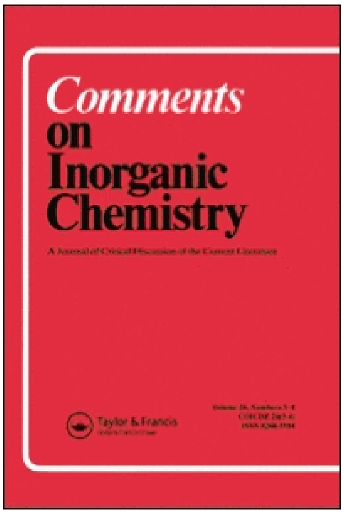

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Synthetic Routes to Microporous Manganese Oxides

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Synthetic Routes to Microporous Manganese Oxides

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Microporous manganese oxides with layer and tunnel structures have been synthesized by methods such as redox precipitation, thermal and hydrothermal alteration, sol-gel processing, and microwave heating. The open frameworks of these materials are composed of edge and corner shared MnO_6 octahedra, with the internal pores being occupied by cations and water molecules. Birnessite-type (OL-1) manganese oxides have layered structures with interlayer spacings that depend on hydration. Hollandites (OMS-2) and todorokites (OMS-1) have tunnel structures that consist of respective 2 × 2 and 3 × 3 arrays of MnO_6 octahedra. Microporous manganese oxides are of interest because of potential applications in heterogeneous catalysis, chemical absorption, and battery technology. This article describes some recent developments in the synthesis of microporous manganese oxides, with particular attention being given to birnessites, hollandites, and todorokites.

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INTRODUCTION

The MnO_2-type manganese oxides make up a large class of materials that have related structures and subtle variations in stoichiometry.[1–4] More than 30 different phases are known, many of which contain foreign cations and/or water molecules as additional constituents. A large number of these compounds are found as natural forms of mineralized manganese in soils, sediments, ores, and marine manganese nodules. Others have been prepared as synthetic phases.

In general, tetravalent manganese oxides are poorly crystalline and therefore not amenable to studies by single-crystal X-ray diffraction.[2] Most of their structural information instead has been determined through powder X-ray methods. The common structural feature of these materials are their MnO_6 octahedral building blocks, which can combine by edge and corner sharing to form layer and tunnel frameworks.

We are interested in the chemistry of microporous manganese oxides such as birnessites, hollandites, and todorokites (Fig. 1). The internal dimensions of these layered and tunneled materials are large enough to accommodate small molecules as well as interstitial cations. Thus, they exhibit desirable characteristics such as molecular sieving and ion-exchange,[5–7] which are also important trademarks of clays and zeolites. These materials are also mixed-valent with respect to manganese and show semiconducting electronic behavior.[8–10] We employ an identification scheme that designates layered and tunneled manganese oxides as *octahedral layer* (OL) and *octahedral molecular sieve* (OMS) compounds. Birnessites are identified as OL-1 while hollandites and todorokites are designated OMS-2 and OMS-1, respectively.

The structural features, physical properties, and mineral characteristics of microporous manganese oxides suggest a variety of potential applications. Their size-selective pores and active oxide surfaces make them excellent candidates for heterogeneous catalysis.[5,6,11] Birnessite and todorokite are especially interesting, being major constituents of marine manganese nodules, because the nodules are known to catalyze a variety of reactions that include the oxidation of alcohols and CO, reduction of NO, hydrogenation of alkenes, and decomposition of organic sulfur compounds.[12–16] Microporous manganese oxides also have ion-exchange capabilities and open structures that might be utilized in chemical absorption of heavy metal cations and noxious gases.[12,17] They are also being examined as cathode materials for rechargeable lithium batteries.[18–22]

STRUCTURE AND COMPOSITION

Birnessites have characteristic layered structures with cations and water molecules occupying the interlayer region (Fig. 1A).[23–25] The typical layer spacing is 7 Å, but this value fluctuates with hydration. Birnessites have poorly defined stoichiometries that are best described by the general formula $A_x MnO_{2\pm y} (H_2O)_z$, in which A typically represents an alkali metal cation. The average manganese oxidation state ranges from 3.6–3.8 due to Mn(IV) and small amounts of Mn(III). There is also speculation over the presence of Mn(II).

Hollandite-type manganese oxides consist of 4.6 Å tunnels formed from 2 × 2 arrangements of MnO_6 octahedra (Fig. 1B).[26–28] The different members of this class of materials are distinguished by their tunnel cation.

