Formation and transformation of mesoporous and layered manganese oxides in the presence of long-chain ammonium hydroxides

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Mesoporous manganese oxides are prepared by reduction and oxidation mechanisms and by interconversions of layered materials.

Two methods (oxidation and reduction) have been developed to synthesize mesoporous manganese oxides (MnO_x). Organic ammonium cations are introduced into layered birnessite-type MnO_x. Transformations from a mesoporous MnO_x to a layered material and from a layered MnO_x to a mesoporous structure have been observed.

The synthesis of molecular sieves of large micropores (VPI-5[1]) and mesopores (MCM-41[2,3]) has long been a focus of many researchers. Since the development of the Mobil MCM series of mesoporous silicates and aluminosilicates using templates such as long-chain ammonium-type surfactants, several studies[4–7] have been published on the synthesis, characterization, and applications of these mesoporous materials. Some transition metals,[8,9] such as Ti, have also been successfully incorporated into mesoporous structures. In those studies, silica or metallo-silicate gel (usually from the hydrolysis of metal ethoxides) is precipitated around the hexagonally packed micelles of surfactant molecules to form a mesoporous inorganic framework. Neither reduction nor oxidation is generally used in the syntheses of these materials.

However, few studies, to our knowledge, have yet been published of the synthesis and related research on manganese containing mesoporous materials. The conversion from a mesoporous structure to a layered structure, and observations that a typical layered MnO_x can be converted into a mesoporous structure have not been reported.

The oxidation of Mn^{II} and reduction of Mn^{VII} are employed herein to prepare mesoporous MnO_x in the presence of long-chain organic ammonium hydroxides. The two methods are thus referred to as oxidation and reduction syntheses, respectively. A method to incorporate organic ammonium cations into a birnessite-type layered manganese oxide to prepare large d-spacing layered materials is also presented. The conversions from a mesoporous MnO_x to a layered material and that from a birnessite to a mesoporous structure have been investigated.

For a typical oxidation synthesis, 8.0 g of $MnCl_2 \cdot 4H_2O$ in 50 ml deionized distilled water (DDW) was slowly added to a 1 l beaker containing a 200 ml solution of $(C_{12}H_{25})NMe_3OH$ (ca. 30 mass%) with a glass rod, with vigorous stirring with a stirring bar. A gel of $Mn(OH)_2$ having pyrochroite structure was formed and was stirred for 30 min. Oxygen gas from a cylinder was then bubbled in to the solution with a gas flow rate of ca. 100 ml min^{-1} via a glass frit, without stirring. In order to prevent formation of a foam, a few drops of ethanol are added to the beaker every 10 min. Bubbling was continued for ca. 8 h after which the resultant black precipitate was transferred to a 500 ml glass bottle, which was aged in a water-bath at 40 °C.

In the oxidation synthesis, $Mn(OH)_2$ having pyrochroite structure (JCPDS card 18-787) was formed when $MnCl_2$ was added to the $(C_{12}H_{25})NME_3OH$ solution. When oxygen was bubbled for 30 min, $Mn(OH)_2$ was converted to hydrohausmannite [a mixture of β-MnO(OH) and γ-Mn_3O_4, JCPDS 18-804 and 24-734, respectively]. Further bubbling of oxygen

into the system led to oxidation of hydrohausmannite to a substance having only one broad XRD peak at 2θ ca. 18–20°. This broad peak did not change even when oxygen bubbling was continued for a day. The XRD pattern also remained the same when the system was aged at 40 °C for 4 h. However, at $t = 10$ h, an XRD peak at ca. 30 Å d-spacing appears, indicating the evolution of mesoporous MnO_x in the system [Fig. 1(a)]. Both the d-spacing and the intensity of the peak increase with increasing ageing time until at $t = 20$ h the intensity reaches a maximum for the peak at a d-spacing of 46 Å [Fig. 1(b)]. During this period mesoporous MnO_x is formed and its amount is increased with increasing ageing time. The time before formation of mesoporous MnO_x is referred to as the induction period. From $t = 20$ h to $t = 36$ h both the intensity and d-spacing value remain almost constant and this is denoted the steady-state period.

