Effects of Microwave Processing on Chemical, Physical, and Catalytic Properties of Todorokite-Type Manganese Oxide

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A microwave-assisted hydrothermal method of synthesis was used to prepare todorokite. Synthetic todorokite, OMS-1, is a multivalent manganese oxide with a $3\times3\times\infty$ tunnel structure. OMS-1 was synthesized from its layered precursor much faster by the microwave method than by conventional heating (8 vs 48 h). In addition, the microwave-synthesized materials reveal some properties superior to those of the conventionally synthesized ones such as better stability, crystallinity, and catalytic activity in the production of phthalic anhydride. Microwave-prepared todorokite also shows novel cubic morphology, which was not found for conventionally made OMS-1 and is catalytically active in the oxidation of benzyl alcohol. Materials synthesized by microwave as well as conventional methods were characterized with XRD, TGA, SEM, TEM, TPD, and BET. Physical, chemical, and catalytic properties of todorokite prepared by the two different methods were compared based on the experimental results.

Introduction

Todorokite, so-called OMS-1 (octahedral molecular sieves), is a multivalent manganese oxide that can be found naturally in terrestrial manganese ore deposits and deep-sea manganese nodules.[1–6] Figure 1 illustrates the tunnel structure of todorokite that consists of $3\times3\times\infty$ arrangements of edge shared MnO_6 octahedra. This material is useful as a shape selective catalyst due to its tunnel structure.[7] In fact, synthetic todorokites are reported to be catalytically active in the oxidation of CO,[8] H_2O_2 decomposition,[9] and the production of styrene by oxidative dehydrogenation of ethylbenzene.[10–11] Generally, mixed-valent manganese oxides have broad applications in oxidation catalysis, en-
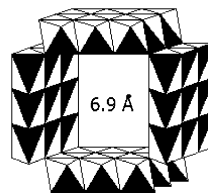

Figure 1. Tunnel structure of todorokite-type manganese oxide (OMS-1).

vironmental catalysis, and rechargeable battery technology.

Synthesis of todorokite generally involves three major steps: (1) synthesis of layered precursor, namely, birnessite (OL-1), (2) ion exchange of the precursor, and (3) hydrothermal aging (Figure 2).[11–14] The use of microwave instead of conventional heating in the hydrothermal treatment step could significantly affect physical and chemical properties of the microwave-synthesized manganese oxides.

Microwave heating is essentially different from conventional heating.[15–23] In microwave processes, heat is

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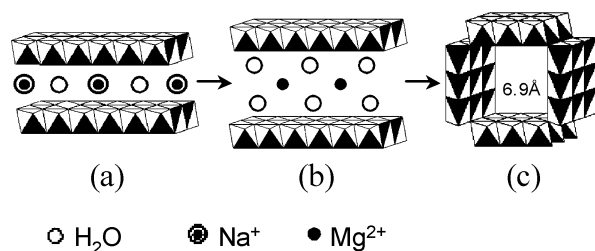
Figure 2. Three-step synthesis procedure of OMS-1: (a) layered Na-OL-1, (b) layered Mg-OL-1, and (c) tunnel-structured OMS-1.

generated directly from the interaction between molecules in the heated material and electromagnetic field created in the microwave oven. In contrast, in conventional processes, heat originates from external heating sources. Microwave heating is considered as volumetric heating, where the flow of heat and thermal gradients are opposite to those in conventional heating. Energy can be delivered to reacting molecules at a much greater rate as compared to conventional heating, which makes it possible to decrease reaction times.[24,25] Therefore, microwave processing allows the heating of materials to be faster and more uniform.[26,27] There has been a great deal of interest in the application of microwave synthesis to a wide range of organic, organometallic, and inorganic reactions.[28-37]

Microwave processing can be beneficial in the processing of materials with high dielectric constants because absorption of microwave radiation by a material depends on its dielectric constant and its dielectric loss factor. Manganese oxides absorb microwave radiation very efficiently due to the high values of dielectric constants, which were reported to be ~10 000.[38] Moreover, water is a very good absorber of microwave radiation at frequencies of 0.915 and 2.450 GHz, so the microwave effect in the synthesis of todorokite could be significantly enhanced.[26]

In this study, todorokite was synthesized by applying microwave heating during the hydrothermal aging step. Although a similar method of OMS-1 synthesis was reported, we have found a novel microstructure and unique properties of microwave synthesized materials. In this paper, we show that not only the time of the microwave synthesis is reduced as compared to conventional methods, but also that the microwave-synthesized todorokite has much better catalytic properties than a conventional one. Therefore, microwave heating can be used to manipulate catalytic properties of materials. Several experiments were performed to confirm the reproducibility of our results. In addition, todorokite was synthesized in a conventional way. The microwave and conventionally synthesized todorokite samples were extensively characterized and compared. X-ray powder diffraction (XRD), elemental analysis (ICP), titration experiments to determine the average oxidation state of manganese in the samples, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal analysis (TGA), temperature programmed desorption (TPD), and surface analysis (BET) techniques were employed to characterize the samples.