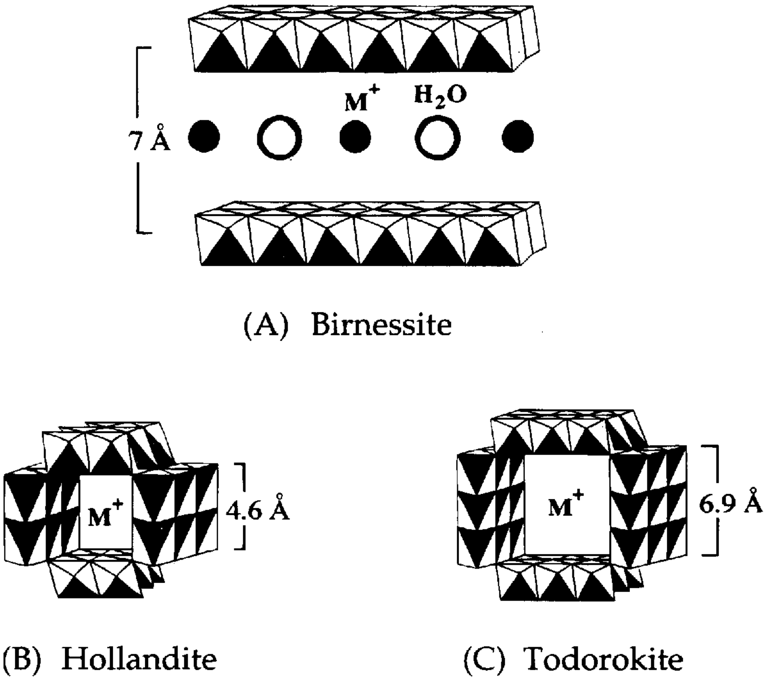


FIGURE 1 Structural frameworks of microporous manganese oxides showing the edge and corner shared MnO_6 octahedra and interstitial species. (**A**) Birnessite (OL-1). (**B**) Hollandite (OMS-2). (**C**) Todorokite (OMS-1).

Hollandite, for example, is used both as a broad title for these materials and as a specific definition for the manganese oxide with Ba^{2+} in the tunnels. The most common hollandite is cryptomelane, which contains K^+.

Todorokites have a 3 × 3 tunnel structure with 6.9 Å × 6.9 Å dimensions (Fig. 1C).[29] Their elemental compositions and manganese oxidation states are similar to birnessite. The tunnels contain significant amounts of water and can accommodate a variety of metal ions. Mineral forms of todorokite usually have Na^+ and/or Ca^{2+} in the tunnels, while synthetic todorokites are prepared with Mg^{2+}, as well as divalent cations of several first-row transition metals.

BIRNESSITES

Birnessites (OL-1) are among the most common manganese-containing minerals. Synthetically, the 7 Å OL-1 material is most prevalent, but other OL-1 phases with different interlayer distances also have been prepared. The 10 Å OL-1 phase known as buserite is generated upon further hydration of the 7 Å birnessite layers.[2,3,5,24,30,31] A dehydrated form of sodium birnessite with an interlayer spacing of 5.5 Å also has been identified.[32–36] Collectively, these materials are often referred to as phyllomanganates because of their lamellar structure.

The most common synthetic birnessites, Na-OL-1 and K-OL-1, are classically prepared by oxidation of aqueous Mn^{2+} in concentrated NaOH or KOH. Typical oxidants include O_2,[4,37–41] Cl_2,[4] $S_2O_8^{2-}$,[4] and MnO_4^-.[5] Hydrothermal routes also have been developed for OL-1 materials, as Na-OL-1 can be prepared from slurries of MnO_2[33,42] and Mn_2O_3[43] in aqueous NaOH, while K-OL-1 can be obtained from MnO_2 in KOH solution[44] or from $KMnO_4$ in mild aqueous acid.[30]

Ion-exchange reactions provide a convenient route to OL-1 materials with non-alkali-metal interlayer cations. This strategy typically utilizes Å and 10 Å Na-OL-1 as ion-exchange precursors in order to take advantage of the highly labile sodium cations. Reactions of 7 Å Na-OL-1 with divalent cations such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} have been shown to produce 10 Å buserites through ion-exchange and concurrent enhancement of interlayer hydration (Fig. 2).[5,24,36] Other foreign cations also participate in ion-exchange, but without expansion of the interlayer region.[24,36] Ion-exchange of 7 Å Na-OL-1 and 7 Å K-OL-1 also has been carried out in two-stage procedures, which involve initial

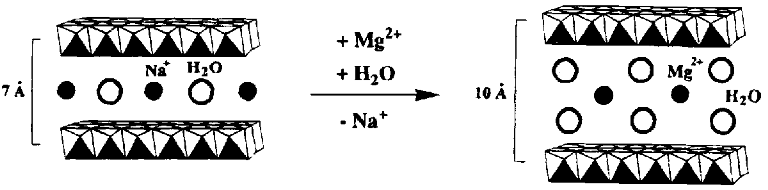


FIGURE 2 Conversion of birnessite (7 Å OL-1) to buserite (10 Å OL-1).

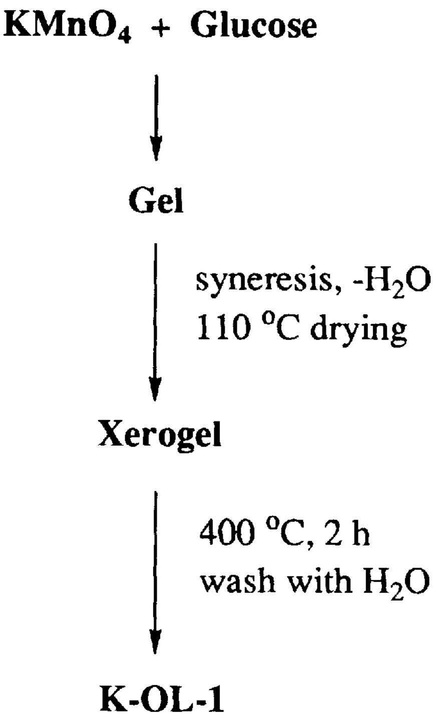
extraction of the alkali cations with aqueous acid followed by insertion of different foreign cations.[42,44] Samples of 10 Å Na-OL-1 typically undergo ion-exchange with retention of the 10 Å layer spacing.[39–41] However, reactions with cations such as dodecylammonium[45] and hexylammonium[46] have been used to generate manganese oxides with larger interlayer distances. A pillared OL-1 material also has been prepared by further reaction of hexylammonium-OL-1 with the polyoxo cation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$.[46]