Beyond an ageing time of 48 h, the XRD peak at 45 Å d-spacing was found to decrease and continued to decrease with increasing time. The d-spacing value also decreased to some extent. Meanwhile, a new set of XRD peaks characteristic of a layered structure appears. The peaks occur at 25.4 Å (001), 12.7 Å (002), 8.6 Å (003), 6.4 Å (004) and 5.1 Å (005) [Fig. 1(c)] where the numbers in parentheses are the reflection indices. The 46 Å peak corresponding to a mesoporous structure is shifted to 39 Å at $t = 48$ h and finally disappears at $t = 4$ d, with the presence of only peaks for the layered structure, whose
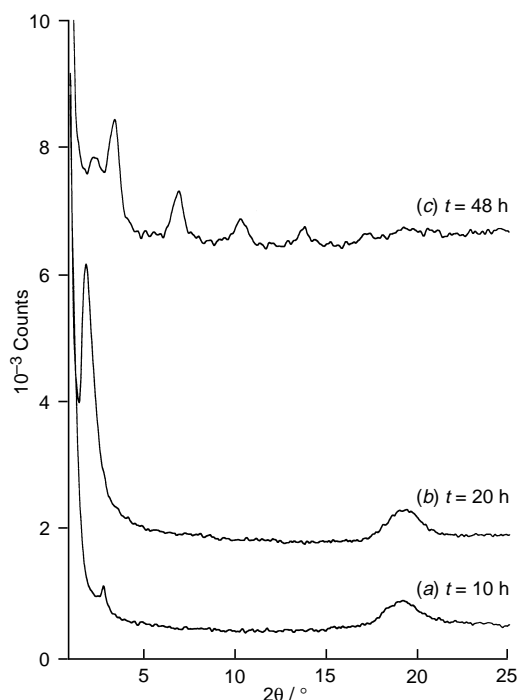

Fig. 1 XRD patterns showing the formation and transformation of mesoporous MnO_x during the oxidation synthesis at different ageing times

d-spacings are also decreased slightly to 23.9 (001), 11.9 (002), 7.9 (003), 6.0 (004) and 4.8 Å (005), respectively. This indicates that the mesoporous MnO_x has completely converted to a layered structure.

The reduction synthesis employs alcohols such as ethanol as reductants to reduce $(C_{12}H_{25})NMe_3MnO_4$ in the presence of $(C_{12}H_{25})NMe_3OH$. Typically a slurry containing 20 g of freshly prepared $(C_{12}H_{25})NMe_3MnO_4$‡ was added to a 100 ml solution of $C_{12}H_{25}NMe_3OH$ (*ca.* 30 mass%) with stirring, forming a uniform slurry. Absolute ethanol (100 ml) was then poured into the slurry. The resultant gel was stirred for *ca.* 30 min and aged at 65–85 °C in an oven.

In the reduction synthesis, the product before ageing was an amorphous MnO_x material. When it was aged at 65 °C for 2 days, the amorphous material became mesoporous, with only one XRD peak at 57 Å. Unlike the mesoporous material produced during the oxidation synthesis, it exhibited no peaks in the range 2θ 18–20. In addition, this material showed no conversion to any layered structure even after ageing at 65 °C for 5 days.

The synthesis of birnessite and subsequent conversion of the layered MnO_x into a mesoporous structure was performed by adding, with stirring, 10 g of $KMnO_4$ dissolved in 150 ml DDW to a mixture of 100 ml absolute ethanol and 50 ml DDW containing 30 g KOH. A brownish gel was formed, which (after 30 min stirring) was kept in an oven at 85 °C for 2 days. After being filtered, the gel was washed with DDW until the pH of the filtrate was < 10. The product was potassium birnessite. While still wet, it was transferred to a beaker containing 200 ml of 1 M HNO_3 and stirred at room temp. for 3 h to allow H⁺ exchange. The exchange was repeated, giving H-birnessite, which was washed, filtered and transferred to a beaker containing 200 ml of DDW while stirring. A solution of 10 ml of 20–40 mass% of different organic ammonium hydroxides was added to introduce different types of ammonium ions into the birnessite.

