Articles

Syntheses of Birnessites Using Alcohols as Reducing Reagents: Effects of Synthesis Parameters on the Formation of Birnessites

Ying Ma,[†] Jian Luo,[†] and Steven L. Suib*[,†,‡]

55 N. Eagleville Road, U-60, Department of Chemistry, Department of Chemical Engineering, and Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06269-3060

Received June 3, 1998. Revised Manuscript Received May 27, 1999

This study shows that synthetic birnessite, an octahedral layered manganese oxide material called OL-1 can be synthesized with Na^+, K^+, Na^+/Mg^{2+}, or K^+/Mg^{2+} ions as interlayer cations by redox reactions between permanganate and alcohols in a strong basic media. The synthesis processes were followed by powder X-ray diffraction (XRD) studies. OL-1 samples have been characterized by XRD, chemical analysis, average oxidation states measurements, and scanning electron microscopy studies. Results show that all OL-1 samples have an interlayer spacing of ∼7.0 Å. The average oxidation states of manganese fall in a range of 3.60−3.70. The chemical compositions for typical Na−OL-1 and K−OL-1 are $Na_{4.7}Mn_{14}O_{27.7}{\cdot}8.7H_2O$ and $K_{4.6}Mn_{14}O_{27.9}{\cdot}6.6H_2O$, respectively. α-MnO(OH) coexists with Na−OL-1 in the synthesis where $NaMnO_4$ aqueous solution is added to the solution containing ethanol, water, and sodium hydroxide. When $Mg(MnO_4)_2$ was used as the oxidant, more Mg^{2+} ions were accommodated in OL-1 than in previous reports. The interlayer space is propped opened by intercalating hexylammonium ions between the layers, confirming the layered structure.

I. Introduction

Birnessite is a common manganese oxide mineral, existing in a variety of geological settings including deep sea nodules, terrestrial ore deposits, and surface coatings and crusts.[1−5] It is also a significant component of some soils and involved in ion-exchange processes and redox reactions related to groundwater chemistry.[6] Birnessite is a layered manganese oxide material with edge-shared MnO_6 octahedra forming the layers and cations and water molecules situated between the negatively charged layers.[7−11] The layer spacing ranges from between 6.9 to 7.0 Å.[7−11] In their natural form, birnessites show potential applications as heterogeneous catalysts in the reduction of NO in the presence of ammonia,[12] oxidation of CO,[13] and hydrogenation of alkenes.[2] Birnessite is also a useful material for nuclear waste absorption due to its microporosity.[2,14] Ion-exchange and redox properties make birnessite an interesting cathode material[15−19] for rechargeable batteries.

Birnessite is also a necessary intermediate for preparing OMS-1 (*o*ctahedral *m*olecular *s*ieve),[20,21] a cata-

* To whom correspondence should be addressed.
[†] Department of Chemistry.
[‡] Department of Chemical Engineering and Institute of Materials Science.

(1) Burns, R. G.; Burns, V. M. *Marine Manganese Deposits*; Glasby, G. P., Ed.; Elsevier: New York, 1977; Chapter 7.
(2) Nitta, M. *Appl. Catal.* **1984**, *9*, 151−176.
(3) Matuso, K.; Nitta, M.; Aomura, K. *J. Catal.* **1978**, *54*, 446−449.
(4) Weisz, P. B. *J. Catal.* **1968**, *10*, 407−412.
(5) Golden, D. C.; Dixon, J. B.; Chen, C. C. *Clays Clay Miner.* **1986**, *34*, 511−520.
(6) Oscarson, D. W.; Huang, P. M.; Liaw, W. K. *Clays Clay Miner.* **1981**, *29*, 219−225.
(7) Ching, S.; Petrovay, D. J.; Jorgensen, M. L.; Suib, S. L. *Inorg. Chem.* **1997**, *36*, 883−890.
(8) Post, J. E.; Veblen, D. R. *Am. Miner.* **1990**, *75*, 477−489.
(9) Drits, V. A.; Silvester, E.; Gorshkov, A. I.; Manceau, A. *Am. Mineral.* **1997**, *82*, 946−961.
(10) Silvester, E.; Manceau, A.; Drits, V. A. *Am. Mineral.* **1997**, *82*, 962−978.
(11) Kuma, K.; Ushi, A.; Paplawsky, W.; Gedulin, B.; Arrhenius, G. *Mineral. Mag.* **1994**, *58*, 425−447.
(12) Wu, S. C.; Chu, C. *Atmos. Environ.* **1972**, *6*, 309−316.
(13) Cabrear, A. L.; Maple, M. B. *Appl. Catal.* **1990**, *64*, 309−320.
(14) Sabine, T. M.; Hewat, A. W. *J. Nucl. Mater.* **1982**, *110*, 173−177.
(15) Bach, S.; Pereira-Ramos, J. P.; Baffier, N. *Electrochim. Acta* **1993**, *38*, 1695−1698.
(16) Bach, S.; Pereira-Ramos, J. P.; Baffier, N.; Messina, R. *Electrochim. Acta* **1991**, *36*, 1595−1603.
(17) Golf, P. L.; Baffier, N.; Bach, S.; Pereira-Ramos, J. P.; Messina, R. *Solid State Ionics* **1993**, *61*, 309−315.
(18) Chen, R.; Zavalij, P.; Stanley Whittingham, M. *Chem. Mater.* **1996**, *8*, 1275−1280.
(19) Chen, R.; Chirayil, T.; Zavalij, P.; Stanley Whittingham, M. *Solid State Ionics* **1996**, *86−88*, 1−7.
(20) Shen. Y.-F.; Zerger, R. P.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O'Young, C.-L. *Science* **1993**, *260*, 511−515.
(21) Shen, Y.-F.; Zerger, R. P.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O'Young, C.-L. *J. Chem. Soc., Chem. Commun.* **1992**, 1213−1214.

10.1021/cm980399e CCC: $18.00
Published on Web 07/17/1999

lytically active manganese oxide material[22,23] containing tunnels formed by 3 × 3 edge-shared MnO_6 octahedra.[20,21,24,25] The interlayer distance of birnessite (~7.0 Å) needs to be increased to and stabilized at 10 Å (buserite) before buserite is hydrothermally treated at 170 °C to produce OMS-1.[20,21,24] This stabilization of interlayer distance at 10 Å is usually carried out by ion exchanging with Mg^{2+} after birnessite is completely washed with distilled deionized water and the pH of the washing water reaches about 9. [20,21,26,27]

Due to its layered structure, birnessite is also a promising precursor for pillared materials. Robust oxides such as Al_2O_3 and SiO_2 and catalytically important transition metal oxides are successfully intercalated into birnessite resulting in greatly improved thermal stabilities, chemical activities, and increased porosity.[28] As birnessite is also a mixed-valent manganese oxide material,[7−9,10,20] pillaring birnessite with transition metal oxides may also result in interesting electrical and photoelectrical properties.[29]

The variable valence states and compositions[9−11] of birnessite minerals make their industrial performance unpredictable and unrepeatable. Synthetic birnessite, prepared here is called M-OL-1 (M is the interlayer cation species) which has controllable valence states and compositions.

