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Sol–Gel Synthesis of Cryptomelane, an Octahedral Molecular Sieve

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The sol–gel synthesis of an octahedral molecular sieve (OMS) having the cryptomelane (2 × 2) MnO_6 tunnel structure (OMS-2) is reported.

We report the sol–gel synthesis of cryptomelane, an octahedral molecular sieve (OMS) having a tunnel structure consisting of two edge-shared MnO_6 octahedra on each side (2 × 2), known as OMS-2.[1] Resultant OMS-2 materials of composition KMn_8O_{16} are highly crystalline with pronounced thermal stability in relation to materials produced by reflux or hydrothermal alteration methods. Some of the major factors that control the crystallinity and thermal stability include the concentration of MnO_4^-, the nature of the cation of the permanganate anion, the nature of the organic acid reducing agent, and the temperature used for calcination. We are not aware of the preparation of tunnel structure materials by the sol–gel route.

Octahedral molecular sieves having the (3 × 3) todorokite [OMS-1][2,3] and (2 × 2) cryptomelane [OMS-2][1,4] structures that have been prepared by hydrothermal alteration and reflux methods, have recently been reported. These materials are mixed-valent manganese oxides that contain tunnels of molecular dimensions, 6.9 Å for OMS-1 and 4.6 Å for OMS-2,[5,6] that are related to natural manganese nodules.[7] The synthetic conditions for such phases are quite demanding and appear to be related to control of the tunnel size[1–9] as well as the degree of mixed valency.[1–4]

Sol–gel methods offer several advantages for the preparation of materials including the relatively inexpensive procedures, the ability to control resultant phases, synthesis at the molecular scale, very pure products, control of particle and pore sizes, and others.[10,11]

A procedure for the preparation of OMS-2 *via* sol–gel methods involves preparation of a solution of $KMnO_4$ (1.5804 g; J. D. Baker) in 100 ml distilled deionized water (DDW). To this solution, maleic acid (0.387 g; Pfaltz and Bauer) is added and the mixture is stirred for 30 min.

A dark brown sol is formed at room temperature which starts to gel in 30 min with syneresis occurring in about 5 min. The resultant H_2O–gel product is 50% H_2O by volume on top of the gel. The H_2O is decanted and the resultant gel is washed 4 to 5 times with 100 ml portions of DDW and the wash water is decanted. The gel is then transferred to a filter funnel under vacuum (water aspirator) for 20 min at room temperature. The gel is then heated in air at 100 °C in an oven for about 10 h, and then calcined in air at 450 °C for 4 h. The resultant chemical composition is $KMn_8O_{16}\cdot nH_2O$.†

The resultant powders show sharp X-ray powder diffraction patterns and no evidence of other phases. X-Ray powder diffraction data were collected on a Scintag Model PDS 2000 theta diffractometer with Cu-Kα radiation. Data for sol–gel prepared OMS-2 show d-spacings (Å) and [intensities, (counts)] of 7.107 (90), 4.990 (151), 3.141 (302), 2.480 (72), 2.414 (330), 2.168 (138), 1.952 (45), 1.842 (148) and 1.647 (64). The temperature of calcination needs to be at least 400 °C to observe formation of cryptomelane. Below 400 °C, amorphous materials are produced. Above 800 °C, cubic Mn_2O_3 (c-Mn_2O_3) or synthetic bixbyite is formed.

Bixbyite is a distorted octahedral edge-shared structure similar to that of CaF_2.[12] Optimization of several synthetic factors besides calcination temperature is necessary to avoid the bixbyite phase and to prevent its formation at temperatures as low as 600 °C. For example, $KMnO_4$ yields crystalline, thermally stable OMS-2 as does $CsMnO_4$, however, $NaMnO_4$ leads to OMS-2 materials that are less thermally stable (600 °C), $LiMnO_4$ and $Ca(MnO_4)_2$ lead to mixtures of OMS-2 and bixbyite, and $Mg(MnO_4)_2$ only produces bixbyite at temperatures greater than 400 °C.

The concentration of MnO_4^- is also a critical factor. For solutions of 0.35 mol dm^{-3} MnO_4^-, a mixture of cryptomelane and birnessite[1–9] [an octahedral layered (OL-1) MnO_6 edge-shared structure] is formed. Addition of organic acid to these higher permanganate ion solutions leads to instantaneous gelation and the resultant products are less thermally stable, yielding bixbyite at 600 °C.

As the temperature of the synthesis is increased from room temperature to 35–40 °C, the reaction rate increases and gels are formed more rapidly. The thermal stability of the resultant materials is diminished with bixbyite being formed at 600 °C.

