Synthesis of Silica-Pillared Microporous Manganese Oxide

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Silica-pillared layered manganese oxides with high surface area and high thermal stability have been synthesized for the first time by the two step intercalation of octylamine followed by tetraethylorthosilicate into birnessite type manganese oxide.

Porous manganese oxides with narrow pores have been prepared by the templating reaction, using metal ions as templating cations.[1,2] Spinel-type, hollandite-type, and todorokite-type manganese oxides have pores with [1 × 3], [2 × 2], and [3 × 3] tunnels of MnO_6 octahedra, respectively. Birnessite-type and buserite-type manganese oxides have pores with [2 × ∞] and [3 × ∞] layers, respectively. They show specific ion-sieve properties depending on the size of tunnel or layer.[1] The pore radii of these samples are less than 0.3 nm, belonging to ultramicroporous materials. Thus, these samples are not suitable as adsorbents for gaseous molecules or as catalysts.

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. However, there have been relatively few studies on the pillared reaction of layered manganese oxides or related oxides by the intercalation of large molecules.[3-6] Pillared manganese oxides with Keggin ions or organic molecules as guest molecules have been reported,[3,4] but they have relatively small surface areas and do not show clear evidence for the formation of a pillared structure. The expansion of the interlayer space by preintercalation of large organic molecules is an effective method to enable smooth intercalation of pillared materials, preserving the layered structure.[7,8] In the present study, we prepared silica-pillared layered manganese oxide using a two-step intercalation reaction: uniform expansion of the interlayer with octylamine, followed by the intercalation of tetraethylorthosilicate (TEOS). Subsequent heat treatment at an appropriate temperature gave microporous manganese oxide, which had good porosity and thermal stability.

The starting material, layered manganese oxide (birnessite) was prepared by the method reported in the literature.[9] 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 hours in a 2 M NaOH solution. The precipitates 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 sample with the chemical composition, $Na_{0.21}H_{3.49}\,Mn_{12}O_{23}\cdot 9.5\,H_2O$. Since the starting birnessite does not react directly with TEOS, the octylamine intercalated sample was prepared first in order to expand the interlayer, similar to the case of layered titanium niobium oxide.[10] The acid-treated sample (1 g) was mixed with a 1.5 M octylamine solution and stirred at 50 °C for a week. After mixing, the solution was separated by centrifugation, and the precipitates were washed with ethanol (40 cm^3) three times and dried at room temperature. The octylamine-intercalated birnessite is hereafter abbreviated as OILMO. Sample OILMO (1 g) was then added to 150 cm^3 of TEOS liquid (Wako Chemicals Co.) and stirred at 65 °C for a week. After the reaction, the precipitate was filtered, washed with ethanol, and then dried for 2 days at room temperature. The product is hereafter abbreviated as SPLMO.

Total carbon (TC) and total nitrogen (TN) contents of OILMO and SPLMO were measured by GC with a SUMIGRAPH type GCT-12N analyzer. The octylamine amount reached 1.61 mmol/g for OILMO, which reached 71% of the ion exchange capacity (2.72 mmol/g). For sample SPLMO, the TC/TN ratio was similar to that of OILMO, but the octylamine amount decreased to 1.14 mmol/g. The Si content determined by ICP spectroscopy was 5.5 mmol/g, corresponding to a Si/Mn mole ratio of 1 : 1; indicating that a considerable amount of Si is incorporated in SPLMO.

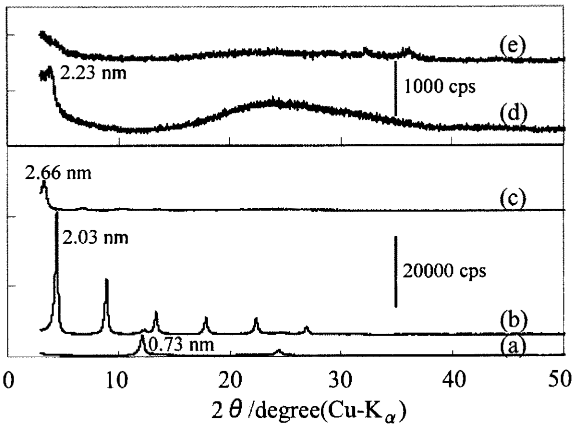

Figure 1. XRD patterns of (a) birnessite(H); (b) OILMO; (c) SPLMO; (d) SPLMO(400); and (e) SPLMO(600).

The XRD patterns of the starting material, OILMO, and SPLMO are given in Figure 1. The starting birnessite has a basal spacing of 0.73 nm. The octylamine-intercalated sample OILMO shows the diffraction pattern of a layered structure with basal spacing of 2.03 nm, which is almost three times larger than that of the starting birnessite. The presence of higher order diffraction peaks suggests a stacked structure of the expanded manganese oxide sheets. The interlayer space is calculated as 1.6 nm, which is a little larger than the geometric length of octylamine (about 1.2 nm). The basal spacing further increases to 2.66 nm by treatment with TEOS; this suggests that TEOS molecules are intercalated into the interlayer space. Higher order diffraction peaks are weakened by the TEOS treatment, suggesting that the stacked structure is weakened.