Experimental Procedures

Synthesis. Conventional and microwave-prepared OMS-1 was synthesized according to the two-step procedure. First, sodium-birnessite (Na-OL-1) was prepared by oxidation of Mn^{2+} with potassium permanganate in sodium hydroxide solution. Then layered Na-OL-1 was aged hydrothermally as a slurry in a magnesium chloride ($MgCl_2$) solution at 160 °C. In this process, ion exchange and hydrothermal aging were performed in one step. The resulting OMS-1 was washed with a large amount of hot (~100 °C) distilled deionized water. Teflon autoclaves transparent to microwave radiation were used for microwave processing. Metal autoclaves with Teflon liners were used for the synthesis in a convection oven. Synthesis of todorokite in a microwave oven took 8 h, and the synthesis of todorokite in a convection oven took 2 days. Details of this procedure are reported in the literature.[11]

X-ray Diffraction. The X-ray powder diffraction patterns of the samples were collected using a Bruker D5005 diffractometer with CuKα X-ray radiation with a 1.5418 Å wavelength. A beam voltage of 40 kV and a 40 mA beam current were used. Crystallite size was calculated using the Scherrer equation.[39]

Elemental Composition. Elemental composition analyses were done at the Environmental Research Institute, Storrs, CT. An inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique with a Perkin-Elmer 7-40 instrument equipped with an autosampler was used.

Average Oxidation State Determination. A potentiometric titration was employed to measure the average oxidation state of manganese in all of the samples. This method consists of a two-step procedure. The first step involves the determination of the total manganese content in a sample. In the second step, the amount of available oxygen in the sample is measured. A complete titration procedure is reported in the literature.[40,41]

Morphology. Morphologies of microwave and conventionally synthesized samples were inspected with an Amray 1645 Scanning Electron Microscope. Samples were prepared for

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taking the micrographs by being spread uniformly on a carbon tape attached to an aluminum sample holder. An Amray model PV 9800 EDX was used for energy-dispersive X-ray analyses.

Transmission electron microscopy (TEM) images were obtained with a JEOL 2010 FasTEM at an accelerating voltage of 200 kV. Powder samples were dispersed ultrasonically in ethanol, and the suspension was deposited on a Quantafoil holey carbon coated copper grid (R1.2/1.3).

Thermal Stability. A thermogravimetric analysis (TGA) technique was employed to study the thermal stability of the samples. The experiments were performed with a TA instrument Model 2950 in a N_2 atmosphere. Temperature was increased from 30 to 700 °C at a rate of 10 °C/min during the experiments.

Specific Surface Area and Pore Size Distribution Measurements. A Micrometrics ASAP 2010 accelerated surface area system was used for nitrogen sorption measurements. The experiments were done at 77 K after initial pretreatment of the samples by degassing them at 120 °C for 12 h. The specific surface area of the samples was determined by the Brunauer−Emmett−Teller (BET) method. The pore size distribution was measured using the Horvath and Kawazoe model.

Acidity and Basicity of OMS-1. NH_3 and CO_2 temperature programmed desorption (TPD) was used to study the acidic and basic properties of OMS-1. TPD experiments were done using 20 mg of each sample. The samples were positioned in a quartz tube and secured with quartz wool plugs. NH_3 and CO_2 were passed over the samples for 30 min at room temperature. Then, the reactor was purged with He to remove gases physisorbed on the samples. The temperature was increased from 25 to 700 °C at 10 °C/min. The evolution of gases from the samples was monitored with an MKS-UTI PPT quadruple mass spectrometer.

Catalytic Activity: Oxidation of Indene. Oxidation of indene was done by the following procedure. In a 50 mL round-bottomed flask, 1 mmol of indene was dissolved in 10 mL of CH_3CN (acetonitrile), and 0.05 g of either microwave or conventionally made OMS-1 was added to the solution. Subsequently, 2 equiv of TBHP (*t*-butyl hydroperoxide) was added dropwise using a pipet at room temperature. The reaction temperature was gradually increased to 70 °C and kept constant during the oxidation experiment. The mixture was stirred and refluxed overnight. Then, the reaction mixture was cooled and filtered. $MgSO_4$ (magnesium sulfate) was added to remove water. The desiccator was filtered out, and the reaction mixture was analyzed and quantified with GC/MS.

Catalytic Activity: Oxidation of Benzyl Alcohol. The following procedure was used for the oxidation of benzyl alcohol. A total of 1 mmol of benzyl alcohol and 10 mL of toluene was placed in a 50 mL round-bottomed flask. The catalyst (0.05 g) either conventionally or microwave-synthesized OMS-1 was added to that mixture. The reaction mixture was stirred and refluxed at 100 °C for 4 h and then filtered. The products of the experiment were analyzed and quantified with GC/MS.

