

## Octahedral Molecular Sieves: Preparation, Characterization and Applications

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Synthesis and characterization of a thermally stable analogue of synthetic todorokite, octahedral molecular sieve (OMS-1), is reported.

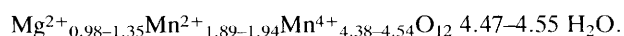
We report the synthesis of thermally stable crystalline synthetic octahedral molecular sieves having a structure similar to the mineral todorokite, a 3 octahedra by 3 octahedra manganese oxide tunnel structure, having a pore size of 6.9 Å. These materials are ion-exchangeable, can sorb hydrocarbons as large as CCl<sub>4</sub>, have Brønsted and Lewis acid sites and remain crystalline with an open pore structure to 500 °C. This octahedral molecular sieve (OMS-1) also shows unusual electrical conductivity properties.

OMS-1 was prepared by exchanging synthetic birnessite<sup>†</sup> (produced with [MnO<sub>4</sub>]<sup>2-</sup> oxidizing agent) with Mg<sup>2+</sup> ions and autoclaving the exchanged material at 155–170 °C for 10–40 h. The resultant powder was washed with distilled deionized water, dried at room temperature and then calcined at temperatures between 300 and 500 °C. X-Ray powder diffraction data for OMS-1 yield an *a* lattice parameter of 9.516 Å based on a pseudo-orthorhombic unit cell.<sup>1</sup>

Transmission electron microscopy studies of OMS-1 reveal plates of area 2500 by 6000 Å with hexagonal features of 100 Å width and 250 Å length (see Fig. 1) that are not present in natural mineral samples. Lattice parameters *b* = 10.31 Å and *c* = 2.97 Å were determined from electron diffraction

data and suggest that OMS-1 is most closely associated with natural todorokite from Charco Redondo, Cuba<sup>2</sup> although greater crystallinity, larger particle sizes, less twinning and higher purities in composition are generally found for OMS-1 than for natural forms.<sup>3,4</sup> Synthetic todorokite has been reported previously,<sup>5</sup> however, the thermal stability of resultant material prepared in our laboratories by this route is about 300 °C, significantly lower than for OMS-1. These materials also have different ion-exchange and structural properties and this may suggest that at least two phases may exist for synthetic todorokites.

Wet chemical and atomic absorption analyses show that the general composition of OMS-1 is:



The percentage of exchangeable Mg<sup>2+</sup> ions in synthetic todorokite is larger than in natural todorokite<sup>6</sup> as evidenced by ion-exchange isotherm data. Further characterization of OMS-1, natural todorokites and related manganese oxide materials<sup>7</sup> was done by using cyclic voltammetry. Cathodic and anodic potentials and peak shapes measured at pH 4, 7 and 10 readily distinguish these different structures.

Electron paramagnetic resonance data confirm the presence of Mn<sup>2+</sup> ions. Thermogravimetric analyses coupled with sorption studies of cyclohexane, which has a kinetic diameter of about 6.2 Å, show significant uptake for OMS-1 with a considerable falloff in sorption after heating to 500 °C as

<sup>†</sup> Synthetic birnessite was prepared by adding a sol of 40 ml 0.50 mol dm<sup>-3</sup> MnCl<sub>2</sub> to 50 ml 5.0 mol dm<sup>-3</sup> NaOH thoroughly stirred to a 0.1 mol dm<sup>-3</sup> Mg(MnO<sub>4</sub>)<sub>2</sub> solution. The resultant powder was washed until no Cl<sup>-</sup> was further detected.



Fig. 1 Transmission electron micrograph of OMS-1, 380 000 $\times$

shown in Fig. 2. Loss of the tunnel structure above 500  $^{\circ}\text{C}$  was confirmed by X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) measurements. Negligible sorption of 1,3,5-triethylbenzene (8.4  $\text{\AA}$ ) or hexachlorocyclopentadiene (7.5  $\text{\AA}$ ) was observed for materials activated at all temperatures. The equilibrium uptake of  $\text{CCl}_4$ , which has a kinetic diameter of 6.9  $\text{\AA}$ , of about 18 g per g of OMS-1 is similar to that for cyclo- $\text{C}_6\text{H}_{12}$ . Notably the layered birnessite precursor sorbs all of these molecules (as expected), although uptake curves for cyclohexane show considerably different rates and amounts of uptake than for OMS-1.<sup>8</sup>

The fact that uptake increases up to 500  $^{\circ}\text{C}$  is consistent with the retention of crystallinity of OMS-1 to temperatures greater than 500  $^{\circ}\text{C}$ . X-Ray powder diffraction experiments for OMS-1 calcined at 500  $^{\circ}\text{C}$  show that the resultant material retains its crystallinity and has sharper and more intense reflections than a similarly treated natural todorokite from Saipan.<sup>9</sup> In addition, BET surface area measurements show that porosity is retained after calcination at 500  $^{\circ}\text{C}$ .<sup>9</sup>

Fourier transform infrared studies of calcined OMS-1 which was allowed to sorb pyridine at room temperature (followed by removal of physisorbed pyridine at 80  $^{\circ}\text{C}$  for 8 h) showed bands at 1460  $\text{cm}^{-1}$  attributed to Lewis and Brønsted acid sites observed near the 1540  $\text{cm}^{-1}$  region. We are not aware of other reports concerning acidity of these materials.

Electrical conductivity studies done with a layer of OMS-1 between two electrodes showed insulating behaviour until temperatures of 275  $^{\circ}\text{C}$  when good electrical conductivity ( $>100 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) was observed. Mixed valent transition metal oxides are expected to conduct, however, a Nernstian response or exponential increase in conductivity is expected for semiconducting materials. No corresponding phase change was observed in this temperature range by either XRD or differential scanning calorimetry methods. A reversible

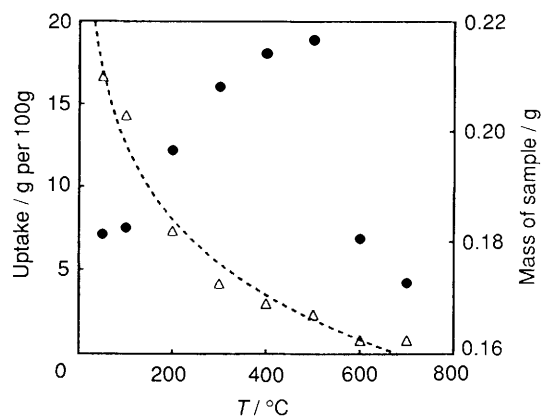


Fig. 2 Plot of cyclohexane uptake (●) and mass gain ( $\Delta$ ) as a function of dehydration temperature of OMS-1

change in the electronic band structure of OMS-1 may be occurring near 275  $^{\circ}\text{C}$ , as when the temperature is lowered below 275  $^{\circ}\text{C}$ , insulating character is restored over at least ten cycles. Electrical conductivity of other forms of manganese oxide such as  $\text{Li}_x\text{MnO}_2$  is well known in applications of rechargeable, secondary nonaqueous batteries.<sup>10</sup>

Further syntheses of ion-exchanged OMS-1 materials having divalent ions substituted for  $\text{Mn}^{2+}$  have resulted in materials containing  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  ions that have similar structures and thermal stabilities.

These results obtained to date have demonstrated that a new family of tunnel structure materials has been synthesized and characterized with interesting sorptive, catalytic and electrical properties. Synthetic and structural studies of these and related materials will be reported in subsequent publications.<sup>9</sup>

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