Many ways have been reported to synthesize OL-1, e.g., passing O_2 through suspensions of $Mn(OH)_2$ obtained by reactions of NaOH and Mn^{2+} to prepare synthetic sodium birnessite,[24,30] hydrothermal treatment of NaOH, MnO_2, and Mn_2O_3 to produce Na−OL-1,[31,32] and hydrothermal treatment of $NaMnO_4$ or $KMnO_4$ at 170 °C in a slightly acidic solution (pH 3.5) to prepare Na− or K−OL-1,[18,19] KOH reacting with MnO_2 can produce K−OL-1.[33] Redox reactions between permanganate and Mn^{2+} in basic solution followed by aging the reaction precipitate produce OL-1.[24,27,34] Sol−gel processes combined with calcination can lead to OL-1.[7,16,17,35] By ion-exchanging synthetic Na−birnessite with monovalent or divalent cations, synthetic birnessites with the same crystal symmetry but slight modifications of unit cell parameters are obtained[8−11] except for exchange with Ca^{2+} ions, where different structural and chemical features result.[36]

Table 1. Synthesis Combinations of Cations of MnO_4^- and OH^-

combination	MnO_4^- cation	OH^- cation	product
a	Na^+	Na^+	Na−OL-1
b	K^+	K^+	K−OL-1
c	Mg^{2+}	Na^+	Na/Mg−OL-1
d	Mg^{2+}	K^+	K/Mg−OL-1
e	K^+	Na^+	Na/K−OL-1

We report here the synthesis of OL-1 materials using alcohols as reducing agents. E. J. Witzemann summarized reactions between permanganate and organics in neutral, acidic, and basic media,[37] and the focus of that research was to obtain amorphous manganese oxide colloids. Experiments described here are systematic investigations of the synthesis parameters in monoalcohol systems to understand and optimize crystallization of OL-1.

II. Experimental Section

Syntheses. *Method 1*. Aqueous permanganate solution (150 mL, 0.316 M) was added to a mixed solution containing 0.125−0.375 mol of alkali hydroxide, 50 mL of ethanol, and 50 mL of distilled deionized water (DDW) with vigorous stirring. The resultant brown mixture was stirred for another 30 min before being allowed to age at different temperatures (60, 80, and 95 °C) for several days. The resultant dark gray to gray precipitate was thoroughly washed with distilled deionized water (DDW) until the pH of water was 9. The sample was dried at 80 °C for 24 h. Upon drying, it was ground to fine powder for characterization.

Method 2. This method is similar to Method 1 except that hydroxide was mixed with permanganate solution instead of with ethanol aqueous solution.

Method 3. Aqueous solution containing both permanganate (150 mL, 0.316 M) and hydroxide (0.833−2.50 M) was prepared first, and a solution consisting of 50 mL of water and 50 mL of ethanol was added to this solution dropwise, as compared to Methods 1 and 2 where MnO_4^- species were added to alcohol. The resultant mixture was stirred for another 30 min before being allowed to age at different temperatures (60, 80, and 95 °C).

In our experiments, different reaction systems have been studied to investigate the effects of interlayer cations on the formation of OL-1 materials. These combinations are shown in Table 1. Both Methods 1 and 2 were used to produce these materials. Table 2 lists the sample preparation conditions for all materials.

Characterization. *Powder X-ray Diffraction Studies.* A Scintag 2000 PDS diffractometer was used with Cu Kα radiation (1.54060 Å) and the tube voltage and current were set at 45 kV and 40 mA, respectively. Continuous scans with a scanning rate 5° 2θ/min were performed on thin film samples prepared by dripping a slurry of OL-1 on a microscope glass slide which was air-dried. The purpose of this fast continuous scan was to check whether OL-1 (distinguished by two diffraction peaks at 7.0 and 3.5 Å) was formed and to compare the relative widths of the XRD peaks obtained under the same operation conditions. Step scans with a step size of 0.01° 2θ and a counting time of 2 s/step were conducted on finely ground powder to confirm OL-1 materials, and to improve the signal/noise ratio. Side packing of powder samples was used to overcome preferential orientation of OL-1 thin-film samples.

Elemental Analyses. Solid samples were dissolved in concentrated HCl. Upon dilution Mn, Na, K, and Mg were analyzed with atomic absorption spectroscopy on a Perkin-Elmer P-40 instrument.

(22) Shen, Y.-F.; Suib, S. L.; O'Young, C.-L. *J. Am. Chem. Soc.* **1994**, *116*, 11020−11029.
(23) Wang, J.-Y.; Xia, Y.-G.; Yin, Y.-G.; Suib, S. L. *Catal. Organ. React.* Herkes, F. E., Ed. **1998**, 621−626.
(24) Golden, G. C.; Chen, C. C.; Dixon, J. B. *Science* **1986**, *231*, 717−719.
(25) Turner, S.; Buseck, P. R. *Science* **1981**, *212*, 1024−1027.
(26) Tian, Z.-R.; Yin, Y.-G.; Suib, S. L. *Chem. Mater.* **1997**, *9*, 1126−1133.
(27) Strobel, P.; Charenton, J.-C. *Rev. Chim. Miner.* **1986**, *23*, 125−137.
(28) Ma, Y.; Suib, S. L. Manuscript in preparation.
(29) Ma, Y.; Ressler, T.; Suib, S. L. Manuscript in preparation.
(30) Giovanoli, R.; Bürki, P.; Giuffredi, M.; Stumm, W. *Chimia* **1975**, *29*, 517−520.
(31) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 1226−1232.
(32) Hirano, S.; Narita, R.; Naka, S. *Mater. Res. Bull.* **1984**, *19*, 1229−1235.
(33) Feng, Q.; Yamasaki, N.; Yanagisawa, K.; Ooi, K. *J. Mater. Sci. Lett.* **1996**, *15*, 963−969.
(34) Wadsley, A. D. *J. Am. Chem. Soc.* **1950**, *72*, 1781−1784.
(35) Ching, S.; Landrigan, J. A.; Jorgensen, M. L.; Duan, N.; Suib, S. L. *Chem. Mater.* **1995**, *7*, 1604−1606.
(36) Drits, V. A.; Lanson, B.; Gorshkov, A. I.; Manceau, A. *Am. Mineral.* **1998**, *83*, 97−118.
(37) Witzemann, E. J. *J. Am. Chem. Soc.* **1915**, *37*, 1079−1091.

