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Microwave-Assisted Hydrothermal Synthesis of Cryptomelane-Type Octahedral Molecular Sieves (OMS-2) and Their Catalytic Studies

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Manganese oxide octahedral molecular sieves (OMS) are important materials in environmental chemistry, electrochemistry, and heterogeneous catalysis. Here, a rapid process to prepare cryptomelane-type octahedral molecular sieve (OMS-2) nanomaterials using a microwave assisted hydrothermal technique (MW-HT) is presented. With the assistance of microwaves in the hydrothermal reaction, the preparation time of OMS-2 can be as short as 10 s; up to 4 days are required in a conventional hydrothermal reaction. Direct observation of reaction temperature and pressure in the hydrothermal reaction can be achieved in real time in the reaction process. Reaction time and temperature are two parameters chosen to examine the formation conditions of OMS-2 materials. A reaction temperature below 80 °C resulted in the formation of amorphous manganese oxide material, whereas crystalline phase OMS-2 materials were formed at increased reaction temperatures to 100 °C or above. Studies by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) showed that the OMS-2 nanowires were produced from thin nanoflakes with increasing reaction temperatures. The N_2 physisorption study showed that the material formed at 100 °C had the highest BET surface area and pore volume. This technique was also used to test the cinnamyl alcohol oxidation of as-prepared OMS-2 materials.

1. Introduction

Porous manganese oxide octahedral molecular sieve (OMS) materials have drawn great interest in the past several decades due to their abundant chemical and physical properties.[1−3] The mixed valent semiconducting character of OMS materials shows promise for use as catalysts,[4] gas sensors,[5−7] electrodes,[8−10] magnetic,[11] and battery materials.[12,13] The porous nature of OMS materials can lead to opportunities for ion-sieving,[14−17] adsorption,[18−20] and catalytic[21,22] applications. Among several different kinds of known tunnel-structured OMS materials developed so far,[1] the 2 × 2 tunnel-structured manganese oxide, known as OMS-2 or α-phase MnO_2, has been the most useful and most widely studied material, due to its versatile morphologies, excellent structural stability, and good catalytic activity.

OMS-2 is a class of manganese dioxides having a tunnel size of 0.46 nm ×0.46 nm, constructed from edge-shared double MnO_6 (mainly $Mn^{4+}O_6$, minor $Mn^{3+}O_6$) octahedral chains, part of which are corner-shared to form one-dimensional tunnels. Barium and potassium are ideal hard templates for maintaining the tunnel structure of OMS-2. A small amount of water molecules is present in the tunnels of cryptomelane. The potassium/barium ions in the tunnel sites can be substituted with other inorganic cations with suitable sizes to form doped OMS-2 materials, denoted as M-OMS-2.[23,24] The dopants can also exist

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in the framework when the cationic size of the ion source is close to that of Mn^{2+}, which can be accomplished with controlled syntheses. Different M-OMS-2 materials may show different electrochemical performance, photosensitivity, and catalytic activity or selectivity.

The conventional preparative routes for OMS-2 include reflux, hydrothermal, solvent-free, high-temperature calcination, and sol−gel with reaction time varing from hours to days. For example, De Guzman et al.[25] used a reflux technique to prepare OMS-2 under a redox reaction in 24 h. Several different oxidants have been used to oxidize $MnSO_4$ in a hydrothermal reaction to synthesize OMS-2 materials. Yuan et al.[26] used $K_2Cr_2O_7$ and $MnSO_4$ to prepare OMS-2 materials in 12 h. Yuan et al.[27] also used $K_2S_2O_8$ and $MnSO_4$ to prepare OMS-2 nanowires in a hydrothermal reaction in 3 days. Microwave heating has been introduced to assist in the preparation of OMS-2 materials recently. For example, Malinger et al.[29] studied microwave frequency effects on the synthesis of OMS-2 materials. Nyutu et al.[30] used a microwave-assisted reflux method to study the formation of OMS-2 materials under different solvent conditions. These reactions were performed either in an open system without controlling the pressure or involving multiple steps, and thus were time-consuming. Rapid and facile synthesis of OMS-2 is desirable.