The nature of the organic acid reducing agent is of considerable importance. Syntheses with fresh fumaric, glutaric and phthalic acids lead to a mixture of cryptomelane and bixbyite whereas maleic acid leads to pure cryptomelane. The solubilities and acid dissociation constants of these dicarboxylic acids are all quite different;[13] however, we believe that oxidation of maleic acid leads to a mixed-valent manganese redox state[1] that favours the formation of cryptomelane. The nature of the organic reducing agents also appear to be important for the preparation of lithium manganese oxide spinel materials.[14,15]

Thermogravimetric analytical data for an OMS-2 gel prepared by the sol–gel route are shown in Fig. 1. The mass change between room temperature and 200 °C is due to loss of H_2O, from 200 to 500 °C to decomposition of the organic acid, at 500–550 °C to formation of cryptomelane, and from 800 to 900 °C to oxidation of cryptomelane to bixbyite. FT-IR data have been used to identify loss of H_2O and maleic acid. Such precise phase changes can often be observed for sol–gel preparations, such as with the preparation of spinels.[10]

Temperature-programmed desorption (TPD) data for O_2 evolved as OMS-2 gel is heated from 273 to 873 K are shown in Fig. 2. Integration of the TPD data shows that only 0.48 atoms of O per 16 atoms in the unit cell are evolved for this material.

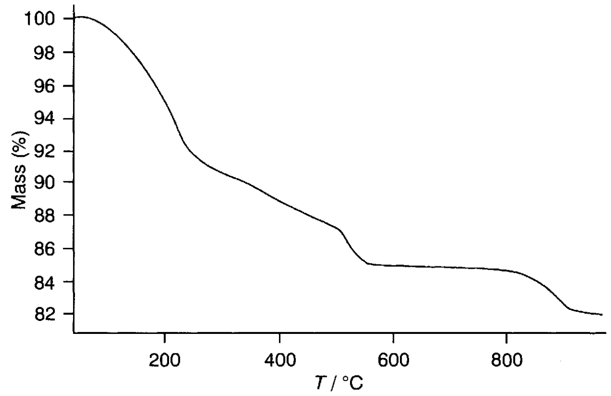

Fig. 1 Thermogravimetric analysis of OMS-2 gel prepared by sol–gel methods

Calcined OMS-2 prepared by hydrothermal alteration methods leads to the loss of 9.41 atoms of O. The thermal stability of the sol–gel OMS-2 system is clearly superior to the materials prepared by hydrothermal alteration.[1,4] The physical properties are also different.[1,4,16] Scanning electron microscopy data such as that of Fig. 3 show that the sol–gel materials have an irregular morphology as large as 8–9 μm in comparison to reflux materials[1,4] which are needles on the order of 2000 Å in length and 250 Å in diameter.

Oxygen vacancies produced during thermal treatment of OMS-2 materials are important for adsorptive and catalytic applications.[1–4] OMS materials have been shown to be outstanding oxidation catalysts[1–4] and may find applications as battery materials.[1,17] Sol–gel methods for the preparation of tunnel structure OMS materials allow several other advantages, such as easy incorporation of dopants and templating agents directly into the sol.[16] Preparation of thin films *via* spin coating techniques that might be used in electrochemical or sensor applications are also possible.

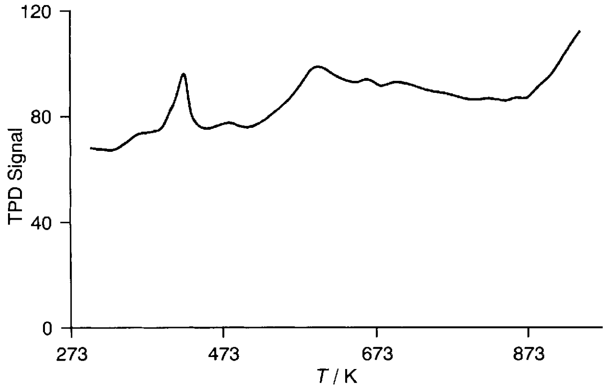

Fig. 2 Temperature programmed desorption of O_2 for calcined OMS-2 gel prepared by sol–gel methods

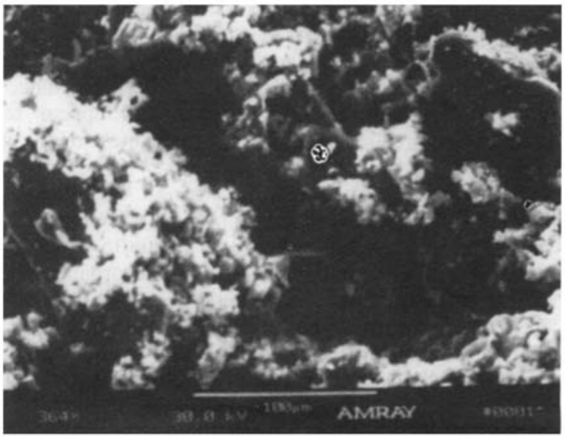

Fig. 3 Scanning electron micrograph of OMS-2 prepared by sol–gel methods

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