Table 2. Directory of Samples[a]

sample	permanganate	base, mol	*T*, °C	aging time,[b] day	Method	product
AC01	$NaMnO_4$	NaOH, 0.125	60	40	2	Na−OL-1
AC02	$KMnO_4$	KOH, 0.125	60	40	2	K−OL-1
AC03	$Mg(MnO_4)_2$	NaOH, 0.125	60	90	2	Na/Mg−OL-1
AC04	$NaMnO_4$	NaOH, 0.375	60	25	2	Na−OL-1
AC05	$NaMnO_4$	NaOH, 0.375	60	30	3	Na−OL-1
AC06	$KMnO_4$	KOH, 0.375	60	30	3	K−OL-1
AC07	$NaMnO_4$	NaOH, 0.125	60	40	1	Na−OL-1
AC08	$KMnO_4$	KOH, 0.125	60	40	1	K−OL-1
AC09	$Mg(MnO_4)_2$	NaOH, 0.125	60	90	1	Na/Mg−OL-1
AC10	$NaMnO_4$	NaOH, 0.375	60	20	1	Na−OL-1
AC11	$KMnO_4$	KOH, 0.375	60	20	1	K−OL-1
AC12	$Mg(MnO_4)_2$	NaOH, 0.375	60	90	1	Na/Mg−OL-1
AC13	$Mg(MnO_4)_2$	KOH, 0.375	60	90	1	K/Mg−OL-1
AC14	$KMnO_4$	KOH, 0.375	80	10	1	K−OL-1
AC15	$KMnO_4$	KOH, 0.375	95	3	1	K−OL-1
AC16	$NaMnO_4$	NaOH, 0.750	60	7	1	Na/K−OL-1
AC17	$KMnO_4$	NaOH, 1.000	60	7	1	Na/K−OL-1
AC18	$KMnO_4$	NaOH, 0.125	60	40	1	Na/K−OL-1

[a] In each synthesis, 150 mL of 0.316 M aqueous permanganate solution was used, and the reducing reagent was 50 mL of ethanol mixed with water with a 1:1 volume ratio. [b] The elapsed time prior to the precipitate being separated from the reaction system. The AOS measurements and elemental analyses were performed on these samples after being washed and dried.

Average Oxidation States (AOS) of Manganese. Standard potentiometric titration measurements[38] were used which involved two steps. The first step determines the total amount of manganese in OL-1 samples. The second step measures total electron transfer when the oxidation states of manganese were brought to 2+ with excess Fe^{2+}. The average oxidation states of Mn in OL-1 were obtained on the basis of the results of these two steps.[38]

Scanning Electron Microscopy. SEM photographs were taken on an AMRAY 1810 scanning electron microscope. Graphite was coated on a sample holder first, and a drop of sample dispersed in 2-propanol was added onto the graphite substrate. The voltage used was 20−25 kV.

Pillaring Process. This method is used to check whether a material is a layered material.[39,40] Our samples were completely washed before mixing with 1 M HCl and stirring overnight. The acid-treated sample was then reacted with hexylamine at room temperature overnight. If the *d* spacing between layers increases, this indicates that the sample has a layered structure.

III. Results

pH of the Reaction System. Acidic, neutral, and basic media were studied. Mn_2O_3 and very poorly crystalline synthetic birnessites were produced in acidic and neutral media, respectively (Figure 1). Only in basic media did the synthesis lead to the formation of pure crystalline OL-1 (Figure 1). As a consequence of these experiments, all subsequent syntheses were done in basic media.

Synthesis Procedures. As mentioned in the Experimental Section, three methods were developed to synthesize OL-1 materials in basic media. Methods 1 and 2 differ from Method 3 in that the oxidant (permanganate) is added to the reducing agent (alcohol) instead of the reverse as in Method 3. Therefore, in Methods 1 and 2 the reducing agent is in excess during the mixing of the reactants, while in Method 3 the oxidant is in excess during the mixing. Method 1 differs from Method 2 in that hydroxide is mixed with alcohol solution while in Method 2 hydroxide is mixed with permanganate solution. Method 1 provides a more constant basic media than Method 2.

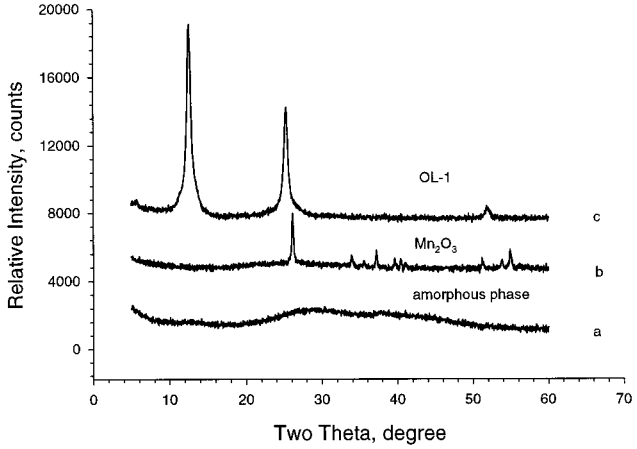

Figure 1. X-ray diffraction patterns of samples (combination a) in the form of thin films. The synthesis procedures of Method 2 were carried out in (a) neutral media, (b) acidic media, and (c) basic media.

The comparison of the three methods was carried out in the Na^+ (combination a, Table 1) system (AC10, AC04, and AC05 in Table 2). XRD results show that the resultant material by Method 3 (AC05) was amorphous. With Methods 1 and 2, crystalline Na−OL-1 materials (AC10 and AC04, respectively) were obtained (Figure 2). For samples prepared with Method 1, an extra peak at a *d* spacing of 3.4 Å indicative of α-MnO(OH) was also present.

Similar results from these three methods were obtained in the K^+ system (combination b, Table 1) as in the Na^+ system. Crystalline K−OL-1 was the only product formed by both Methods 1 and 2. No α-MnO(OH) formed with Method 1 as in the Na^+ system. Amorphous material also resulted from Method 3.

The relative crystallinity of materials, defined as particle size and indicated roughly by the relative peak widths, resulting from all three methods was in the order: Method 1 ≥ Method 2 ≫ Method 3. In the

(38) *Handbook of Manganese Dioxides Battery Grade*; Glover, D., Schumm, B., Jr., Kazowa, A., Eds.; International Battery Material Association (IBA): Cleveland, OH, 1989.
(39) Wong, S.-T.; Cheng, S. *Inorg. Chem.* **1993**, *31*, 1165−1172.
(40) Paterson, E. *Am. Miner.* **1981**, *66*, 424−427.