The microwave-assisted hydrothermal method (MW-HT) has been used to fabricate various metal oxides, such as Sm_2O_3,[31] Co_3O_4,[32] and CoO.[33] However, such a MW-HT technique has not been used to prepare OMS-2 materials. In this paper, we report the MW-HT synthesis of OMS-2 materials. The effect of reaction temperature (T) and time (t) on the MW-HT reaction were systematically studied using a Biotage Initiator microwave apparatus. This systematic study was conducted to examine the formation conditions for OMS-2 materials and reveals a morphological evolution of OMS-2 nanomaterials with different reaction temperatures. This microwave assisted technique was also used to test the catalytic activity of OMS-2 materials. For the catalytic study, the oxidation of cinnamyl alcohol to cinnamyl aldehyde was chosen.

2. Experimental Section

2.1. Setup. A Biotage Initiator microwave synthesizer equipped with a built-in computer and touch-screen was used. This single-mode microwave synthesizer is capable of converting conventional parameters to microwave conditions. The heating temperature can be increased up to 250 °C with ramp rates of 2−5 °C/sec. The pressure for the system can be varied from 0 to 20 MPa at powers of 0−400 W. A 20 mL reactor vial was used throughout the catalyst syntheses. Temperature, pressure, and power of the reaction were monitored in real time and profiled in the process of the reaction.

2.2. Synthesis of OMS-2. Potassium persulfate was chosen as the oxidant and manganese sulfate was used as the reducing reagent. The potassium sulfate was added as a templating reagent.[27,28] All chemicals were purchased from Alfa Aesar and were analytical grade and used as received. In a typical synthesis, 10 mL of 0.2387 mol/L K_2SO_4, 0.2387 mol/L $K_2S_2O_8$, and 0.159 mol/L $MnSO_4 \cdot H_2O$ aqueous solution was prepared in a 20 mL reactor vial and sealed. The apparatus was equipped with a magnetic stirrer. The reactions were carried out in the Biotage Initiator microwave synthesizer, which was programmed to heat from 80 to 200 °C with a hold time of 10 s to 30 min. All synthesized products were washed with DDW several times to remove any possible impurities.

2.3. Catalytic Study. Cinnamyl alcohol (1 mmol) was dissolved in 3 mL of toluene in a 10 mL glass vial. A Teflon-coated magnetic stirrer and 50 mg of catalyst were added in a previously prepared vial. The vial was sealed and allowed to stir for 30 s before catalysis. All the microwave-assisted catalytic reactions were performed at 200 °C for 10 min. As a comparative catalytic study, the OMS-2 sample prepared at 200 °C for 30 min was studied in the conventional reflux route.[4] All the resultant reaction mixtures were analyzed immediately after the reaction was complete.

The gas chromatography−mass spectroscopy (GC-MS) method was used for the identification and quantification of the resulting reaction mixture. The analytical sample was prepared by diluting 3 mL of the filtered reaction mixture with 3 mL of toluene. GC-MS analyses were done using an HP 5890 series II chromatograph with a thermal conductivity detector coupled with an HP 5970 mass selective detector. An HP-1 column (nonpolar cross-linked siloxane) with dimensions of 12.5 m × 0.2 mm × 0.33 μm was used in the gas chromatograph analysis.

Caution: Heating a closed reactor vial containing volatile solvents can produce an explosion. We performed these experiments in a hood. Readers are advised to take appropriate precautions.

2.4. Characterization. *2.4.1. Structure.* The crystalline phases of as-synthesized materials were analyzed using powder X-ray diffraction (XRD) with a Scintag 2000 XDS with a Cu Kα X-ray source ($\lambda = 1.54$ Å). A beam of 45 kV voltage and 40 mA current was used. The as-prepared powder sample (100 mg) was loaded on a glass slide and the data were collected in the 2θ range 5−75° with a continuous scanning rate of 2°/min.

High-resolution transmission electron microscopy (HR-TEM) experiments were performed using a JEOL 2010 instrument with an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in ethanol. A drop of the homogeneous-like dispersion was loaded on a carbon coated copper grid and allowed to dry before analysis.

2.4.2. Morphology (SEM/TEM). FE-SEM images were taken on a Zeiss DSM 982 Gemini emission scanning microscope with a Schottky Emitter at an accelerating voltage of 2 KV under a beam current of 1 μA. The samples were ultrasonically dispersed in ethanol for analysis. The suspensions were deposited on a silicon wafer and allowed to dry overnight in vacuum.

Transmission electron microscopy (TEM, Tecnai T12) was used to measure the morphology of the as-prepared materials.

