A Novel TiO_2-pillared Microporous Manganese Oxide

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A novel TiO_2-pillared microporous manganese oxide was first synthesized by preliminary expanding the interlayer of birnessite-type manganese oxide using dodecylamine, followed by TiO_2 pillaring and subsequent heat treatment.

Recently, intense research efforts have been devoted to the pillaring of semiconducting materials into layered inorganic solids, since the pillaring method can not only synthesize novel porous materials but also improve the functional activity of pillared agents.[1–3] It was reported that the pillaring of semiconducting materials such as CdS–ZnO, Fe_2O_3, and TiO_2 gave rise to a remarkable enhancement of their functional activity, and the functional activity of semiconducting pillared agents depended on the type of the host layer.[4] Layered manganese oxides are a classical type of inorganic host layer and can be used as molecular sieves, catalysts, battery materials, and precursors for synthesizing porous manganese oxides.[5,6] TiO_2 is an interesting semiconductor pillar because of its unique photocatalytic and electrochemical properties.[7] Therefore, TiO_2-pillared microporous manganese oxide has been sought, which is expected to possess the hybrid properties of manganese and titanium. But so far, such materials have not be synthesized because there are the high surface charge density of the interlayer and the thin layer characteristic of manganese oxide sheets, as well as the strong hydrolysis of titanium isopropoxide in aqueous solution.[8,9] In this work, a novel pillaring method has been developed in which dodecylamine was chosen as a preintercalation agent to expand the interlayer space of layered manganese oxide and a mixed solution of titanium isopropoxide (TIIP) and ethanol was done as a reactant medium to control the hydrolysis of TIIP. A novel TiO_2-pillared microporous manganese oxide with a specific surface area of $140\,m^2/g$ was successfully synthesized by a preliminary expansion, followed by introducing a pillaring agent (TiO_2) and subsequent heat treatment.

The starting material, layered manganese oxide (birnessite-type) was prepared by the method reported in the literature.[9] A mixed solution of 0.6 M NaOH and 2 M H_2O_2 (100 mL) was poured quickly into a 0.3 M $Mn(NO_3)_2$ solution (50 mL) and the mixture was stirred for 25 min before filtration. Then the washed precipitate was subjected to hydrothermal treatment at 150 °C for 16 h in a 2 M NaOH solution. The precipitate obtained had a chemical formula of $Na_{0.39}Mn_{0.94}O_2{\cdot}0.67H_2O$. 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 $Na_{0.02}H_{0.34}Mn_{0.94}O_2{\cdot}0.64H_2O$ abbreviated as H-BirMO. H-BirMO (1 g) was mixed with an ethanol solution of 0.5 M dodecylamine (50 mL) and stirred at room temperature for a week. The suspension was filtered and the obtained precipitate was washed with ethanol for 3 times and dried at room temperature. The dodecylamine-intercalated sample was obtained, which was hereafter abbreviated as DOIMO. Sample DOIMO (0.2 g) was soaked to a mixed solution of TIIP and ethanol (50 mL) with a volume ratio of 1:25 in a Teflon-lined stainless steel vessel and autoclaved at 50 °C under autogenous pressure for 2 days. After reaction, the suspension was filtered and the precipitate was washed with ethanol for 3 times, and then dried at room temperature for 2 days. The TiO_2-pillared layered manganese oxide was obtained, which was hereafter abbreviated as TIIMO. Sample TIIMO was heat-treated in air at 300 °C for 2 h, TiO_2-pillared microporous manganese oxide was obtained, which was abbreviated as TIIMO(300). Mn and Na contents in above samples were determined by atomic absorption spectrometry after they were dissolved in a mixed solution of HCl and H_2O_2, and Ti contents were determined by UV spectrometry after the samples were dissolved in a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4. X-ray diffraction pattern (XRD), N_2 adsorption at 77 K, TG-DTA analysis, and SEM observation were performed with a Rigaku D/Max2550VB+/PC system, a Beckman Coulter-made volumetric apparatus, a SDT Q600 thermal analyzer, and a Philips type Quanta 200 high-resolution scanning electron microscope, respectively. In addition, different volume ratios of TIIP to ethanol in the mixed solution (1:50, 3:25, and 4:25) were used to observe the effect on the synthesized materials.

The XRD diffraction patterns of samples at different stages are shown in Figure 1. The precursor H-BirMO has a layered structure with a basal spacing of 0.73 nm, with crystal water and exchangeable H^+ in the interlayer space (Figure 1a). The layered structure is maintained after the intercalation of dodecylamine into the interlayer, while the basal spacing increases to 2.62 nm (Figure 1b), which is almost 4 times larger than that of H-BirMO. High-order diffraction peaks indicate a stacked structure of expanded manganese oxide sheets. The interlayer space is calculated as 2.17 nm, suggesting that dodecylamine is intercalated perpendicular to the manganese oxide sheets be-

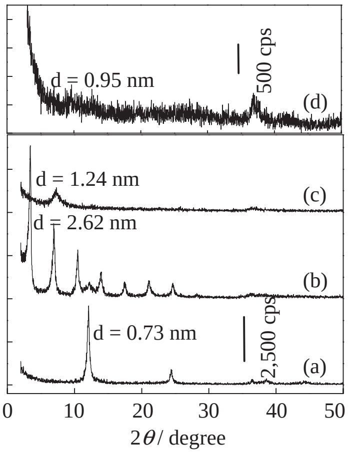

Figure 1. XRD diffraction patterns of samples: (a) H-BirMO, (b) DOIMO, (c) TIIMO, and (d) TIIMO(300).