GC/MS. A Hewlett-Packard Model 5890 Series II chromatograph coupled to a Hewlett-Packard Model 5971 mass selective detector was used to analyze and quantify the reaction products. The instrument was equipped with an HP-1 column (a cross-linked methyl siloxane) of the following film dimensions: 12.5 m × 0.2 m × 0.33 μm.

Results

XRD. XRD patterns for conventionally and microwave-prepared materials are shown in Figure 3. All the samples have patterns corresponding to synthetic todorokite ($NaMn_6O_{12} \cdot 13H_2O$, JCPDS 38-475). The patterns of materials synthesized in the convection oven as well as materials prepared in the presence of microwave field do not reveal any extra phases. Todoro-
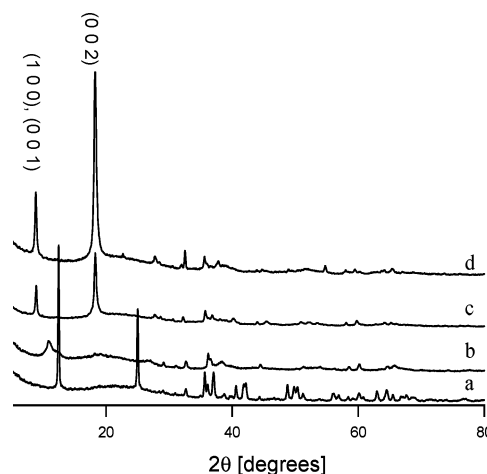

Figure 3. X-ray diffraction patterns of: layered precursors Na-OL-1 (a) and Mg-OL-1 (b), conventionally prepared OMS-1 (c), and microwave-prepared OMS-1 (d).

Table 1. Average Oxidation Number (AON), Average Crystallite Size (ACS), and ICP-OES[a] Elemental Analyses Results for OMS-1 Materials

sample	AON for Mn (± 0.02)	ACS	Mg/Mn	Na/Mn
conventionally synthesized OMS-1	3.69	26	0.132	5.7×10^{-3}
microwave synthesized OMS-1	3.76	20	0.135	1.8×10^{-3}

[a] Inductively coupled plasma-optical emission spectroscopy.

kite reflections at 9.5 and 4.7 Å d spacing are present in all samples. The diffraction peak at 4.7 Å d spacing is the most intense, which is a characteristic of synthetic todorokite. Microwave samples are much more crystalline than conventionally prepared ones based on the peak intensities.

The average crystallite size for the samples was calculated from fwhm (full width at half maximum) of (002) peak (the most intense peak) using the Sherrer equation.[39] The average crystallite size value is larger for conventionally prepared materials as compared to that of the microwave synthesized samples of tordorokite. The calculated values are listed in Table 1.

Elemental Analysis and Average Oxidation Number Determination. Table 1 shows the elemental composition. Materials are mainly composed of manganese, magnesium, and oxygen. The average charge on Mg is slightly higher for the microwave OMS-1. The sodium content in the microwave prepared materials is significantly lower as compared to the sodium content in the conventionally prepared samples. The Na/Mn ratio for microwave OMS-1 is 1.8×10^{-3} and 5.7×10^{-3} for conventional OMS-1. The average oxidation number for manganese in the microwave samples is higher as compared to conventionally made materials. The calculated values are displayed in Table 1. This difference might influence the catalytic properties of todorokite in oxidation reactions.