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The samples for TEM analyses were obtained by placing a small amount of the as-prepared OMS-2 diluted in ethanol onto a copper grid and evaporated in air at room temperature. TEM images were taken at an accelerating voltage of 300 kV.

2.4.3. Surface Area and Porosity. A Micromeritics ASAP 2010 system was employed to determine the surface area (SA) and pore size distribution measurements. N_2 gas was used as the adsorbate at 77 K by a multipoint method. The Brunauer−Emmett−Teller (BET) method was used to measure the surface area and the Barrett−Joyner−Halenda (BJH) desorption method was used to calculate the pore size distribution. The sample (120 mg) was degassed at 150 °C for 12 h before analysis.

2.4.4. Structural Stability. The temperature-resolved X-ray diffraction (TR-XRD) technique was used to investigate the structural stability of as-prepared material. The analysis was performed in an XTRA X-ray diffractometer (Cu Kα radiation) equipped with an Anton Parr XRK 900 heater chamber. The OMS-2 sample prepared by the MW-HT method at 200 °C, 30 min was investigated from room temperature (RT) to 850 °C under air flow. The OMS-2 material was ramped at 10 °C min^{-1} until reaching the analysis temperature. XRD patterns were obtained in the range of 5−75° 2θ degrees at a scanning rate of 2° min^{-1}.

3. Results

3.1. Formation and Crystallization of OMS-2 Nanomaterials. The redox reaction between $S_2O_8^{2-}$ and Mn^{2+} under suitable hydrothermal conditions resulted in the formation of crystalline cryptomelane-type OMS materials.[28] Time-dependent and temperature-dependent studies were conducted to examine the conditions for the crystallization of OMS-2 materials. In the time-dependent study, the reaction temperature was set at 200 °C and reaction time was varied from 10 s to 30 min, while in the temperature-dependent study, reaction times were held at 5 min and reaction temperature was varied from 80 to 200 °C. Figure 1 shows the XRD patterns obtained in the time-dependent study. All observed peaks can be indexed to those of pure tetragonal cryptomelane (space group $I4/m$) with lattice parameters $a = b = 9.82$ Å and $c = 2.85$ Å. Peaks with low intensity and broadness were observed when the reaction time was less than 1 min, indicating the low crystallinity.

Better crystalline phases were obtained when the reaction time was extended to 1 min or longer. Notably, the crystalline phase OMS-2 can be obtained in as short a time as 10 s. Figure 2 shows the XRD patterns of as-prepared materials in the temperature-dependent study. A reaction temperature at 80 °C resulted in the formation of amorphous manganese oxide (AMO) materials. Crystalline phase OMS-2 materials were obtained when the reaction temperature was increased to 100 °C. More crystalline peaks were observed when the reaction temperature was increased to 120 °C. The OMS-2 sample prepared at 200 °C in 5 min was examined with high-resolution transmission electron microscopy (HR-TEM). Figure 3a shows that the morphology of OMS-2 materials is fibrous. The insert of Figure 3b shows an image of lattice fringes on the (200) planes ($d_{(200)} = 0.47$ nm), which reconfirms the formation of the OMS-2 crystalline phase.

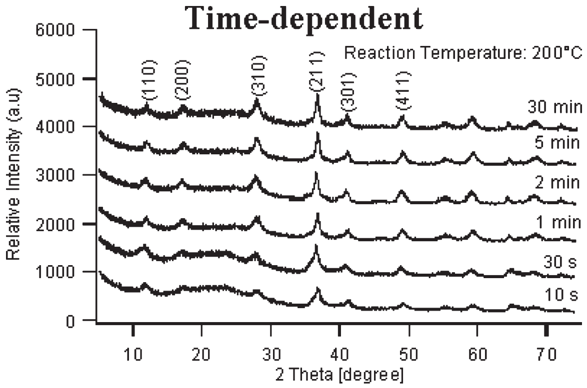


Figure 1. XRD patterns obtained in a time-dependent study. Reaction temperatures were set to 200 °C and reaction times varied from 10 s to 30 min.