The sol-gel process is a less studied route to layered manganese oxides that offers an interesting alternative to traditional synthetic procedures.[47–49] Advantages of sol-gel chemistry include homogeneous reactant mixing on the molecular level, and possible control over the identity, shape, morphology, and particle size of the resulting phases. A major problem in developing sol-gel processes for manganese oxides with near-MnO_2 stoichiometry is the lack of suitable Mn(IV) molecular precursors in aqueous solution.[50] However, this difficulty has been circumvented using redox reactions between aqueous permanganate and organic reducing agents such as fumaric acid,[50] sugars, and other poly alcohols.[51,52]

The sol-gel synthesis of birnessite-type manganese oxides was first reported by Bach and co-workers, who used reactions of $NaMnO_4$ or $KMnO_4$ with fumaric acid (E-butenedioic acid) to generate monolithic gels that yielded OL-1 materials upon drying and calcination.[50] The cation-extracted OL-1 phases could be obtained after treatment with sulfuric acid.[50,53] Analogous reactions with other permanganates such as $LiMnO_4$ and $(NR_4)MnO_4$ produced non-birnessite manganese oxide phases.

Our research has produced a sol-gel synthesis of birnessite-type manganese oxides from reactions of $KMnO_4$ or $NaMnO_4$ with various sugars and other organic polyalcohols.[51,52] The formation of MnO_2 "jellies" from reactions of $KMnO_4$ and sugars was initially reported by Witzrmann in 1915,[54] but these gels remained poorly characterized[55,56] and were not subjected to drying and calcination. The formation of birnessite was established by our reinvestigation of this work.

We find that reactions between concentrated solutions of $KMnO_4$ and glucose produce gels that ultimately yield potassium birnessite (K-OL-1) upon drying and calcination (Scheme 1).[51] This reaction is easily extended to other sugars, as well as a variety of polyalcohols such as ethylene glycol, glycerol, and poly(vinyl alcohol). Gelation is believed to result from manganese oxide sites being cross-linked by partially oxidized organic fragments (Fig. 3). The synthesis is optimized using concentrated reactants with high glucose/$KMnO_4$ ratios.[52] More dilute reaction mixtures and low glucose/$KMnO_4$ ratios produce other manganese oxide phases such as cryptomelane and Mn_2O_3 (Scheme 2).



SCHEME 1 Sol-gel synthesis of K-OL-1.

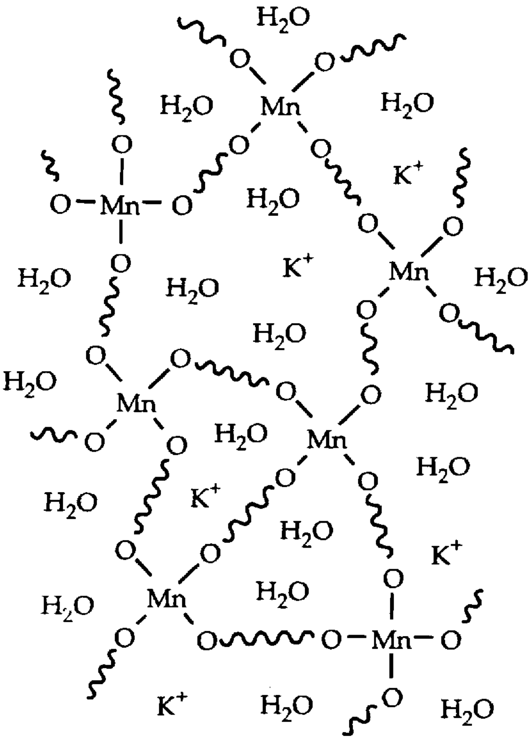
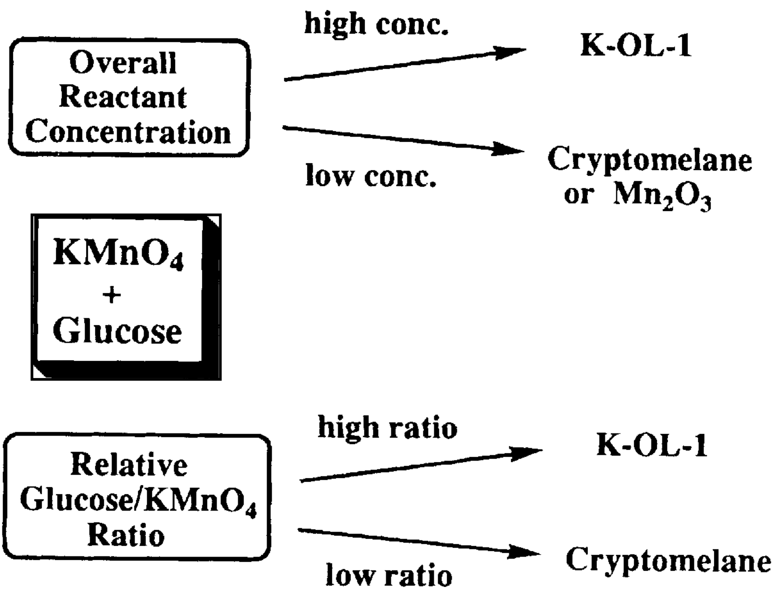


FIGURE 3 Proposed structure of the manganese oxide gel matrix.

