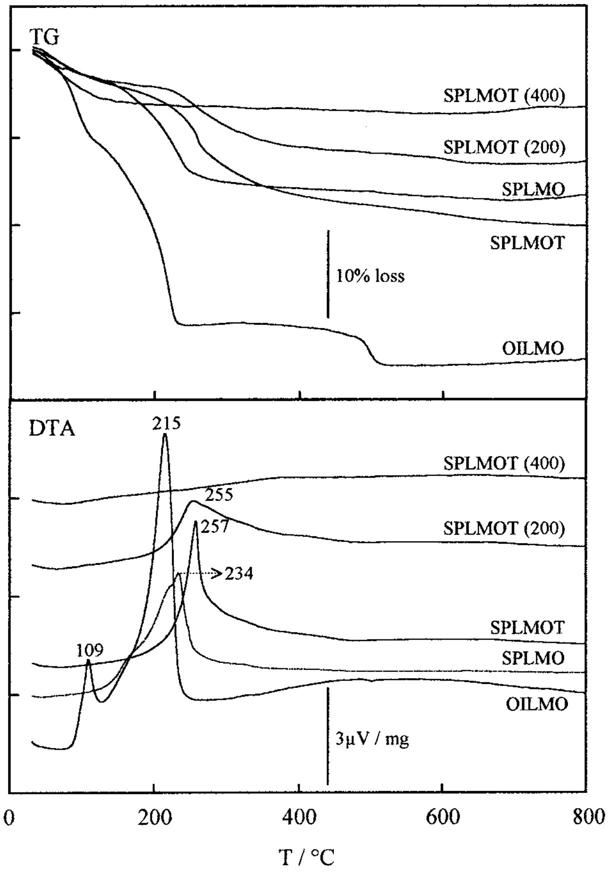

Figure 4. DTA (bottom) and TG (top) curves of OILMO, SPLMO, SPLMOT, SPLMOT (200), and SPLMOT (400).

DTA-TG Analysis. DTA curves of OILMO, SPLMO, and SPLMOT show a characteristic exothermic peak around 250 °C, which corresponds to the decomposition of octylamine molecules (Figure 4). The weight losses between 130 and 300 °C were 23.5, 11.6, and 10.3% for OILMO, SPLMO, and SPLMOT, respectively. In OILMO and SPLMO, the weight losses correlated with their octylamine contents. But in SPLMOT, the weight loss

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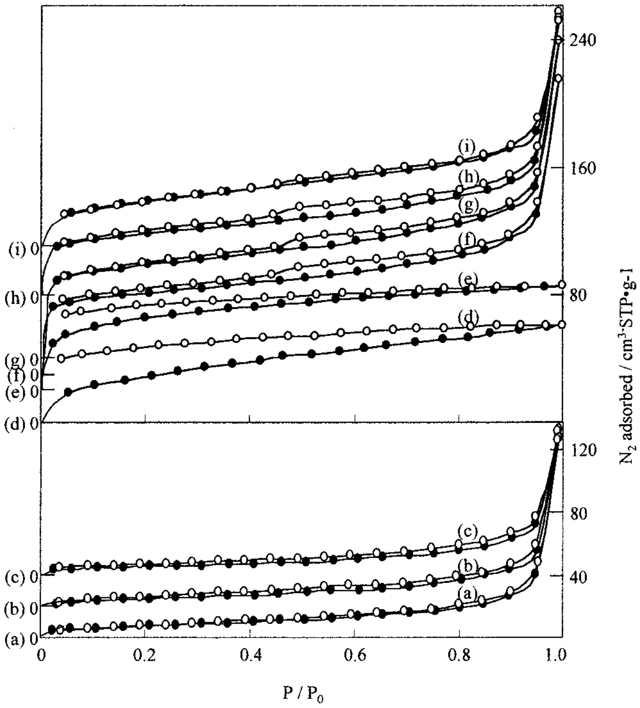

Figure 5. Nitrogen adsorption(●)−desorption(○) isotherms of samples: (a) BirMO(H), (b) OILMO, (c) SPLMO, (d) SPLMOT, (e) SPLMOT (200), (f) SPLMOT (300), (g) SPLMOT (400), (h) SPLMOT (500), and (i) SPLMOT (600).