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Thermal analyses showed that sample OILMO had a rather low thermal stability. It had large exothermic peaks around 150 and 230 °C with marked weight loss and the layered structure collapsed with heat treatment at 250 °C. On the other hand, sample SPLMO has a higher thermal stability than OILMO. The exothermic peak around 150 °C weakened markedly with TEOS treatment although the exothermic peak around 230 °C had similar strength. The XRD patterns of SPLMO heat-treated at 400 and 600 °C are given in Figure 1 (the heat-treated samples are abbreviated as SPLMO(400) etc., where the numbers in the parenthesis indicate heating temperature). SPLMO(400) preserved a layered structure although the peak intensity decreased. The basal spacing decreased a little to 2.23 nm by heating at 400 °C due to the decomposition of organic materials in the interlayer, but was much larger than that of the starting birnessite and OILMO. Further heating at 600 °C resulted in the disappearance of the layered structure. The interlayer silicon remained after the heating treatment; Si content of SPLMO(400) was 5.6 mmol/g with a Si/Mn ratio of 1.0. These results indicate that the intercalation of TEOS results in the stabilization of the layered structure against thermal treatment. Since TEOS changes to silica with heating, colloidal silica particles may be formed in the interlayer by the heating treatment, which act as pillars to prop up the manganese oxide layers after the interlayer organic materials are removed.

SEM observation was carried out using a Hitachi type S-2460N scanning electron microscope. The SEM images of SPLMO and SPLMO(400) resembled each other. They consisted mainly of plate-like particles corresponding to a layered structure. Silica particles were not clearly observed in either the sample, indicating that silica particles were rarely deposited on the external surface of the particles.

Nitrogen adsorption/desorption isotherms were obtained with Quantachrome type 1-C apparatus for samples degassed at 30 °C for 4 hours below 10^{-3} mmHg (Figure 2). The isotherms for starting birnessite, OILMO, and SPLMO belong to BDDT type II with a little hysteresis loop, which corresponds to non-porous or macroporous materials. The BET surface areas are between 27 and 21 m^2/g (Table 1). The V_l-t plots (with t values by de Boer) give straight lines with S_t between 26 and 22 m^2/g. These results indicate that the surface areas of non-heated samples correspond to external surfaces of manganese oxide particles and no micropore is formed in the interlayer. On the other hand, the heated samples show isotherms of either BDDT I or BDDT IV classification, which correspond to microporous or mesoporous material, respectively. A small hysteresis loop around $P/P_0 = 0.5$ for SPLMO(400) indicates the presence of a small amount of mesopores. The surface area (S_{BET}) increased to 159 m^2/g for SPLMO(100) and 282 m^2/g for SPLMO(400). The V_l-t plots for SPLMO(100) and SPLMO(400) show downward deviations from the straight lines around t = 0.45 and 0.7 nm, respectively which shows the presence of micropores for both the samples. The micropore size increases a little with heating temperature. Micropore surface area (S_{mp}) and external surface area (S_{ext}) were calculated from the V_l-t curves (Table 1). Micropore surface area increases markedly with heat treatment, but the increase of external surface area is not so marked. These results clearly show that internal micropores are formed between the manganese oxide sheets. Sample SPLMO(600) has a relatively small surface area (102 m^2/g), owing to the destruction of layered structure.

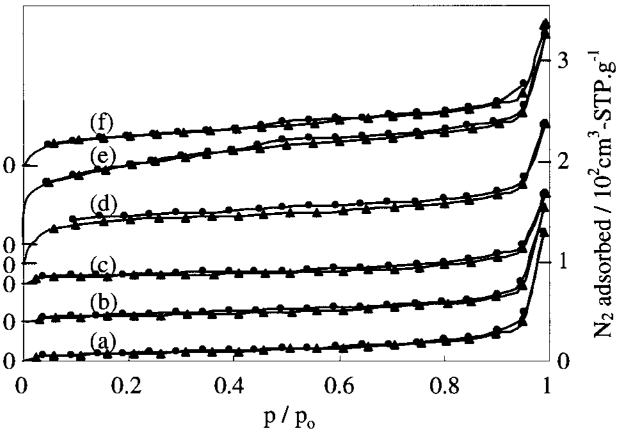

Figure 2. Nitrogen adsorption (▲)-desorption (●) isotherms of (a) birnessite(H); (b) OILMO; (c) SPLMO; (d) SPLMO (100); (e) SPLMO (400); and (f) SPLMO(600).

Table 1. The basal spacing and surface properties of manganese oxide samples

Sample	d^a	$S_{BET}{}^b$	C_{BET}	$S_t{}^b$	$S_{mp}{}^b$	$S_{ext}{}^b$
Birnessite(H)	0.73	27	65	26	-	26
OILMO	2.03	21	20	24	-	24
SPLMO	2.66	22	96	22	-	22
SPLMO(100)	2.55	159	144	156	127	29
SPLMO(400)	2.23	282	205	278	245	33
SPLMO(600)	-	102	75	104	61	43

^{a}Basal spacing (nm). ^{b}Unit: m^2/g.

In conclusion, silica-pillared microporous manganese oxide was successfully prepared by the two-step intercalation reaction. The silica-pillared manganese oxide is attractive as a novel catalyst, since it consists of mixed surfaces (-Mn-O-Mn- and Si-O-Si- surfaces) with different acid strengths and different oxidation abilities.

References and Notes

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