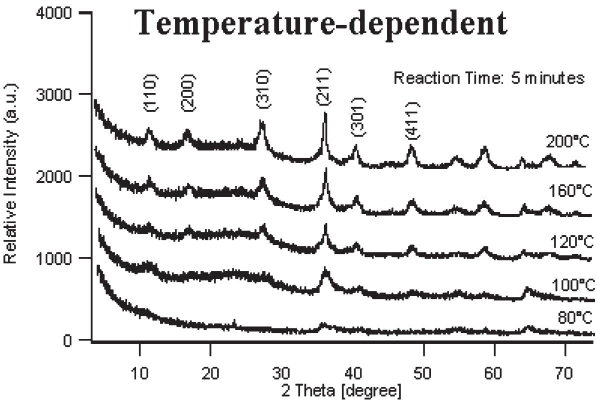


Figure 2. XRD patterns obtained in a temperature-dependent study. Reaction times were set to 5 min and reaction temperature varied from 80 to 200 °C.

3.2. Morphology. The OMS-2 materials synthesized under different conditions had typical fibrous shapes, which are similar to those OMS-2 materials prepared by other methods. Figure 4 shows OMS-2 morphologies in the time-dependent study. The fibers have a tendency to increase their length with increased reaction time, indicating better crystallinity. A small amount of flakes was observed at short reaction times of 10 and 30 s. Figure 5 shows the morphologies of samples prepared in the temperature-dependent study. At 80 °C, a flower-like morphology was obtained for amorphous manganese oxide (AMO) materials, which were assembled from thin nanoflakes. A flower-like morphology was retained when 100 °C was used as the reaction temperature, but fibers were formed by splitting the flakes. Figure 5d shows the destructured flower-like OMS-2 materials, which were prepared at 120 °C. Fibrous OMS-2 materials became more and more prominent with increasing reaction temperatures. Low-resolution TEM images shown in Figure 6 confirmed this flake-to-fiber morphological evolution process with increased reaction temperatures. When the reaction temperature was increased to 200 °C, well-defined fibrous OMS-2 was the main morphology with fiber diameters of about 20 nm and several micrometers in length.

3.3. Structural Stability. The stability of OMS-2 samples prepared at 200 °C in 5 min was investigated by temperature-resolved in situ X-ray diffraction (TR-XRD).

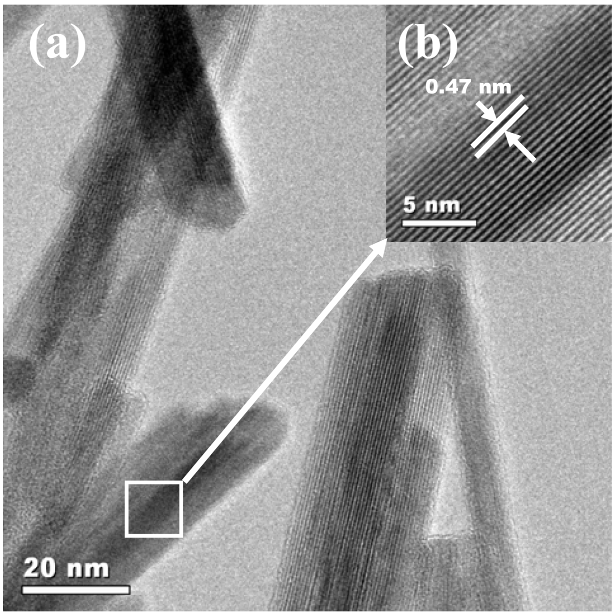


Figure 3. (a) HR-TEM pattern for the OMS-2 sample prepared at 200 °C, 5 min. (b) Image of lattice fringes, $d_{(110)} = 0.67$ nm.

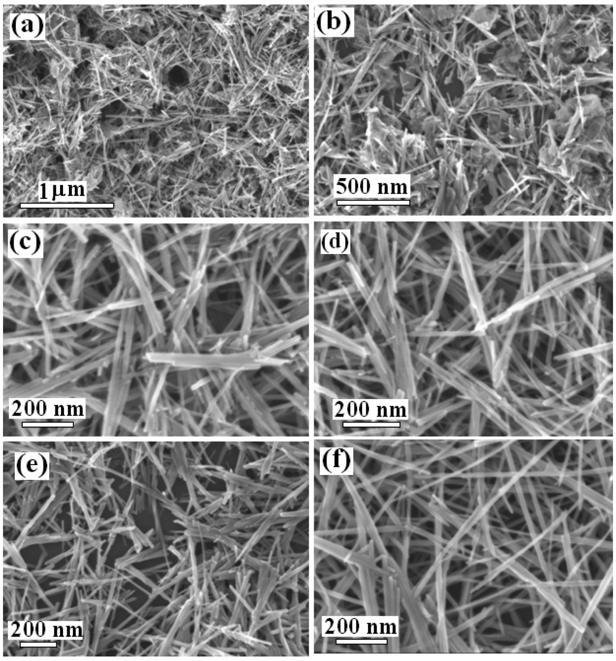


Figure 4. FE-SEM images obtained in time-dependent study. Images were OMS-2 prepared in (a) 10 s, (b) 30 s, (c) 1 min, (d) 2 min, (e) 5 min, and (f) 30 min at a reaction temperature of 200 °C.