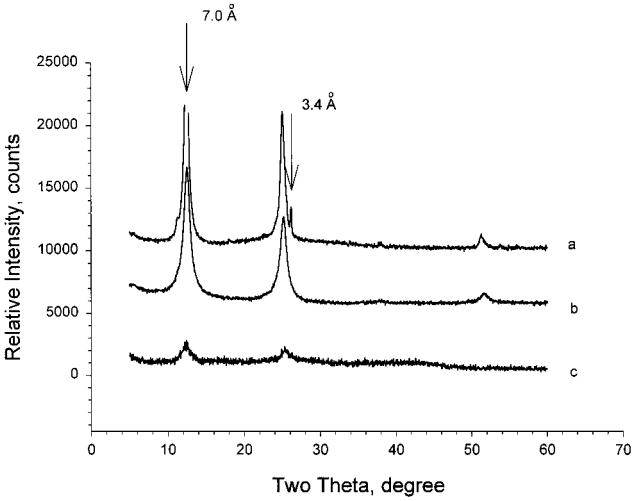

Figure 2. X-ray diffraction patterns of Na−OL-1 materials in the form of films: (a) AC10, (b) AC04, and (c) AC05. The synthesis conditions and aging times for these samples are listed in Table 2.

following experiments, Methods 1 and 2 were used unless otherwise stated.

Choice of Organic Species. To test the generality of these preparation methods, besides ethanol, other organic species were also tried, including methanol, (ethanol,) 1-propanol, 2-propanol, 2-butanol, pentanol, hexanol, and cyclohexanol. OL-1 formed in all of these organic systems. Under the same synthesis conditions, the rates of OL-1 growth in these organic systems decreased in the above order of organic species, which agrees with the decreasing order of reducing ability of these organic species. Organic species did not interfere with the growth of OL-1, and they function in this synthesis system only as reducing reagents. In our following experiments, ethanol was used as the reducing reagent in consideration of safety and efficiency.

Aging Temperature. The same effects of temperature on crystal growth were observed in this system as reported before in other systems.[41] Higher temperatures shortened the full growth of OL-1, which is defined as the elapsed time from the beginning of aging to whenever the intensities of XRD peaks of the resultant materials no longer increase. For example, the full growth of K−OL-1 by Method 1 was shortened from 20 days at 60 °C (AC11) to 10 days at 80 °C (AC14) and 3 days at 95 °C (AC15) (Table 2). K−OL-1 materials prepared at 80 and 95 °C exhibited decreased intensities in their XRD peaks (corresponding to *d* spacings of both 7.0 and 3.5 Å) 5 and 2 days, respectively, after these peaks reached their maximum intensities. Elemental analyses show that AC14 and AC15 accommodated less interlayer cations than AC11 (Table 3). The 60 °C sample showed constant peak intensities after the maximum intensities of the peaks were achieved indicating sample stability. Therefore, in the following experiments, an aging temperature of 60 °C was used instead of 80 and 95 °C, unless otherwise stated.

Choice of Interlayer Cations. Interlayer cations, usually the alkali and alkaline earth cations, have been the subject of a great deal of research in the synthesis and characterization of OL-1 materials.[7−11,15−19] Among these cations, sodium, potassium, and magnesium are the most extensively studied. In our synthesis systems, the following pure cations or their combinations, for example, Na^+, K^+, Na^+/Mg^{2+}, K^+/Mg^{2+}, and Na^+/K^+ (Table 1), were studied as interlayer cations in the preparation of OL-1 materials. XRD patterns of combinations a−d (AC10−13) are shown in Figure 3. All patterns exhibit the two diagnostic peaks of OL-1 at 7.0 and 3.5 Å, together with other reflection peaks characteristic of OL-1 materials.[7]

a. Na−OL-1. For combination a (Table 1), Na-OL-1 was the only phase resulting from Method 2 (AC01 and AC04). With Method 1, a peak at 3.4 Å in addition to Na−OL-1 peaks was also detected by XRD indicative of another phase (Figure 3a). The 3.4 Å peak became more obvious when the concentration of base in the synthesis was increased (AC16, Figure 4) and was ascribed to α-MnO(OH). SEM photograph (Figure 5a) of the Na−OL-1 sample prepared with Method 1 (sample AC16 with 45 days aging) shows the coexistence of this second phase (with a regular morphology) and Na−OL-1 (with an irregular morphology). By comparison, both Na−OL-1 prepared with Method 2 (Figure 5b) and K−OL-1 prepared with Method 1 (Figure 5c) exhibit irregular but uniform morphology.

During the aging of Na−OL-1 samples prepared with Method 1, the intensity ratio of the main diffraction peak of α-MnO(OH) (3.4 Å) to that of Na−OL-1 (7.0 Å) kept increasing until this ratio became constant after, for example, 40 days aging in the case of AC16 (Figure 4).

b. K−OL-1. For samples of combination b (Table 1), K−OL-1 was always the only phase observed with both Method 1 (AC08 and AC11) and Method 2 (AC02). K−OL-1 did not transform to any other phase, e.g., α-MnO(OH), even with 9 months aging at 60 °C.

In combination e (AC17 and AC18, Table 2) where Na^+ and K^+ ions existed together as interlayer ions while the molar ratio of Na^+ to K^+ was kept larger than 10, α-MnO(OH) also formed in addition to Na/K−OL-1 with Method 1, as we also observed in the Na^+ system. In contrast, when the molar ratio of K^+/Na^+ was larger than 10, no α-MnO(OH) formed.

c. Na/Mg−OL-1 and K/Mg−OL-1. When $Mg(MnO_4)_2$ was used as an oxidizing agent, NaOH or KOH was used instead of $Mg(OH)_2$ to provide the necessary concentrations of OH^- groups for the preparation of OL-1.

Table 3. Average Oxidation States and Chemical Formulas[a] of OL-1 Materials

sample	chemical formula	AOS of Mn
AC01	$Na_{4.64}Mn_{14}O_{27.9}\cdot 6.4H_2O$	3.65
AC02	$K_{4.24}Mn_{14}O_{27.4}\cdot 5.77H_2O$	3.67
AC04	$Na_{4.58}Mn_{14}O_{27.48}\cdot 7.1H_2O$	3.61
AC06	$K_{4.66}Mn_{14}O_{28.1}\cdot 6.58H_2O$	3.68
AC07	$Na_{4.62}Mn_{14}O_{27.8}\cdot 7.65H_2O$	3.63
AC08	$K_{4.46}Mn_{14}O_{28.4}\cdot 7.58H_2O$	3.73
AC10	$Na_{4.70}Mn_{14}O_{27.7}\cdot 8.65H_2O$	3.62
AC11	$K_{4.61}Mn_{14}O_{27.9}\cdot 6.58H_2O$	3.66
AC12	$Na_{4.05}Mg_{7.2}Mn_{14}O_{34.51}\cdot 18.0H_2O$	3.61
AC13	$K_{3.49}Mg_{7.16}Mn_{14}O_{34.66}\cdot 17.5H_2O$	3.68
AC14	$K_{4.01}Mn_{14}O_{27.49}\cdot 5.71H_2O$	3.64
AC15	$K_{3.45}Mn_{14}O_{27.42}\cdot p4.36H_2O$	3.67

[a] The calculation of the chemical formulas were only performed on relatively pure materials (defined as the intensity of the 7.0 Å peak 20 times that of the main diffraction peak of the impurity phase).