The XRD pattern of the prepared H-birnessite is shown in Fig. 2(*a*). Only two main peaks with *d*-spacings of 7.3 and 3.6 Å were present in this preferentially oriented XRD pattern.
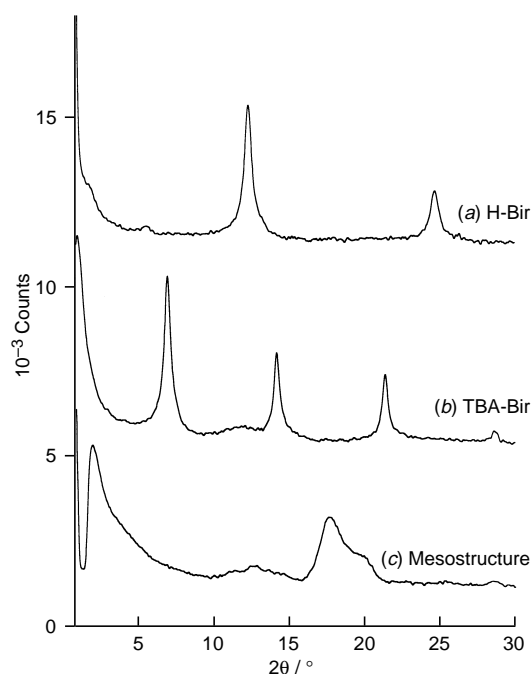
When an organic ammonium species is introduced, the interlayer spacing is increased to an extent which depends on the dimension of the individual organic ammonium ion. For a $(C_{12}H_{25})NME_3$-birnessite, the preferentially oriented XRD reflections were at 24.1 (001), 12.0 (002), 8.0 (003), 6.0 (004), 4.8 (005) and 4.0 Å (006). This is almost identical to that of a layered MnO_x converted from a mesoporous MnO_x which was prepared from the oxidation of Mn^{II} with oxygen in the presence of $(C_{12}H_{25})NMe_3OH$. When a smaller organic ammonium ion, *e.g.* tetrabutylammonium hydroxide (TBAOH), is used the XRD reflections of the layered MnO_x are at 12.8 (001), 6.4 (002), 4.2 (003) and 3.2 Å (004) [Fig. 2(*b*)], *i.e.* at substantially lower values than for $(C_{12}H_{25})NMe_3$-birnessite.

When $Mg(MeCO_2)_2 \cdot 6H_2O$ (20 g) in 50 ml DDW was added to H-birnessite prior to the addition of the organic ammonium hydroxide, no exchange of Mg^{2+} for H⁺ was observed even if the system was stirred for more than a week. However, when TBAOH was added to H-birnessite containing Mg^{2+} ions and the system was stirred for two days, the layered material was converted to a mesoporous MnO_x structure [Fig. 2(*c*)]. The layered mesoporous MnO_x material exhibits a basal XRD reflection at 42.3 Å, with several broad small peaks at 2θ 15–20°. This XRD pattern is quite similar to that of the mesoporous MnO_x produced in the oxidation syntheses.

IR studies show that the mesoporous materials all have a strong absorption around 700 cm⁻¹, arising from Mn–O bond vibrations. The layered materials, including both those converted from mesoporous MnO_x formed during oxidation syntheses and those containing organic ammonium introduced into birnessites, all have framework vibrations similar to those of birnessite. Detailed characterization of the materials, including TEM, thermal properties, sorptive properties, Mn oxidation state, acid–base properties and catalytic properties are under way. The mechanisms of formation and transformations associated with the mesoporous MnO_x are also being studied.

Footnotes

References

1 M. E. Davis, C. Saldarriaga, C. Montes, J. Graces and C. Crowder, *Nature*, 1988, **331**, 698.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
3 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Cresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.
4 C. F. Cheng, Z. Luan and J. Klinowski, *Langmuir*, 1995, **11**, 2815.
5 C. Chen, H. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17.
6 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. G. Chmelka, *Science*, 1993, **261**, 1299.
7 N. Coustel, F. D. Renzo and F. Fajula, *J. Chem. Soc., Chem. Commun.*, 1994, 967.
8 A. Corma, M. T. Navarro and J. Perez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
9 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014.

Fig. 2 XRD patterns showing the conversion of a layered MnO_x birnessite into a mesoporous material