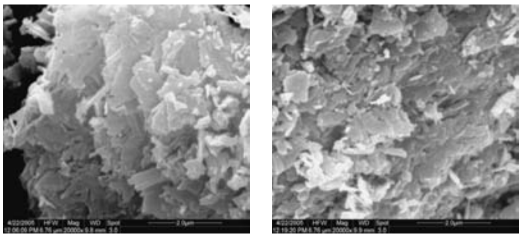

Figure 2. SEM photographs of sample TIIMO (left) and TIIMO(300) (right).

cause the chain length of dodecylamine is 2.08 nm. A new layered structure with a basal spacing of 1.24 nm, TIIMO, is obtained after sample DOIMO is treated with a mixed solution of TIIP and ethanol (1:25). The intercalated dodecylamine molecules are replaced by TIIP, resulting in the decrease of the basal spacing (Figure 1c). Disappearance of high-order diffraction peaks suggests that the stacked structure is weakened. After sample TIIMO is heat-treated at 300 °C for 2 h, only a weak peak corresponding to a basal space of 0.95 nm can be observed. This indicates that the layered structure is nearly destroyed and the sample TIIMO has relatively low stability against heat-treatment. A mixed solution with different volume ratios of TIIP to ethanol is used to react with sample DOIMO. Experimental results show that both the position and strength of XRD diffraction peaks depend on the content of the intercalated TIIP. Figure 2 shows the SEM images of TIIMO and TIIMO(300). They consist mainly of plate-like particles corresponding to a layered structure. Titanate particles are not clearly observed, indicating that titanate particles rarely deposit on the external surface and exit in the interlayer space. For sample TIIMO(300), the size of the particles merely seems to become smaller because of the heat-treatment. Figure 3a shows the N_2 adsorption isotherm at 77 K on TIIMO(300), whose shape seems to be a mixture of type I (an initial steep rise at $p/p_o < 0.05$) and type IV (a gradual increase at $p/p_o > 0.15$) with a small hysteresis loop, indicating that some mesopores may be formed by heating treatment sample TIIMO at 300 °C for 2 h.[10] V_l–t plot is made from adsorption isotherm using de Boer's t values.[11] The V_l–t plot shows downward deviation from the straight line around 0.65 nm due to pore filling of nitrogen, indicating that micropores with widths around 0.65 nm is formed (Figure 3b). Table 1 shows the chemical analysis results and special surface area (S_{BET}) of TIIMO(300) in comparison with H-BirMO, DOIMO, and TIIMO. Except for TIIMO(300), all the samples have a S_{BET} value below 40 m^2/g, indicating that only the expanding of the precursor H-BirMO can not cause the increase of S_{BET}. A external surface area (S_{ext}) of 31 m^2/g is calculated from V_l–t plot curve and the proportion of micropore surface area reaches 78%, suggesting that the heat treatment results in the production of main micropores for sample TIIMO(300). After TIIP is intercalated into the interlayer, the water molecules in the interlayer space make the TIIP hydrolyze to form titanate, which only causes a small increase of the special surface area. The heat treatment at high temperature accelerates the ripening of titanate to compact and form voids among the titanate particles, resulting in a microporous composite with the relatively large surface area.

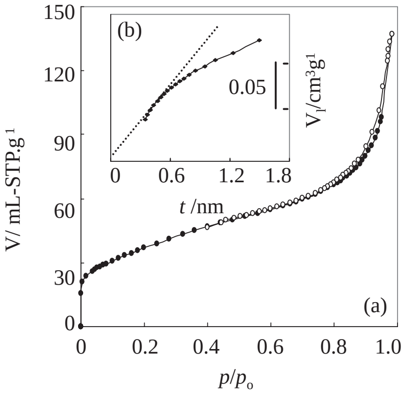

Figure 3. Nitrogen adsorption (●)–desorption (○) isotherm and V_l–t plot from nitrogen adsorption data for sample TIIMO(300).

Table 1. Chemical analysis results and BET surface areas of samples

Sample	Mn (mmol/g)	Ti (mmol/g)	TC (mmol/g)	S_{BET} (m^2/g)
H-BirMO	8.92	—	—	31
DOIMO	5.77	—	15.9	28
TIIMO	7.01	1.74	−4.73	39
TIIMO(300)	7.54	1.92	<0.05	140

In conclusion, TiO_2-pillared microporous manganese oxide is successfully prepared by preliminarily expanding the interlayer of birnessite-type manganese oxide using dodecylamine, followed by TiO_2 pillaring through a heat treatment of TIIP intercalated sample. The titanium–manganese nanocomposite has the potential to be developed as a novel catalyst, a selective adsorbent, or as a cathode material for lithium ion battery, since it consists of mixed surfaces (–Mn–O–Mn– and –Ti–O–Ti– surfaces).

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