Morphology. Figures 4 and 5 show SEM and TEM micrographs of the OMS-1 samples, respectively. SEM images reveal a novel morphology of microwave-prepared materials. Among the characteristic todorokite platelike shaped particles, cubes are present in the microwave samples. The average size of a cube is 4 μm.
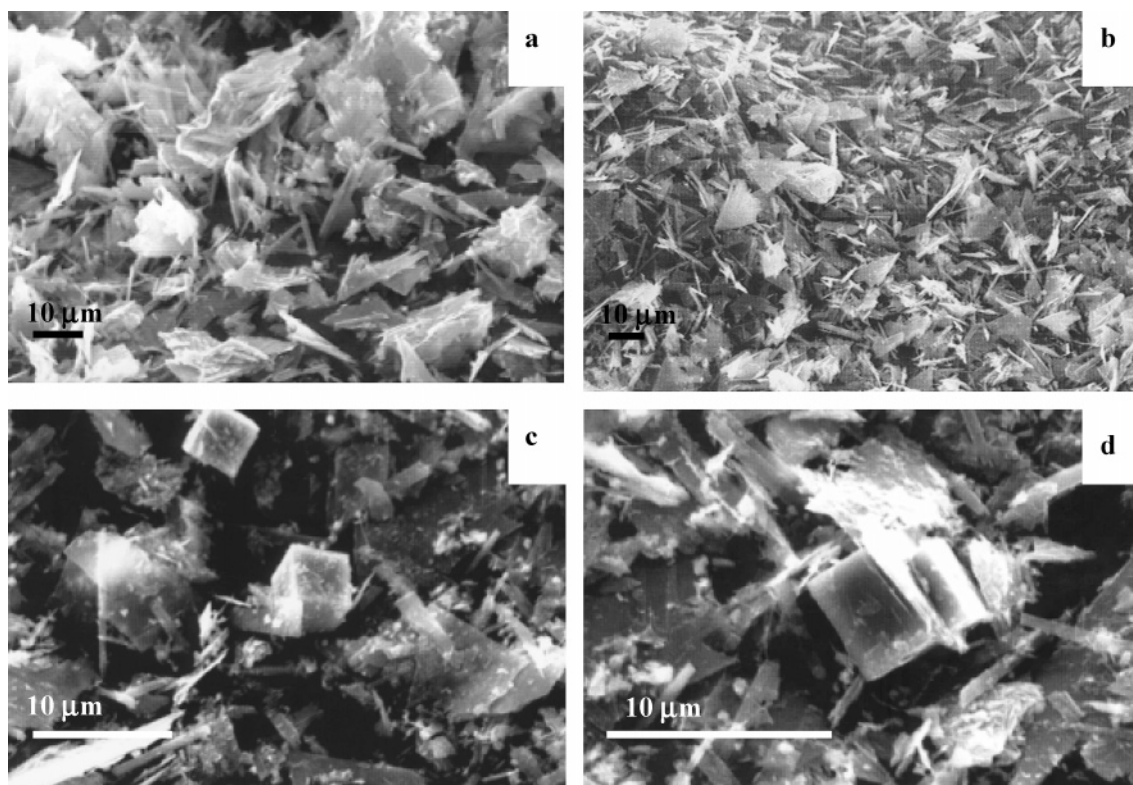
Figure 4. SEM micrographs of (a) precursor OL-1, (b) conventional OMS-1, and (c and d) OMS-1 synthesized in the presence of a microwave field.

The cubic morphology was found in all microwave-prepared OMS-1 materials. Conventionally made todorokite has a typical platelike morphology very similar to the morphology of its precursor, Mg-OL-1. EDX analyses showed that typical elemental metallic composition of the cube surface is ~10% Mg and ~90% Mn. Surface composition of plates was 25−35% Mg and 75−65% Mn. The same precursor was used for microwave as well as for conventional synthesis of OMS-1. The unique cubic morphology arises from microwave-assisted hydrothermal treatment of the OMS-1 precursor.

TEM characterization confirmed the results found by both SEM and XRD data. Figure 5 shows the cubic todorokite particles and a selected area electron diffraction pattern of the cubic particles. After tilting the sample to the [060] zone axis, the selected area electron diffraction pattern (when compared to the JCPDS file) confirmed that the cube is composed of todorokite. Additionally, the electron diffraction pattern was simulated using Desktop Microscopist, which provided additional confirmation of the todorokite structure. TEM results indicate that the cubes are composed of uniform OMS-1 fibers stacked and oriented along the same direction. TEM of conventional OMS-1 shows long fiber strands and flakes, but there is no agglomeration into the cubic structure seen for microwave-made materials. Therefore, the TEM results indicate that the microwave synthesis of todorokite provides a mechanism for arranging the single OMS-1 fibers and flakes.

Thermal Analysis. Figure 6 shows TGA profiles for microwave and conventionally synthesized materials. Both samples reveal similar initial water loss (around 2%) followed by two transitions centered at 325 and 575 °C. The conventionally made sample also shows a small weight loss at 275 °C. The weight loss at 325 °C is 9%

for the microwave-synthesized sample and 12% for conventionally made material. Both samples display 4−5% loss at 575 °C. X-ray patterns were collected for the samples at each stage of thermal decomposition. Identical crystal structures were found for conventionally and microwave made materials at each phase of thermal decomposition. Figure 7 shows the XRD patterns for samples subjected to thermogravimetric analysis. The 9.5 Å d spacing is lost after heating to 375 °C, but the 4.7 Å d spacing remains still sharp. The weight loss is due to evolution of water sorbed chemically in the tunnels and on the surface. Initial oxygen evolution could also take place at this stage. This causes the breakage of OMS-1 tunnels. After heating to 575 °C, todorokite transforms to hausmannite (JCPDS 24-734). It is a result of oxygen evolution from the framework of the material. These observations are consistent with stability studies of OMS-1 done previously.[10]