Analogous sol-gel reactions between $NaMnO_4$ and glucose yield mixtures of two related Na-OL-1 materials, one with the typical 7 Å interlayer distance and one with a 5.5 Å layer spacing.[52] The 5.5 Å Na-OL-1 is a dehydrated form of the 7 Å phase and readily converts to 7 Å Na-OL-1 after prolonged exposure to water (Fig. 4). Infrared spectroscopy of 5.5 Å Na-OL-1 reveals the absence of an O–H stretching band for water, which is present in the IR spectrum of 7 Å Na-OL-1. The 5.5 Å phase is obtained exclusively by calcining the manganese oxide xerogel at 800°C instead of the usual 400°C temperature. Interestingly, the 7 Å birnessite is not a precursor to the 5.5 Å material, since 7 Å Na-OL-1 decomposes to Mn_3O_4 at temperatures above 600°C whereas 5.5 Å Na-OL-1 is stable to at least 800°C. The chemistry of the sol-gel Na-OL-1 phases is summarized in Scheme 3.



SCHEME 2 Sol-gel reactions between $KMnO_4$ and glucose with different overall and relative reactant concentrations.

Ion-exchange reactions have been performed on sol-gel Na-OL-1 and K-OL-1 using a variety of monovalent and divalent metal cations.[52] However, unlike their non-sol-gel counterparts, these OL-1 materials do not undergo 100% exchange. This is particularly surprising for sol-gel Na-OL-1, given the lability of the sodium ions in classically prepared birnessites. The sol-gel OL-1 materials also differ from non-sol-gel birnessites by not forming 10 Å buserites when exchanged with divalent cations such as Mg^{2+} and Cu^{2+}. We speculate that these unusual ion-exchange characteristics might be related to the poor interlayer hydration found in these sol-gel materials. Less water between the layers results in

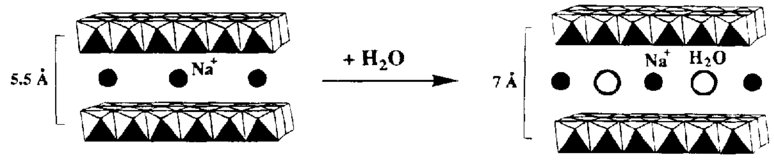
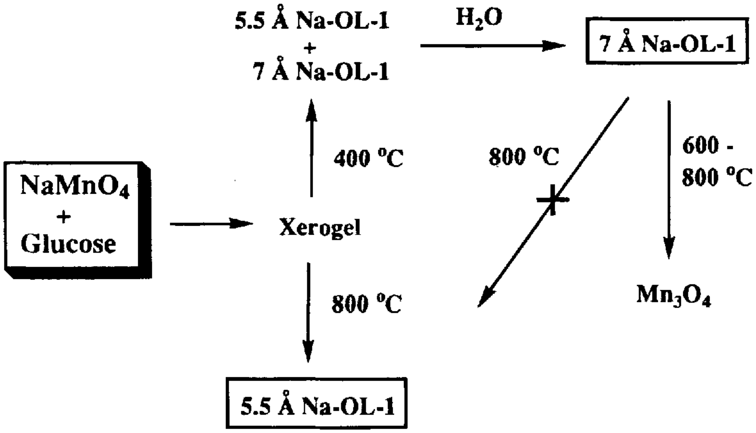


FIGURE 4 Conversion of 5.5 Å Na-OL-1 into 7 Å Na-OL-1 by hydration.



SCHEME 3 Sol-gel synthesis of Na-OL-1 materials.

lower hydration of the interstitial cations. This, in turn, could restrict the mobility and accessibility of the cations between the layers. The inherently poor water content of sol-gel Na-OL-1 and K-OL-1 also works against the formation of 10 Å buserites since the resulting layer expansion calls for even greater interlayer hydration (Fig. 2).

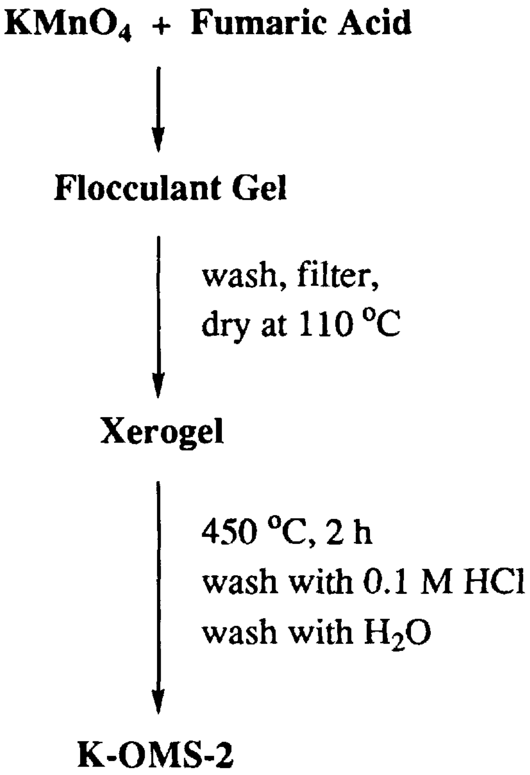
Sol-gel reactions are capable of producing thin films of K-OL-1 on glass and copper substrates.[57] Mixtures of sucrose and $KMnO_4$ have been used to prepare manganese oxide films by different methods such as immersion, spray, spin, and spatula coating. Crystalline K-OL-1 thin films result from coatings that involve immersion, spray, and spatula techniques, with spray coating giving the most homogeneous films. Spin coating generates amorphous thin films that are manganese deficient. In general, the films are good conductors and free from large amounts of impurities, such as carbonaceous deposits, that might be formed during synthesis.