(41) Luo, J.; Suib, S. L. *J. Phys. Chem. B* **1997**, *101*, 10403−10413.

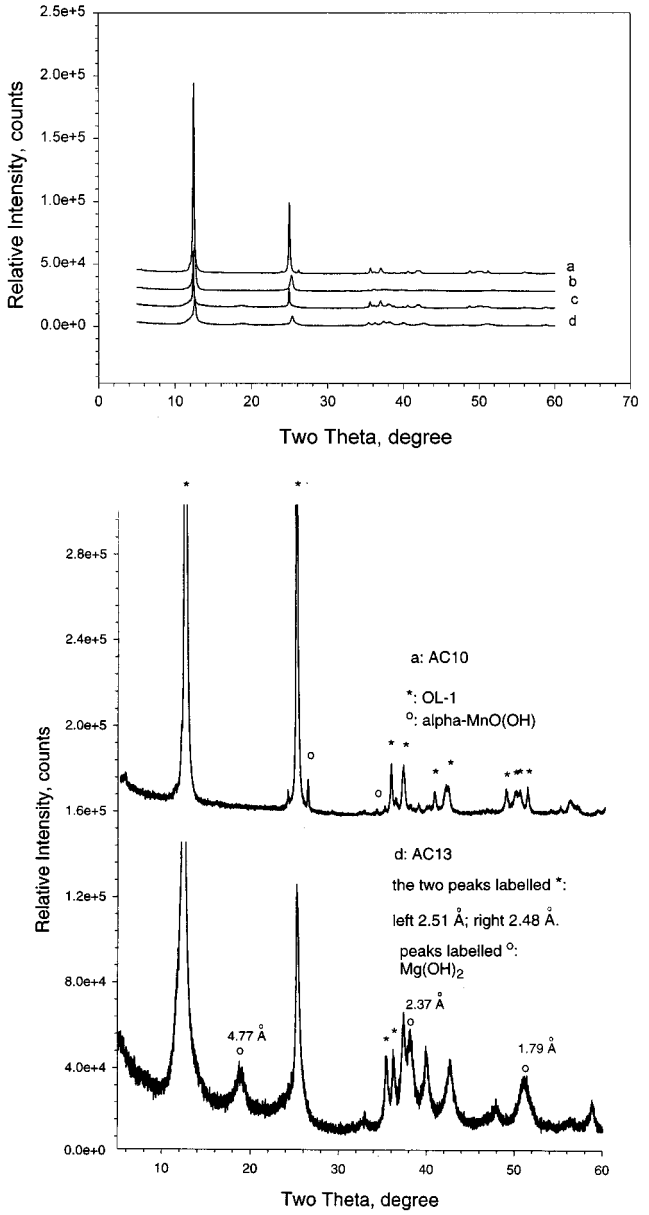

Figure 3. X-ray diffraction patterns of finely ground OL-1 materials with different interlayer cations: (a) Na−OL-1 (AC10), (b) K−OL-1 (AC11), (c) Na/Mg−OL-1 (AC12), and (d) K/Mg−OL-1 (AC13). The synthesis conditions and aging times for these samples are listed in Table 2. The lower part is the enlarged curves of a and d shading the existence of impurity phases which are notdistinguishable in the upper part of the figure.

Samples from combinations c and d showed different growth pathways than samples from combinations a, b, and e. A fairly strong diffraction peak at ∼4.8 Å (Figure 6) was detected at the beginning of aging, and the intensity of this peak decreased while the intensity of the main peak of OL-1 (7.0 Å) increased. The 4.8 Å peak became narrower and shifted to 4.77 Å upon aging.

Compared to the XRD pattern of Na−OL-1 (AC10, Figure 3a), in addition to the 4.77 Å peak, a peak at 2.37 Å was detected for Mg-containing samples (AC13, Figure 3d). The intensity ratio of the 2.48 Å peak to the 2.51 Å peak also increased from 1:7 in Na−OL-1 to about 1:1 in Mg-containing OL-1. These results were compared with ICDD patterns 23−1046 (synthetic birnessite), 23−392 (magnesium manganese oxide), 7−239

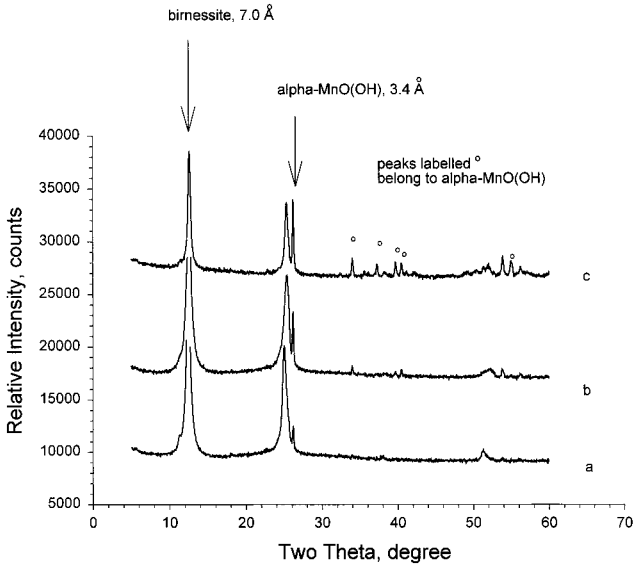

Figure 4. X-ray diffraction patterns of a Na−OL-1 sample prepared with Method 1 in the form of thin films, showing the growth of α-MnO(OH): (a) with 7 day aging, (b) with 20 day aging, and (c) with 45 day aging. The samples were synthesized under the same conditions as those used for AC16 except for different aging times.

(magnesium hydroxide), 18−787 (manganese hydroxides), and 18−804 (β-MnO(OH)). The peaks at 2.37 and 4.77 Å are diagnostic peaks for $Mg(OH)_2$, while the peak at 2.48 Å can be due to either synthetic birnessite or $MgMn_2O_4$ or an unidentified phase. The relative intensity of this peak to the 2.51 Å peak in the same pattern is consistent with $MgMn_2O_4$. None of these reflections (4.77, 2.37, and 2.48 Å) match X-ray data of β-MnO(OH) or $Mn(OH)_2$.