Surface Area and Pore Size Distribution. The N_2 isotherm adsorption data for OMS-1 materials are displayed in Figures 8 and 9. The isothermal plot observed for microwave-prepared materials is similar to that obtained for conventionally made materials. This plot corresponds to a type II adsorption isotherm with micropore filling at low p/p_0s and capillary condensation at high p/p_0s. The inserts of the figures show the macropore size distribution calculated by the BJH method. Microwave-made materials show larger macropore sizes as compared to conventional ones. The BET surface area of microwave OMS-1 was measured to be lower than that of conventionally made OMS-1. The values are shown in Table 2. The specific surface area for both materials appears to be low with respect to the todorokite tunnel size of 6. 9 Å.[4,6] The measurements suggest that the pores might not be accessible, due to

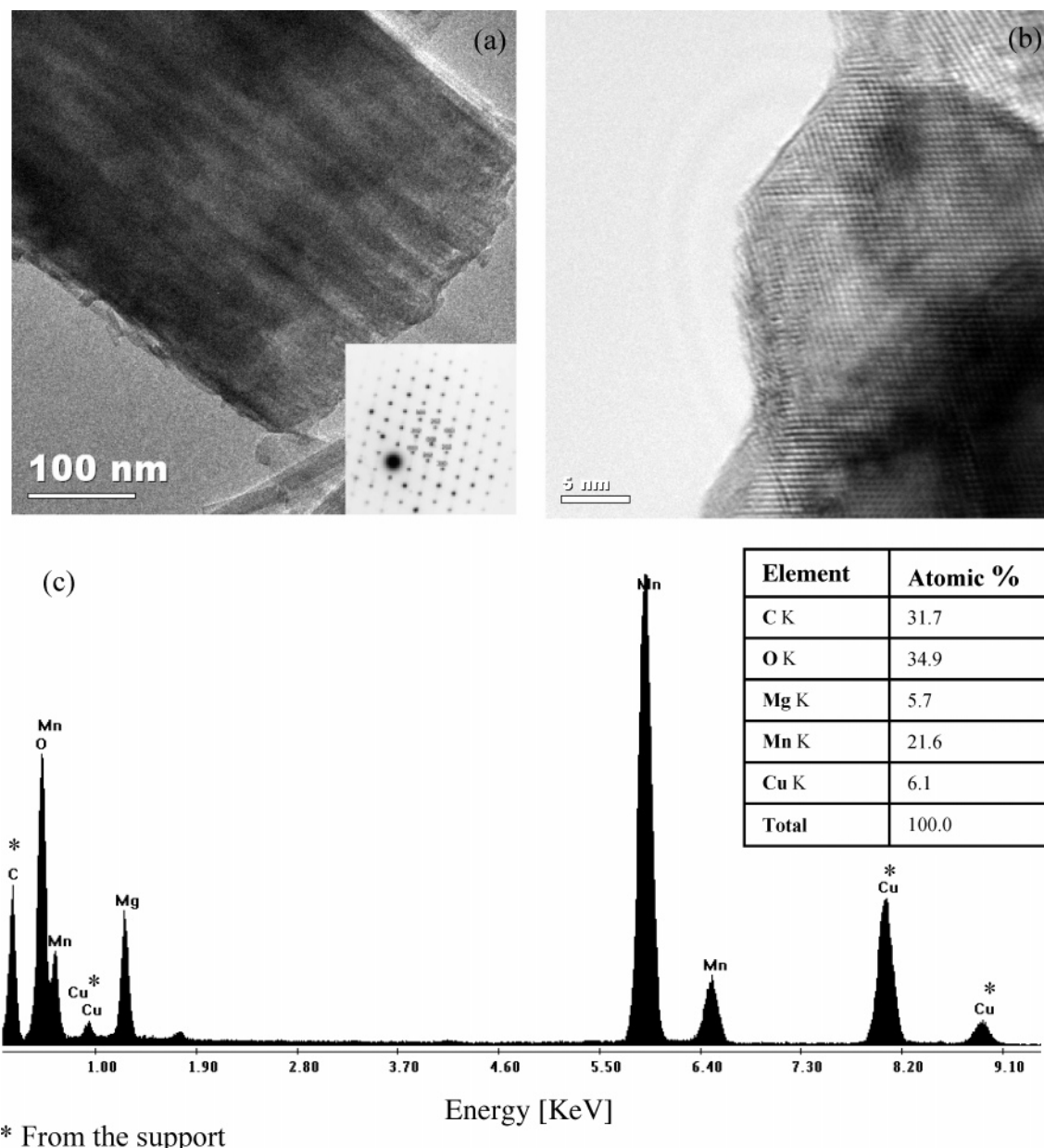| Element	Atomic %
C K	31.7
O K	34.9
Mg K	5.7
Mn K	21.6
Cu K	6.1
Total	100.0

* From the support

Figure 5. TEM bright-field image of a todorokite cubic-shaped particle (a), high-resolution magnified image of that particle (b), and its EDX (c). The inset of panel a is the [060] zone axis.

water molecules and sodium and magnesium cations present inside of them.