Tetraalkylammonium cations have been used as structure directors for the preparation of OL-1 manganese oxides with larger layer spacings.[58] Tetramethyl, tetraethyl, tetrapropyl, and tetrabutylammonium cations react with $KMnO_4$ to produce alkylammonium permanganates that are then treated with water/butanol solutions to generate tetraalkylammonium manganese oxide sols. After aging up to two days and drying at 80–90°C, pillared OL-1 materials are obtained with interlayer distances that match the given alkylammonium cation. These manganese oxides are stable to 150–200°C.

Cryptomelane (K-OMS-2) is the most readily synthesized manganese oxide in the hollandite group. Its prevalence can be attributed to the effectiveness of the potassium cations in stabilizing the 2 × 2 tunnel structure. Conventional routes to K-OMS-2 include thermal[7,17,24,59] and hydrothermal[50] treatment of layered manganese oxides such as K-OL-1. Other common syntheses employ redox reactions between Mn^{2+} and oxidizing agents such as $KMnO_4$,[7,61] $K_2S_2O_8$,[4,62,63] and O_2[64] in aqueous acid. The stoichiometry of K-OMS-2 can be expressed generally as $KMn_8O_{16}(H_2O)_x$. An average manganese oxidation state of 3.9 reflects a vast majority of Mn(IV) with very small amounts of Mn(III). The room-temperature conductivity of K-OMS-2 as pressed pellets is on the order of $10^{-2}\ \Omega^{-1}\ cm^{-1}$, which is several orders of magnitude greater compared to birnessites and todorokites.[8]

We have developed a sol-gel synthesis of K-OMS-2 as an outgrowth of the sol-gel chemistry that we and others have established for OL-1 manganese oxides.[50–52] Reactions between dilute solutions of $KMnO_4$ and fumaric acid produce flocculant gels that are precursors to K-OMS-2 (Scheme 4).[65,66] Similar reactions by Bach and co-workers showed that highly concentrated solutions of $KMnO_4$ and fumaric acid yield monolithic gels that are precursors to layered manganese oxide phases.[50] Our previous experience with sol-gel systems of $KMnO_4$ and glucose indicates that reactant concentration strongly influences the nature of the resulting products (Scheme 2).[52] A similar reactivity pattern appears to be followed in sol-gel systems involving $KMnO_4$ and fumaric acid.

We have investigated possible reasons for the preferential formation of K-OL-1 and K-OMS-2 in the $KMnO_4$/fumaric acid system.[66] Our conclusion is that the potassium content plays a key role in determining the final product from a given manganese oxide gel. The elemental analysis of $KMnO_4$/fumaric acid xerogels supports this view (Table I). The data show a clear preference for K-OMS-2 when the %K and K/Mn ratio are relatively low. By contrast, the higher values favor K-OL-1 formation. These results are consistent with the fact that K-OMS-2 contains less potassium than K-OL-1. Low potassium contents are brought on by washing, which creates flocculant gels and promotes extraction of K^+. Indeed, the monolithic gels used by Bach and co-workers to produce K-OL-1[50] can be converted K-OMS-2 precursors if they are dispersed



SCHEME 4 Sol-gel synthesis of K-OMS-2 (cryptomelane).

and thoroughly washed with water (Table I, last two entries). However, retention of K^+ in the gel, even after washing, results in K-OL-1 as the end product. Such is the case for flocculant gels formed in KOH solution, which generate K-OL-1 (Table I, entry 4).

Changes in acidity and basicity also alter the sol-gel pathway (Table II).[66] Reactions of $KMnO_4$ with fumaric acid in 0.1 M HNO_3 result in precipitates that yield Mn_2O_3, whereas the same reactions in 0.1 M KOH produce K-OL-1. Bach and co-workers found that K-OMS-2 is generated by increasing the solution acidity and decreasing the fumaric acid/$KMnO_4$ ratio. However, this reaction apparently occurs by precipitation rather than through a sol-gel mechanism.[67]

TABLE I

Xerogel Analyses and Manganese Oxide Products from Sol-Gel Reactions Between $KMnO_4$ and Fumaric Acid.