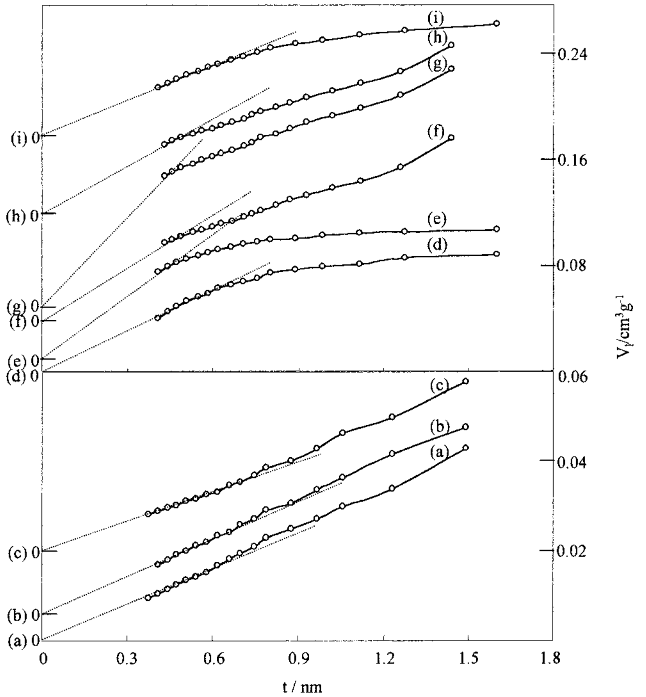

Figure 6. $V_l - t$ plots from nitrogen adsorption data for samples: (a) BirMO(H), (b) OILMO, (c) SPLMO, (d) SPLMOT, (e) SPLMOT (200), (f) SPLMOT (300), (g) SPLMOT (400), (h) SPLMOT (500), and (i) SPLMOT (600).

Table 2. Basal Spacings and Surface Properties of Samples at Different Stages

sample	d^a	$S_{BET}{}^b$	C_{BET}	$S_t{}^b$	$S_{mp}{}^b$	$S_{ext}{}^b$
BirMO(H)	0.73	27	65	26		26
OILMO	2.01	21	20	24		24
SPLMO	2.43	22	96	22		22
SPLMOT	2.44	110	41	105	80	25
SPLMOT (200)	2.29	165	143	156	136	20
SPLMOT (300)	2.22	150	450	159	125	34
SPLMOT (400)	2.09	260	310	265	231	34
SPLMOT (500)	2.04	138	270	142	110	32
SPLMOT (600)		75	99	75	61	14

[a] Basal spacing (nm). [b] Unit: m^2/g.

was caused by the decomposition of octylamine and the dehydration of the silica polymer in the interlayer. OILMO showed an additional unidentified exothermic peak around 109 °C with weight loss. The weight loss around 500 °C was due to the reduction of manganese from tetravalent to trivalent accompanied by the evolution of oxygen. SPLMOT showed a gradual weight loss between 300 and 500 °C, probably because of the calcination of silica particles.

The exothermic peak around 250 °C shifted to a higher temperature as a result of the TEOS intercalation; it further shifted to a higher temperature by the subsequent solvothermal treatment and the peak shape became sharper. These results suggest that the lamellar structure of octylamine formed in OILMO was fractured by TEOS intercalation and octylamine molecules form small isolated clusters in SPLMO. The cooperative destruction of the small isolated clusters may further progress in SPLMOT, and the peak character suggests that the octylamine clusters become small and uniform as a result of the solvothermal treatment. These results indicate that the solvothermal treatment improves advantageously the thermal stability of the silica-pillared manganese oxide.

Surface Properties. Nitrogen adsorption/desorption isotherms and the corresponding V_l vs t curves are shown in Figures 5 and 6, respectively. The V_l vs t plots are carried out with the curve by de Boer for samples with $C_{BET} < 200$ and that by Cranston for samples with $C_{BET} > 200$.[29] The isotherms for BirMO(H), OILMO, and SPLMO belong to BDDT type Π with a small hysteresis loop, which corresponds to nonporous or macroporous structures. The BET surface areas are between 27 and 21 m^2/g with C_{BET} constants around 60 (Table 2). The V_l vs t plots give nearly straight lines with S_t between 26 and 22 m^2/g (Table 2). These results indicate that the surface areas of these samples correspond to the external surfaces of manganese oxide particles and no micropores are formed in the interlayer.

The adsorption isotherms of samples SPLMOT and SPLMOT (200) belong to BDDT type I, corresponding to microporous materials. A characteristic feature is that the hysteresis loops do not close, even at low relative pressures. This kind of isotherm has been observed for xerogels of silica and stannic oxide, etc.[30] The open hysteresis may be caused by the influence of the specific interaction of the interlayer octylamine with nitrogen molecules. The V_l vs t plots for samples SPLMOT and SPLMOT (200) show downward deviations from the straight lines around 0.7 and 0.5 nm, respectively, due to pore filling of nitrogen. These results indicate that micropores with widths around 0.7 and 0.5 nm, respectively, are formed for these samples. The solvothermal treatment changes the nonporous struc-