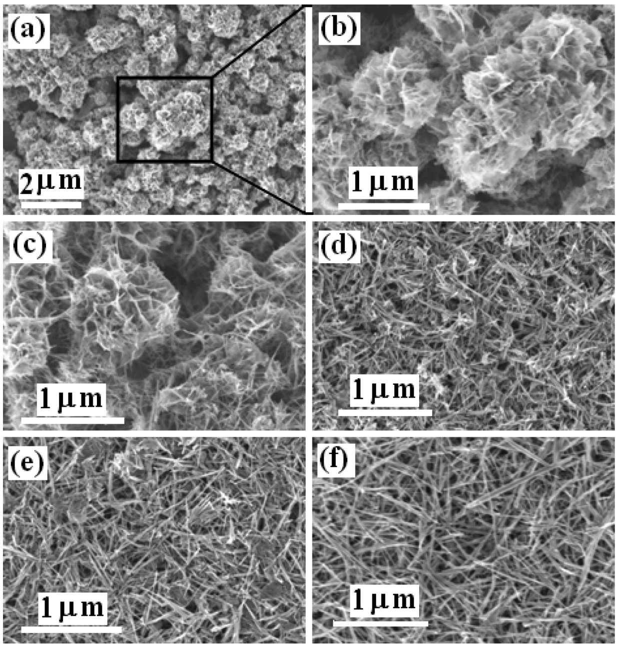


Figure 5. FE-SEM images obtained in temperature-dependent study. Images were AMO prepared at (a) and (b) 80 °C, and OMS-2 prepared at (c) 100 °C, (d) 120 °C, (e) 160 °C, and (f) 200 °C in 5 min.

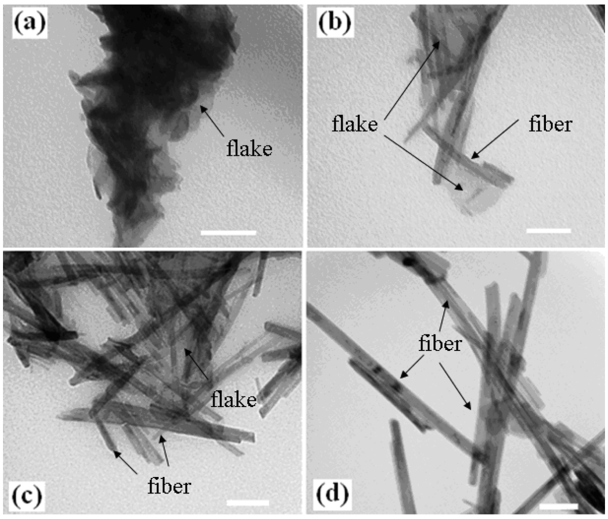


Figure 6. TEM images for flake-to-fiber evolution of OMS-2 materials in temperature-dependent study: (a) AMO prepared at 80 °C; OMS-2 prepared at (b) 100 °C, (c) 120 °C, and (d) 200 in 5 min. Scale bar: 50 nm.

OMS-2 is stable in air atmosphere up to 500 °C (Figure 7). When the heating temperature is above 600 °C, OMS-2 was transformed to the bixbyite phase Mn_2O_3, which agrees with other reported results.[27] This high temperature stability allows OMS-2 materials to be used in high-temperature catalysis.