Reaction Conditions (Gel Treatment)	Xerogel Analysis %K	K/Mn	Product
(1) 0.100 M $KMnO_4$/0.033 M fumaric acid (filtered, washed)	7%	0.13	K-OMS-2
(2) 0.100 M $KMnO_4$/0.033 M fumaric acid (filtered, unwashed)	18%	0.46	K-OL-1
(3) 0.100 M $KMnO_4$/0.033 M fumaric acid (unfiltered, unwashed)	23%	0.89	K-OL-1
(4) 0.100 M $KMnO_4$/0.033 M fumaric acid/ 0.1 M KOH (filtered, washed)	14%	0.51	K-OL-1
(5) 0.250 M $KMnO_4$/0.083 M fumaric acid (unfiltered, unwashed)	15%	0.45	K-OL-1
(6) 0.250 M $KMnO_4$/0.083 M fumaric acid (dispersed, filtered, washed)	7%	0.21	K-OMS-2 + Mn_2O_3

TABLE II

Reactions of $KMnO_4$ and Fumaric Acid with Different Acidity.

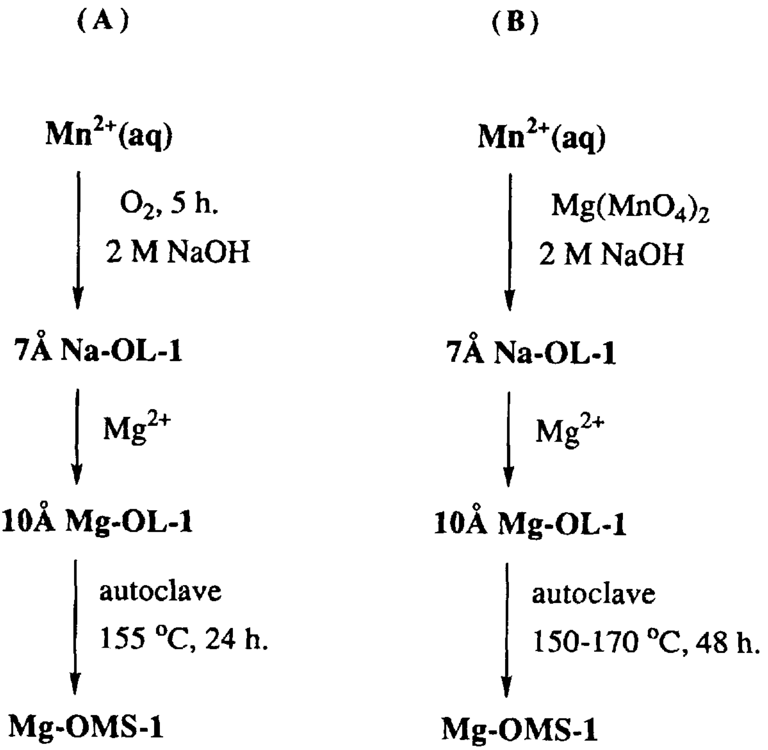
Reaction	Initial Phase	Product
$KMnO_4$ + Fumaric Acid (no acid or base)	precipitate	K-OMS-2
$KMnO_4$ + Fumaric Acid (0.1 M HNO_3)	flocculant gel	Mn_2O_3
$KMnO_4$ + Fumaric Acid (0.1 M KOH)	flocculant gel	K-OL-1

TODOROKITES

Todorokite (OMS-1) is a major component of marine manganese nodules and a potentially useful material for chemical sorption and heterogeneous catalysis. These proposed applications originate from observations that the marine nodules are capable of concentrating transition metal cations and serving as multifunctional catalysts.[12] Since natural todorokite samples often lack the purity required for detailed chemical and mineralogical studies, there has been strong motivation to prepare synthetic OMS-1. Such procedures have been discovered relatively recently.

Todorokite was first synthesized by Golden and co-workers using a multi-step procedure that involves (a) preparation of 7 Å Na-OL-1 by oxidizing Mn^{2+} with O_2 in aqueous NaOH, (b) conversion of 7 Å NaA-OL-1 into 10 Å Mg-OL-1 by ion-exchange, and (c) hydrothermal treatment of Mg-OL-1 for 8 hours at 155 °C (Scheme 5A).[37] The larger hydrated radius of Mg^{2+} is credited with stabilizing the 3 × 3 tunnel structure. Todorokites with Ni^{2+} La^{3+} and also have been generated by this route.[38] Cation-exchange studies on Mg-OMS-1 prepared by this method have shown that 60% of the tunnel Mg^{2+} can be extracted using 1 M HNO_3.[68]

Alternatively, OMS-1 has been synthesized using Na-OL-1 precursors from reactions of Mn^{2+} with $Mg(MnO_4)_2$ in NaOH solution (Scheme 5B). The desired OMS-1 product is generated after aging, Mg^{2+} ion-exchange, and hydrothermal treatment.[5] The Mg-OMS-1



SCHEME 5 Two synthetic routes to Mg-OMS-1: (**A**) the method of Golden and co-workers; (**B**) the method of Suib and co-workers.

obtained from this procedure shows thermal stability to 500°C, which is comparable to natural todorokite samples. By contrast, Mg-OMS-1 prepared by the method of Golden and co-workers was found to collapse near 300°C. Powder X-ray diffraction patterns of OMS-1 and its 10 Å OL-1 precursor both contain two major peaks, one in the range of 9.5–10.0 Å and another at 4.8 Å (Fig. 5). Although the peaks for OMS-1 and 10 Å OL-1 have different relative intensities, the layered and tunneled materials are not distinguishable by XRD data alone. Further information from structural, thermal, and surface analytical methods are required. The OMS-1 synthesis can be extended to other 3 × 3 materials with tunnel cations having similar hydrated radii to Mg^{2+}. Other cations that can be used as templates to prepare OMS-1 include Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The tunnel cations also serve to influence a number of OMS-1 properties such as crystallinity, thermal stability, surface acidity, and hydrocarbon uptake.[6]