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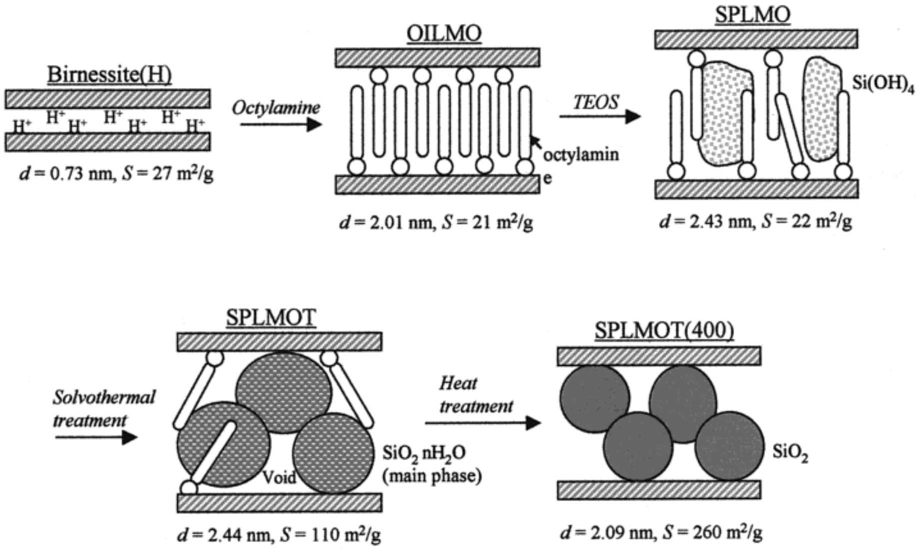

Figure 7. Model for the formation of silica-pillared manganese oxide.

ture of layered manganese oxide to a microporous one. The decrease of pore width by heat treatment is correlated with the decrease of the basal spacing.

The isotherms for the samples heat-treated at temperatures between 300 and 500 °C belong to BDDT type IV with hysteresis loops, which is characteristic of mesoporous material. However, the fraction of mesopores is not so large because the hysteresis loop is not so clear compared to those in typical mesoporous materials. SPLMOT (400) shows the maximum BET surface area and has a markedly high C_{BET} constant. The V_l vs t plot for SPLMOT (400) shows a downward deviation from the straight line around $t = 0.5$ nm. This shows the formation of narrow micropores with a pore diameter around 0.5 nm. The curve gives a total surface area (S_t) of 265 m^2/g and external surface area (S_{ext}) of 34 m^2/g; the proportion of micropore surface area reaches 88%. This shows that the heat treatment results in the production mainly of micropores. SPLMOT (600) has a markedly small BET surface area because of the destruction of the pillared structure.

In the preceding paper,[26] we studied the pillared reaction of the layered birnessite(H) without solvothermal treatment. The preceding data showed the maximum BET surface area at 200 °C heating and a marked decrease at 300 °C due to the destruction of the layered structure. In that report, the sample heat-treated at 200 °C gave a small amount (0.02 mmol/g) of octylamine remaining in the interlayer. The C_{BET} constants are <200 for all the preceding samples. Because the C_{BET} value is a measure of the strength of interaction between the nitrogen molecule and pore surface, the low C_{BET} value indicates the weak interaction between the nitrogen molecule and micropore surface due to the presence of relatively wide micropores. Comparing the present result with the preceding one, we can conclude that the solvothermal treatment is a superior method for obtaining porous materials with high thermal stability and low impurities.

Formation Reaction of Silica-Pillared Manganese Oxide. A schematic representation of the formation of silica-pillared manganese oxide is given in Figure 7. The reaction of BirMO(H) with octylamine forms octylamine-intercalated manganese oxide with a basal spacing of 2.01 nm. The subsequent reaction with TEOS results in the replacement of the octylamine with TEOS. The water molecules in the layers make the TEOS hydrolyze to form silicate precursor, but the surface area does not increase. The solvothermal treatment of SPLMO with TEOS liquid causes further replacement of octylamine with TEOS. The characteristic feature is that the solvothermal treatment causes a considerable increase of surface area, although the chemical species in the interlayer do not change. We think that solvothermal treatment at relatively high temperature accelerates the ripening of silicate polymer to compact hydrous silica particles ($SiO_2 \cdot nH_2O$). The transformation from silicate polymer to silica particles causes the formation of voids among the silica particles, which lead to the relatively large surface area. Further heat treatment results in the decomposition of octylamine to form silica pillars in the gallery. The Si content by the solvothermal treatment effectively increases the thermal stability of the layered structure.

We had carried out a hydrothermal treatment of SPLMO in water at 170 °C to increase the thermal stability of pillared manganese oxide, but it resulted in the change of the crystal phase from layered birnessite to α-Mn_2O_3.

In conclusion, the solvothermal treatment is a unique method for producing a silica-pillared manganese oxide with high porosity as well as high thermal stability.

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