The 4.77 Å peak of $Mg(OH)_2$ did not completely disappear even after 90 days aging (Figure 6), although the intensity of the 4.77 Å peak was only about 5% of the intensity of the 7.0 Å peak. These results are different from other reported processes (Mn^{7+} and Mn^{2+} systems),[41] where almost the same reflection peak (4.8 Å) remained at the beginning of aging but was completely transformed to OL-1 after about 45 days aging.

Concentration of Base. In the K^+ system, the effects of higher base concentrations were to shorten the periods of crystal growth (AC08 and AC11, Table 2) without changing the synthesis products (K−OL-1).

In combinations a and e (Table 1), more base led to not only shorter synthesis periods, but also relatively more α-MnO(OH) with respect to OL-1. The intensity ratios of the 3.4 Å peak (α-MnO(OH)) to the 7.0 Å peak (OL-1) were 0.45, 0.05, and 0.02 for Na−OL-1 samples AC16, AC10, and AC07, respectively, and 0.40 vs 0.03 for Na/K−OL-1 samples AC17 vs AC18.

In combinations c and d (Table 1), with less base (0.125 mol), the intensity of the 4.77 Å peak was almost the same as that of 7.0 Å peak (AC03 and AC07) after 45 days aging, and no significant change was observed even after ∼6 months aging. With 0.375 mol of base (AC12 and AC13), after aging for 90 days, the 4.77 Å peak (impurity) decreased in intensity (5% that of the 7.0 Å) and this ratio then kept constant (Figure 6).

Composition of OL-1. Since OL-1 is electronically neutral, it is assumed that the total amount of oxygen in the dehydrated material is used to balance the

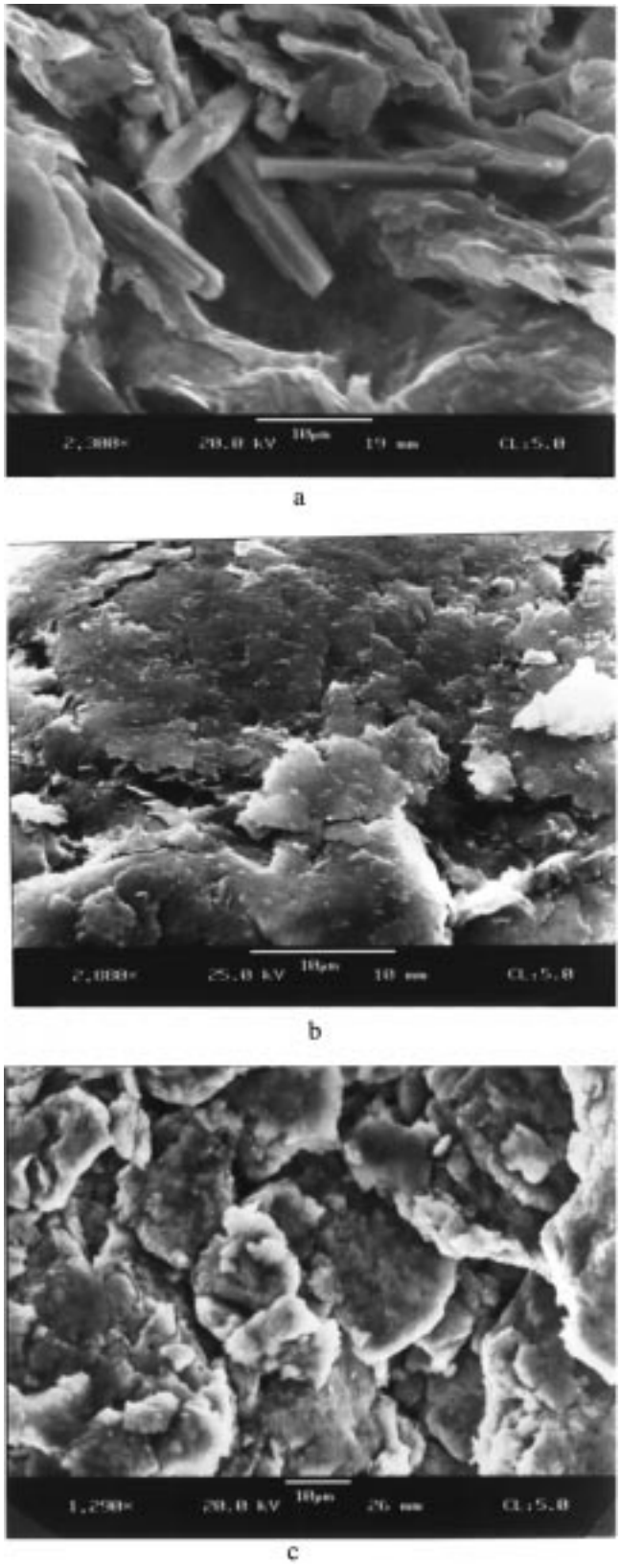

Figure 5. SEM photographs of OL-1 materials: (a) Na−OL-1 prepared with Method 1, showing the coexistence of α-MnO(OH) and Na−OL-1 in AC16; (b) Na−OL-1 (AC04) prepared with Method 2; and (c) K−OL-1 (AC11) prepared with Method 1. No α-MnO(OH) is observed in samples AC04 and AC11.

positive charges of Mn, and interlayer cations such as Na^+, K^+, and Mg^{2+}. The weight of the dehydrated samples was calculated in the following way:

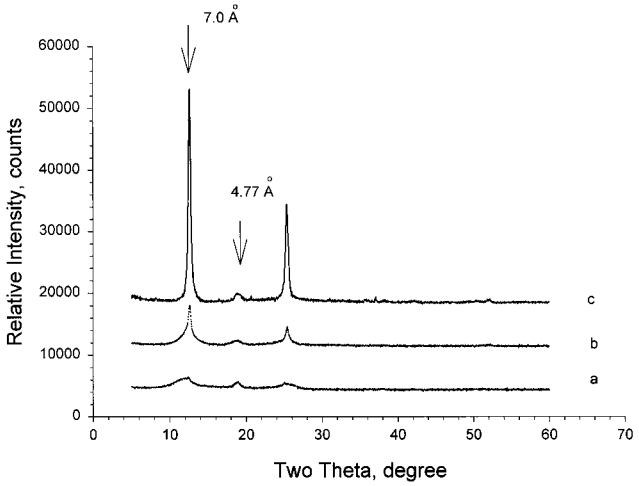

Figure 6. X-ray diffraction patterns of Na/Mg−OL-1 (AC12) samples in the form of thin films, showing the transformation of the metastable phase (characterized by the 4.8 Å peak) to OL-1: (a) with 4 day aging, (b) with 25 day aging, and (c) with 90 day aging.

$$W_d = W_{Mn} + (W_{Mn}/54.94)*(AOS/2)*16.0 + W_{Na} + (W_{Na}/22.99)*0.5*16.0 + W_K + (W_K/39.1)*0.5*16.0 + W_{Mg} + (W_{Mg}/24.3)*1*16.0 \quad (1)$$

where W_d is the weight of dehydrated sample (μg) in 1 g of sample; W_{Mn}, the weight of Mn (μg) in 1 g of sample; W_{Na}, the weight of Na (μg) in 1 g of sample; W_K, the weight of K(μg) in 1 g of sample; and W_{Mg}, the weight of Mg (μg) in 1 g of sample.