Todorokite also has been prepared using microwave heating in place of hydrothermal treatment.[69] Since microwave heating of solids occurs from the interior of a sample to the surface, different results may be observed compared to standard thermal processes. Some advantages of microwave heating are that quicker and more uniform heating can be achieved compared to thermal processes; delays in heat transfer from the surface to the interior of a sample can be reduced or eliminated; improvements in the quality of crystals can be observed; and new phases may be produced. Microwave treatment of Mg-OL-1 produces Mg-OMS-1 in 2–4 hours,[69] decreasing the overall preparation time for OMS-1 by an impressive 7 days. The accelerated synthesis comes about because the microwave procedure does not require the long aging and hydrothermal steps that were previously used to prepare OMS-1.[5,6]

Synthetic todorokites have given excellent initial performances as molecular sieves and heterogeneous catalysts. The OMS-1 materials demonstrate selective uptake of different-sized organic absorbates, with the exclusion of molecules that are larger than the 6.9 Å tunnel operung (Table III).[5] Catalytic activity has been shown in reactions involving the conversion of methane to C_2–C_4 hydrocarbons,[5] oxidation of CO to CO_2,[6,11] and decomposition of isopropanol.[6] Studies with Cu-OMS-1 found conversions of CO to CO_2 in the range of 89–99% at 60–100°C.[11]

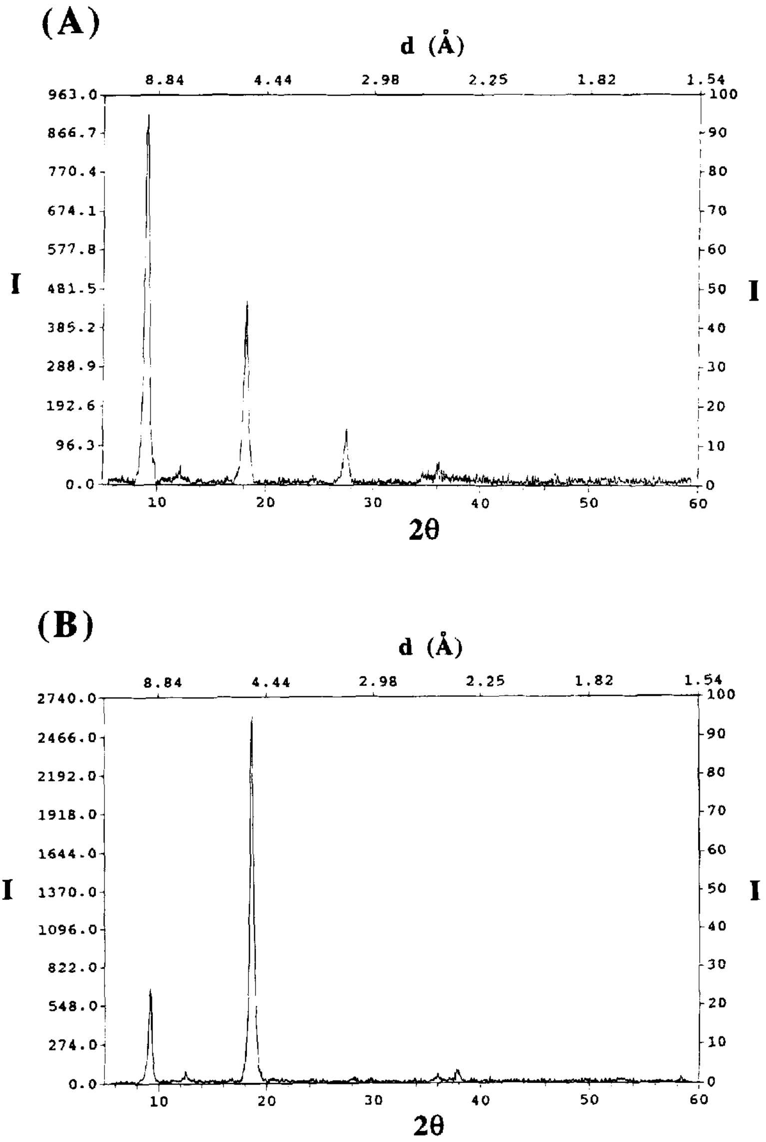


FIGURE 5 Powder X-ray diffraction patterns of (**A**) buserite (10 Å Mg-OL-1) and (**B**) todorokite (Mg-OMS-1).

TABLE III

Uptake of Absorbates in Mg-OMS-1 Heated to 500°C.

Absorbate	Dimension (Å)	Uptake (g/100 g)
cyclohexane	6.1	18.2
carbon tetrachloride	6.9	20.0
1,3,5-triethylbenzene	8.4	0
hexachloropentadiene	7.7	0

LARGER TUNNEL DIMENSION

A new 4 × 4 tunneled material called OMS-3 has been recently synthesized by a redox precipitation reaction between $Mn(O_2CCH_3)_2$ and $KMnO_4$.[70] This manganese oxide is prepared by dissolving 3.0 millimoles of $Mn(O_2CCH_3)_2$ in 500 mL of boiling ethanol, then adding 2.0 millimoles of $KMnO_4$. The resulting solution is heated while covered for one hour, concentrated to 100 mL, and allowed to dry at ambient temperature for one week. The resulting black solid is heated to 70°C over 45 minutes with periodic grinding. The product gives X-ray diffraction peaks at 12.71, 6.37, 4.20, and 3.13 Å, which is consistent with the 4 × 4 OMS-3 structure having 9.2 Å tunnel dimensions (Fig. 6).