Acidic and Basic Properties Measurements. Temperature programmed desorption of NH_3 and CO_2 was used to study acidity and basicity, respectively. The NH_3 and CO_2 desorption temperatures reflect the strength of acidic and basic sites, respectively. The area of the desorption peak corresponds to the amount of particular active sites. Figure 10a,b illustrates temperature programmed desorption of NH_3 from OMS-1 samples. Microwave-prepared materials have much stronger acid sites than conventionally made OMS-1, which is reflected in the temperature of the desorption peak. Microwave prepared OMS-1 shows a maximum NH_3 desorption peak at 340 °C, and conventionally made OMS-1 shows a maximum NH_3 desorption peak at 280 °C. Figure 11a,b shows temperature programmed desorption of CO_2 from conventionally and microwave-made OMS-1 samples. The strength of the basic sites
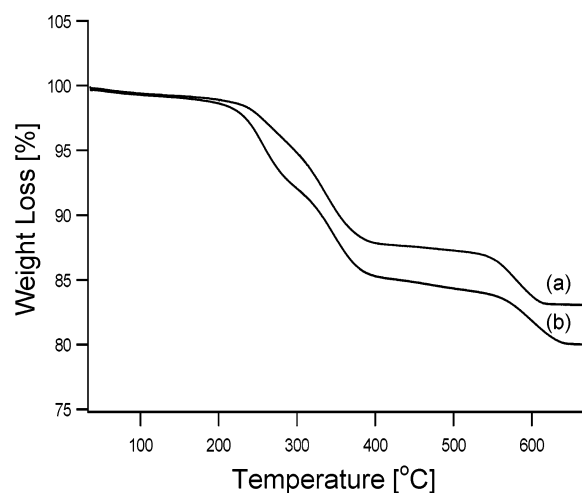

Figure 6. TGA profiles in N_2 for (a) microwave and (b) conventional OMS-1.
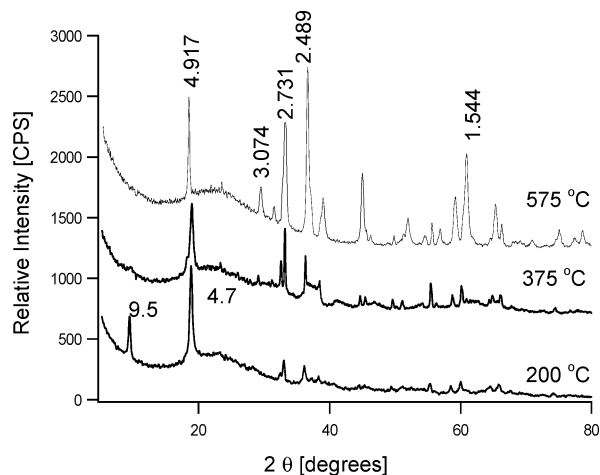
Figure 7. XRD of the microwave-prepared samples subjected to TGA at different decomposition stages.
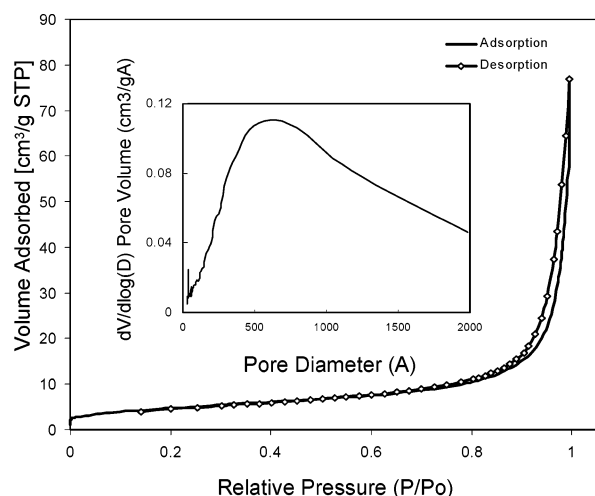

Figure 8. Isotherm plot and BJH desorption dV/dlog D pore volume data for materials synthesized conventionally.

is very similar for both samples; however, the microwave made material contains more weak basic sites than conventionally made samples.

Oxidation of Indene. Application of conventionally synthesized OMS-1 as a catalyst in the oxidation of indene resulted in two products, 40% indenone and 40% phthalic anhydride. The overall conversion for this reaction was 70%. Indenone is an intermediate in the synthesis of phthalic anhydride (Figure 12, Figure 13). Microwave-synthesized todorokite gave 100% selectivity to phthalic anhydride in the oxidation of indene. The average oxidation state of manganese in the microwave-made catalyst is slightly higher than the one calculated for conventional samples. This might be the reason for the greater oxidation ability of microwave-made OMS-1 and therefore better catalytic performance as compared to conventionally made OMS-1.