The above calculation was based on the formulas MnO_x, Na_2O, K_2O, and MgO. $W_{H_2O} = 1 - W_d$, was the weight of hydrated water (μg) in 1 g of OL-1. When the weights of the elements and water were converted to moles, empirical formulas were obtained. Only the formulas of relatively pure materials (defined as the intensity of the 7.0 Å peak of OL-1 being 20 times that of the main diffraction peak of the impurity phase, i.e., α-MnO(OH) or the 4.8 Å phase in combinations c and d) were calculated here (Table 3).

The average oxidation states (AOS) of all the materials fell into the range of 3.60 to 3.70, which agreed well with the literature.[7,9,10] Chemical formulas also matched those in the literature reports.[7,9,10] K−OL-1 contained the least moles of water per mole of manganese, and either Na/Mg−OL-1 or K/Mg−OL-1 contained the most.

Evidence of Layered Materials. One way to confirm that a layered material is present is to use organic ammonium ions to pillar the material.[39,40] The XRD pattern of hexylammonium ion pillared AC10 is shown in Figure 7. For this pillared material, its *d* spacing increased from 7.0 Å for OL-1 to 17.5 Å and diffraction reflections of up to fifth order were observed from {001} planes, which indicates that a well ordered layered material was present.

IV. Discussion

Effects of Procedures on the Synthesis of OL-1. Typical synthesis procedures were described in the Experimental Section. When MnO_4^- solution was added to the alcohol solution, OL-1 formed directly from strong basic media (Methods 1 and 2). Hydroxide was essential

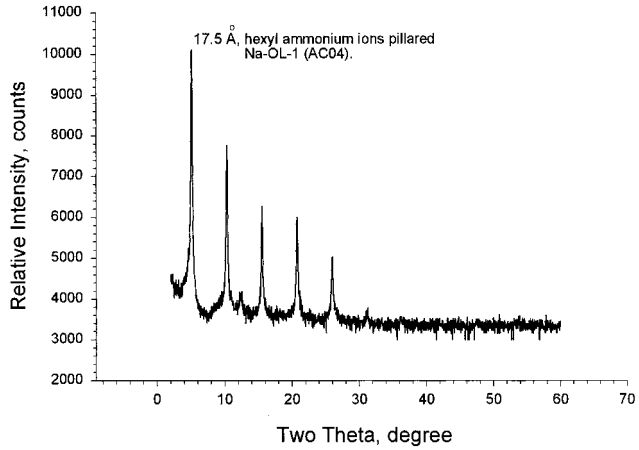

Figure 7. X-ray diffraction pattern of hexylammonium ion pillared Na−OL-1 (AC10) sample as a thin film.

for this reaction, without which the resultant material exhibited very broad and weak XRD diffraction peaks (Figure 1), indicating poor crystallinity.

In both Methods 1 and 2, permanganate was added to alcohol, which was in excess compared to the oxidant (permanganate) during the addition. In this environment, Mn^{7+} was reduced to Mn^{2+} first and formed $Mn(OH)_2$ in the presence of OH^-, as detected by XRD studies. As more permanganate was added, Mn^{2+} was oxidized, and OL-1 was formed. The transformation from $Mn(OH)_2$ to OL-1 is a topotactic reaction as $Mn(OH)_2$ and OL-1 have very similar layered structures. The main difference between the structures of $Mn(OH)_2$ and OL-1 is that the OL-1 structure has hydrated alkali ions between the layers while the $Mn(OH)_2$ structure has none.[27] The transformation from $Mn(OH)_2$ to OL-1 was also observed in other synthesis systems when MnO_4^- reacted with Mn^{2+} to produce OL-1.[41]

In Method 3, alcohol was added to permanganate. Reduction of Mn^{7+} directly to Mn^{2+} was difficult in this case as MnO_4^- was present in excess amounts compared to the reducing reagent (alcohol). XRD studies indicate that no $Mn(OH)_2$ formed during the addition of alcohol to permanganate with only an amorphous phase being formed. This amorphous phase led only to a poorly crystalline OL-1 upon aging (Figure 2).

The chemical composition used in the synthesis is less influential than the synthesis procedures employed in the formation of OL-1 for this particular synthesis system. Samples AC06 and AC11 are two K−OL-1 samples prepared with Methods 3 and 1, respectively. Although these two samples had the same starting compositions and similar empirical formulas for the resultant materials, only sample AC11 (prepared with Method 1) showed clear crystallinity of OL-1.

Although both Methods 1 and 2 lead to the formation of crystalline OL-1, the synthesis products from these two methods show differences in product species and the degree of crystallinity of OL-1. The most remarkable difference was observed in the Na^+ system. With Method 1, α-MnO(OH) was formed together with Na−OL-1 and this Na−OL-1 slowly transformed to α-MnO(OH) during aging until these two phases reached an equilibrium (Figure 5). With Method 2, only Na−OL-1 was produced, and the Na−OL-1 did not transform to α-MnO(OH), even though the starting composition, aging temperature, and the pH of this reaction mixture were the same as that used in Method 1. This phenomenon implies that the transformation from Na−OL-1 to α-MnO(OH) was not automatic and that crystal nuclei of α-MnO(OH) might form in the early stage of synthesis with Method 1 while none formed with Method 2.

No differences in the synthesis products between Methods 1 and 2 were observed in the K^+, Na^+/Mg^{2+}, or K^+/Mg^{2+} systems (combinations b, c, and d, Table 1). In the K^+ system, K−OL-1 obtained with Method 1 exhibited better crystallinity than that from Method 2, as indicated by the narrower peak width of the main reflection peak at 7.0 Å. This is probably due to the more constant basic environment provided by Method 1 as compared to that in Method 2 where OH^- was mixed with permanganate and continuously added to the reducing reagent (alcohol) during the synthesis reaction.

Therefore, as evidenced by X-ray diffraction patterns, the most pure and crystalline OL-1 in the Na^+ system, among all the Na−OL-1s synthesized here, was AC04 where Method 2 and a 60 °C aging temperature were used. The most stable and crystalline K−OL-1 was AC11 where Method 1 and a 60 °C aging temperature were used.