Thermal stability measurements on OMS-3 reveal decomposition at the relatively low temperature of 150°C. The high d-spacing reflections do not shift during thermal analysis, but steadily decrease in intensity. These results indicate that OMS-3 is not a layered material. A comparison of the thermal stability of 2 × 2 cryptomelane (OMS-2), 3 × 3 todorokite (OMS-1), and the 4 × 4 OMS-3 material is shown in Fig. 7. From this data, it is clear that thermal stability decreases as tunnel size increases.

CONCLUDING REMARKS

The synthesis of microporous manganese oxides continues to be an active area of research. Some layered and tunneled phases, such as birnessites (OL-1) and hollandires (OMS-2), already can be obtained by a variety of preparative routes. However, there are still questions concerning their physical properties, thermal stability, chemical transformations,

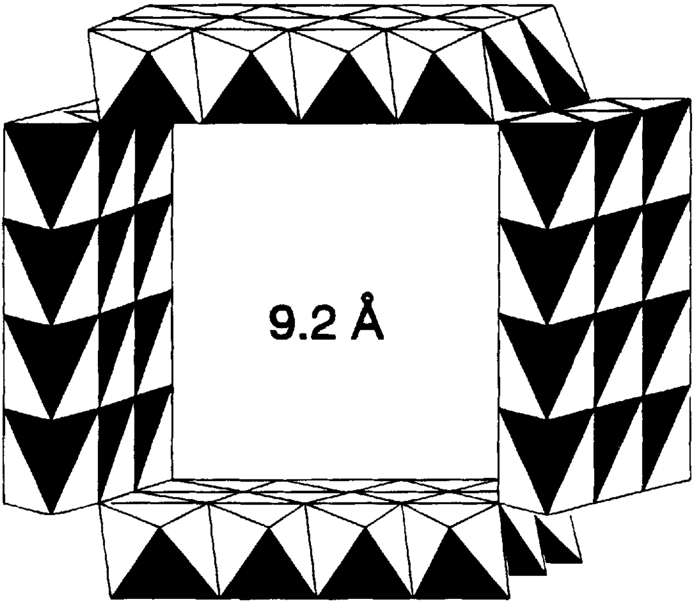


FIGURE 6 Structural framework of the 4 × 4 tunneled manganese oxide, OMS-3.

and catalytic activity. Other manganese oxides, such as todorokites (OMS-1) and the 4 × 4 tunneled materials (OMS-3), are relatively new as synthetic phases. Future investigations may yet uncover routes to other manganese oxides with layer and tunnel structures. New layered phases might be generated with different structures and interstitial species, while new tunneled materials might be prepared with larger or asymmetric tunnel dimensions. Furthermore, the ongoing studies of microporous manganese oxides should continue to provide insight toward the designed syntheses of these novel materials.

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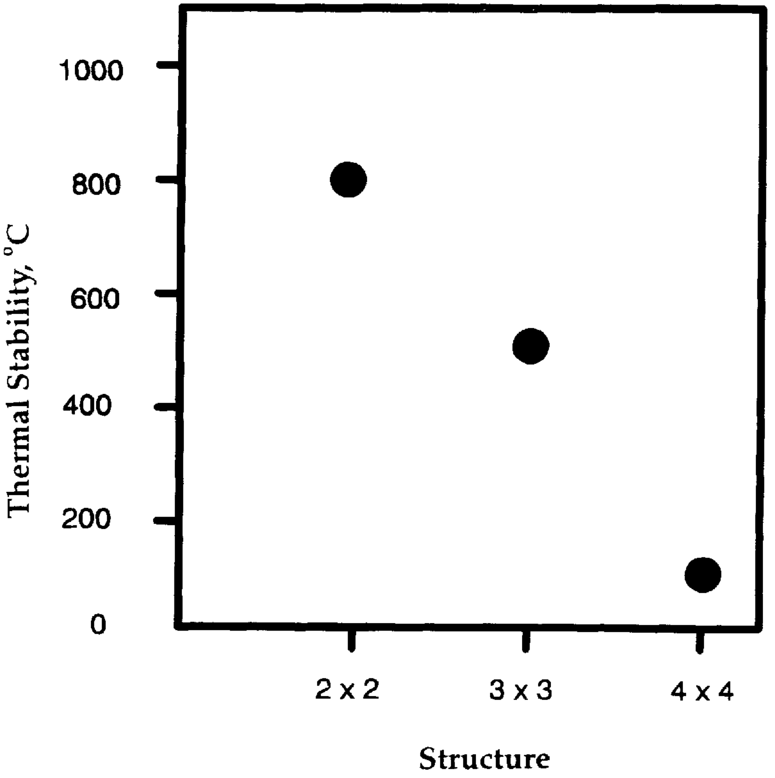

FIGURE 7 Thermal stability vs. structure type for tunneled manganese oxides.

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