Oxidation of Benzyl Alcohol. The experiments showed that conventionally prepared OMS-1 did not have any catalytic activity in the oxidation of benzyl alcohol. However, OMS-1 synthesized by microwave heating provided 16% conversion of benzyl alcohol with the 100% selectivity to benzaldehyde. Crystallinity, average oxidation number, and the morphology of microwave-synthesized OMS-1 can be responsible for that activity. Oxidation of alcohols is known to take
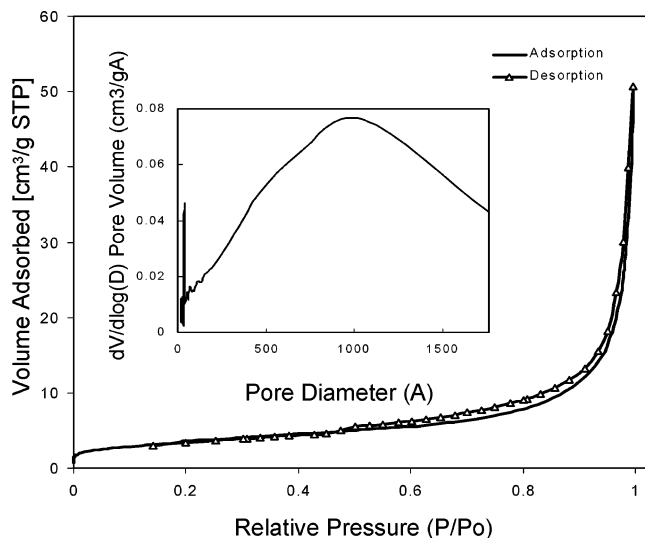

Figure 9. Isotherm plot and BJH desorption dV/dlog D pore volume data for materials made in the presence of microwave radiation.

Table 2. BET Surface Area, BJH Desorption Average Pore Diameter, and BJH Desorption Cumulative Pore Volume Data for OMS-1 Materials

sample	BET surface area [m^2/g]	BJH desorption av. pore diameter [nm]	BJH desorption cumulative pore volume [cm^3/g]
conventionally synthesized OMS-1	17 ± 0.17	25	0.120
microwave synthesized OMS-1	13 ± 0.21	21	0.079

place in acidic medium.[42] According to ammonia TPD experiments described previously, microwave-prepared materials have much stronger acid sites than conventionally made OMS-1. This is reflected in the temperature of NH$_3$ desorption peak. The improved catalytic activity of microwave-made todorokite in the oxidation of benzyl alcohol can be explained by higher acidity of microwave OMS-1.

Discussion

Microwave heating applied during the hydrothermal aging of layered precursors can be used to synthesize todorokite-type manganese oxide. The time of synthesis can be shortened to 8 h versus 2 days. Faster collapsing of OL-1 layers in the presence of microwave heating results in quicker formation of the $3 \times 3 \times \infty$ OMS-1 structure. The acceleration of synthesis time may result from the microwave coupling of water molecules and manganese oxides due to their high dielectric constants.[38,43−45]

Todorokite synthesized by microwave heating is more crystalline than the corresponding conventional materials and has a smaller crystallite size. These factors can

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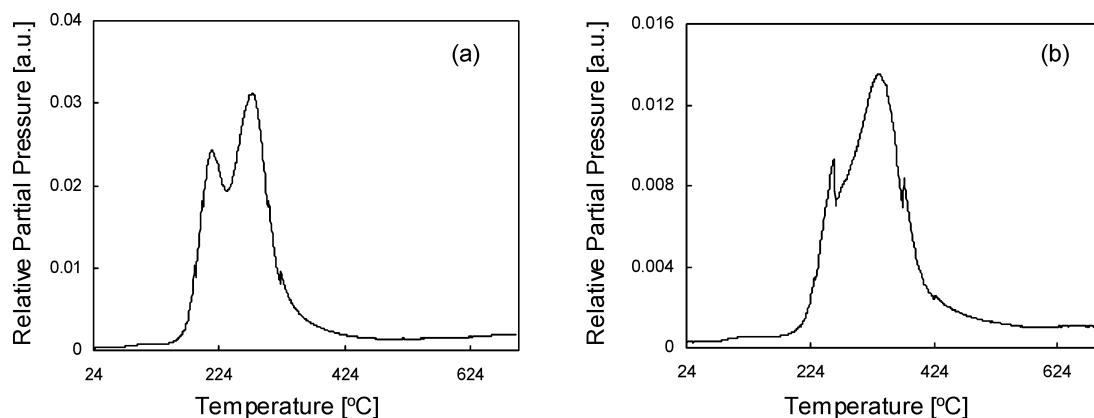
Figure 10. NH$_3$ temperature programmed desorption: (a) from conventional and (b) from microwave-made OMS-1.
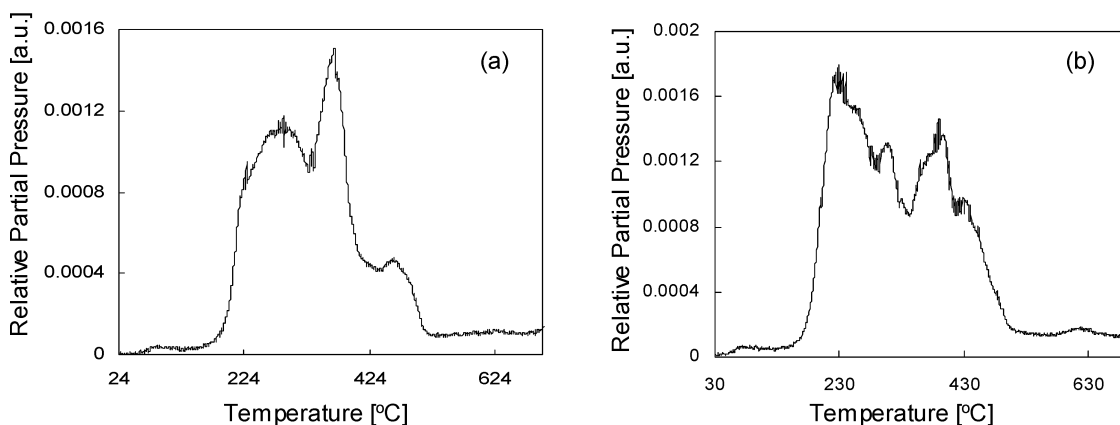