Factors Affecting the Formation of α-MnO(OH) in the Na^+ System. The formation of α-MnO(OH) only occurs when sodium permanganate is added to a solution containing NaOH, ethanol, and H_2O (Method 1). Use of $KMnO_4$ and KOH in replace of $NaMnO_4$ and NaOH in the above synthesis does not result in the formation of α-MnO(OH). It seems that the major difference in these two syntheses is the different degrees of solvation of Na^+ and K^+ ions in the basic aqueous ethanol solutions,[42] and this may account for the difference in synthesis products in the Na^+ and K^+ systems.

Different base concentrations and reaction temperatures were used to understand solvation effects on the formation of α-MnO(OH) with Method 1. Base concentrations did not influence product species, but they did affect product distributions. Higher base concentrations in the Na^+ system led to more solvated Na^+ ions in aqueous ethanol solution, and also led to larger relative amounts of α-MnO(OH) with respect to Na−OL-1. In the K^+ system, K−OL-1 was still the only product formed even with higher base concentrations. The smaller charge/radius value of K^+ ions than that of Na^+ ions suggests a weaker solvation of K^+ ions in aqueous ethanol solution.[42] This phenomenon indicates that the different degrees of solvation of Na^+ and K^+ ions in aqueous ethanol solutions might be one reason for the formation of α-MnO(OH) in the Na^+ system. The stronger the solvation effect, the more α-MnO(OH) is formed.

Two reaction temperatures (temperature at which the preparation of the basic aqueous ethanol solution and the addition of permanganate to the basic aqueous ethanol solution were done) of 25 and 60 °C were used. With a 60 °C reaction temperature, the relative amount of α-MnO(OH) was decreased compared to the amount in the synthesis conducted at 25 °C. The dissolution and solvation of NaOH in aqueous ethanol solution is an

(42) Marcus, Y. *Ion Solvation*; John Wiley and Sons Ltd.: New York, 1985; Chapter 4.

exothermic process. On increasing the reaction temperature, the solvation effect on Na^+ is decreased.[43] As a result, the relative amount of α-MnO(OH) was decreased at the reaction temperature of 60 °C.

α-MnO(OH) was not formed in the Na^+ system when NaOH was mixed with sodium permanganate in water before it was added to aqueous ethanol solution. The higher solvating ability of ethanol than water,[43] the lower cation mobility in ethanol than in water,[43] and the stronger hydrogen bonding between water and ethanol than between water molecules[44,45] might be some of the reasons that α-MnO(OH) was not formed in the Na^+ system when Method 2 was used.

Effects of Magnesium Ions. Many previous studies showed that magnesium ions are very important synthesis parameters in the preparation of OL-1.[20,21,26,41] When $Mg(MnO_4)_2$ was used as the oxidizing reagent, $Mg(OH)_2$ was not used because of its low solubility. NaOH or KOH was used instead and their amounts relative to the amount of $Mg(MnO_4)_2$ were varied to study the effects of different metal ions and concentrations of bases on the formation of OL-1 materials.

In all experiments that started with $Mg(MnO_4)_2$, a 4.8 Å reflection peak with almost the same intensity as that of the 7.0 Å peak was always detected by XRD studies at early stages of synthesis. In the process of aging, this 4.8 Å peak decreased in peak intensity and became narrower and the reflection shifted a little to 4.77 Å at the same time as the 2.37 Å peak appeared. These X-ray data indicate that $Mg(OH)_2$ was present. The broad reflection at 4.8 Å might be due to an overlap of the 4.77 Å peak and other peaks at ∼4.8 Å indicative of an unknown intermediate phase. The 7.0 Å peak gradually increased with time. When the transformation was stabilized, the intensities of the 4.77 and 2.37 Å peaks were about 5% that of the 7.0 Å peak, suggesting that the majority of $Mg(OH)_2$ was transformed to OL-1. OL-1 materials obtained from combinations c and d (Table 1) show much higher Mg content (molar ratio of Mg to Mn about 1:1, Table 3) than for previously reported OL-1 materials.[26,41] This implies that more Mg had been accommodated into these OL-1 materials by the transformation of $Mg(OH)_2$ and other intermediate phase(s) to OL-1. The OL-1 materials with larger amounts of Mg can be very useful catalysts.[23]

V. Conclusions

This systematic study of the hydrothermal preparation of OL-1 materials in basic media used monoalcohols as reducing agents. Na−, K−, Na/Mg−, K/Mg−, and Na/K−OL-1 materials have been synthesized. Two synthesis methods have been used to prepare OL-1. Adding basic permanganate solutions to aqueous ethanol solutions followed by aging (Method 2) is a general procedure that is applicable to all cation combinations to prepare OL-1 materials. Adding permanganate solution to basic aqueous ethanol solution followed by aging (Method 1) leads to better crystallinity in the resultant materials. The most pure, crystalline, and stable OL-1 materials are obtained at a 60 °C aging temperature for both Na−OL-1 (with Method 2) and K−OL-1 (with Method 1).

Synthesis products in the Na^+ and Na^+/K^+ systems are strongly influenced by synthesis procedures. In these two systems, when pure aqueous permanganate solution is added to solutions containing ethanol, water, and sodium hydroxide (Method 1), α-MnO(OH) forms in addition to Na−OL-1 and Na/K−OL-1. The products in the K^+, Na^+/Mg^{2+}, and K^+/Mg^{2+} systems are not influenced by the synthesis procedure. In the K^+ system, synthetic birnessite (K−OL-1) is the only phase resulting from the synthesis.

When $Mg(MnO_4)_2$ is used as the oxidizing reagent, OL-1, $Mg(OH)_2$ and an intermediate phase(s) characterized by a broad 4.8 Å peak are produced simultaneously in the beginning of synthesis and the intermediate phase(s) and $Mg(OH)_2$ eventually transform to OL-1. These OL-1 materials accommodate more Mg than previously reported systems.[26,41] This, in turn, may be a very useful property for OL-1 catalysts.[23]

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for support of work. We thank Drs. M. Smith and F. S. Galasso of the Department of Chemistry, the University of Connecticut for very helpful discussions.

CM980399E

(43) Girdhar, H. L.; Gohil, K.; Matta, R. P. *Indian J. Chem.* **1981**, *20A*, 172−173.
(44) Arnett, E. M.; Bentrude, W. G.; Bruke, J. J.; Duggleby, P. *J. Am. Chem. Soc.* **1965**, *87*, 1541−1553.
(45) Issa, I. M.; Diefallah, E. M.; Mahmoud, M. R.; El-Nady, A. M. *Z. Naturforsch.* **1978**, *33B*, 30−34.