Figure 11. CO$_2$ temperature programmed desorption: (a) from conventional OMS-1 and (b) from microwave-made OMS-1.
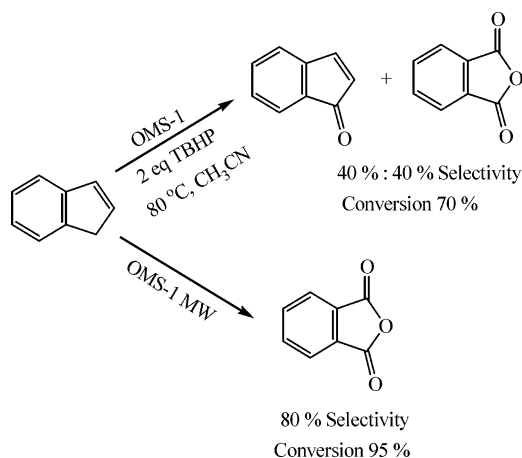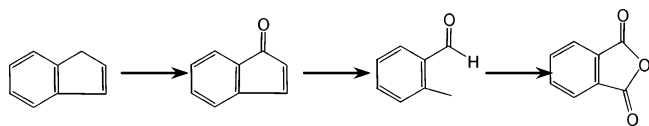

Figure 12. Oxidation of indene.

Figure 13. Mechanism of indene oxidation.

influence its performance as a catalyst. Selective heating could cause unusual morphology of OMS-1 prepared hydrothermally in the presence of microwaves. In addition, oscillating microwave fields may affect the arrangement of todorokite particles. TEM results indicate that the cubes consist of OMS-1 fibers that are uniformly arranged in one direction.

Microwave-made OMS-1 catalyst was more effective in the catalytic oxidation reactions than the correspond-

ing conventionally made OMS-1. Its greater oxidation ability can result from properties that distinguish it from conventional todorokite. These materials have higher oxidation state of manganese detected by potentiometric titration that could give better oxidation activity. The oxidation of indene with intermediate product of indenone is 80% selective to phthalic anhydride. Enhanced oxidation ability of microwave-prepared OMS-1 can drive the reaction to the higher selectivity. On the other hand, conventional OMS-1 gives only a mixture of phthalic anhydride and the intermediate product. It is also possible that the morphology plays a role in improved catalytic performance of microwave-synthesized todorokite. Furthermore, acid properties of microwave OMS-1 may be significant in improvement of the catalytic performance. Microwave OMS-1 has much stronger acid sites than conventionally made OMS-1 that is reflected in the temperature of ammonia desorption. The amount and strength of Brønsted sites would have an effect on oxidation of benzyl alcohol. Microwave-prepared materials are also more stable than conventional according to TGA results. Conventional materials lose more oxygen when heated, which lowers their oxidation properties.

Conclusions

Todorokite-type manganese oxide (OMS-1) has been synthesized conventionally and in the presence of a microwave field. Microwave heating during the hydrothermal aging step of the synthesis has a pronounced effect on chemical, physical, and catalytic properties of the material. Microwave-synthesized OMS-1 demon-

strates excellent conversion and selectivity to phthalic anhydride in the oxidation of indene. Therefore, catalytic performance of microwave OMS-1 in this reaction is superior to conventionally made todorokite. In addition, microwave-synthesized OMS-1 is active in the oxidation of benzyl alcohol to benzaldehyde, while conventionally made OMS-1 does not give any conversion. Improvement in the catalytic activity of microwave made todorokite seems to arise from its higher acidity, higher oxidation state of manganese, and better thermal stability when compared to traditional material.

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