3.4. Surface Area and Porosity. The Brunauer–Emmett–Teller (BET) surface areas and pore volumes of as-synthesized OMS-2 nanomaterials are presented in Table 1. The OMS-2 sample prepared at 100 °C in 5 min possesses the highest surface area and pore volume. The self-assembly of nanoflakes and flake-to fiber transition might be related to this larger surface area. Well-defined nanowires in other samples have similar and relatively lower surface areas, which may be due to the similarity in morphology of these samples. The aggregation and entanglement of nanowires might account for the decrease of the surface area. Figure 8a shows representative N_2 adsorption/desorption isotherms of an OMS-2 sample prepared at 200 °C in 5 min. The adsorption/desorption isotherms show type IV isotherms (IUPAC classification) with a distinct hysteresis loop at high partial pressures ($P/P_0 > 0.9$), which indicates the presence of high textural mesoporosity. At low partial pressures, formation of a monolayer of adsorbed molecules is the prevailing process, while at high partial pressures multilayer adsorption

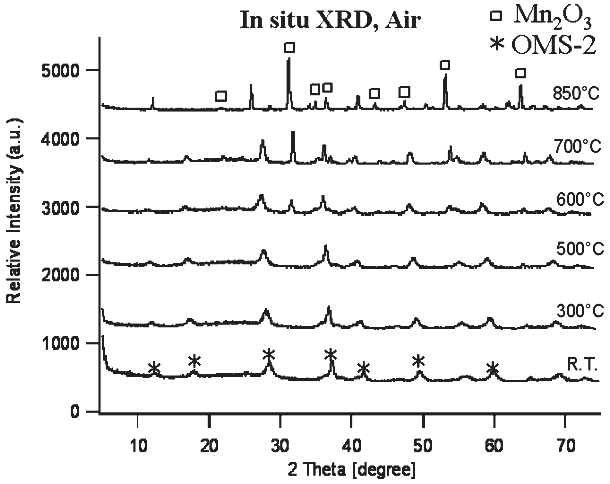


Figure 7. TR-XRD patterns of OMS-2 sample prepared at 200 °C in 5 min.

Table 1. BET Surface Area and Pore Volume of As-Prepared OMS-2 Nanomaterials

sample name	BET surface area (m^2/g)	pore volume (cm^3/g)
OMS-2: 100 °C, 5 min	129	0.97
OMS-2: 120 °C, 5 min	79	0.67
OMS-2: 160 °C, 5 min	84	0.61
OMS-2: 200 °C, 5 min	83	0.56
OMS-2: 200 °C, 30 min	84	0.56

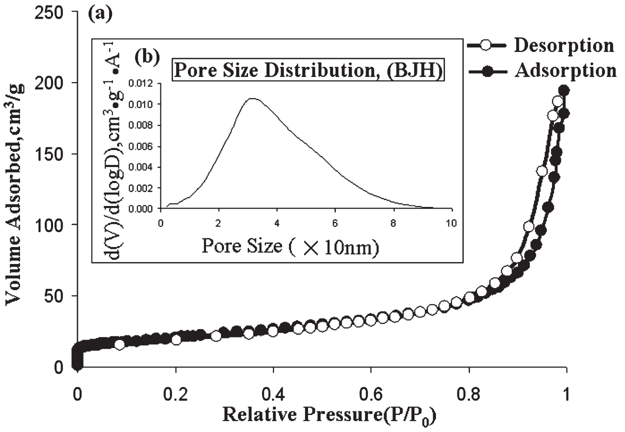


Figure 8. (a) N_2 adsorption/desorption isotherms and (b) Barrett–Joyner–Halenda (BJH) desorption pore size distribution of OMS-2 (200 °C, 5 min).

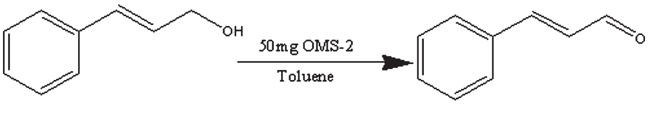
occurs. All the other as-prepared OMS-2 materials possess this type of isotherm, which corresponds to other reported OMS-2 materials.[34] The pore size distribution of the OMS-2 sample was centered at 32 nm by the BJH desorption method (Figure 8b).

3.5. Catalytic Study. The catalytic performances of as-synthesized catalysts were evaluated in a microwave assisted catalysis method (10 min, closed system; Equation 1). The results are shown in Table 2. All the as-prepared catalysts showed 29–32% conversion with 100% selectivity to cinnamyl aldehyde. The OMS-2 materials prepared at 200 °C for 30 min were also tested in a conventional reflux method (4 h, open system),[4] and showed a conversion of 26.1%, which is 6.4% lower than that in microwave assisted methods. An OMS-2 catalyst was made by a conventional hydrothermal method[27] and used to study catalytic activity under the same microwave assisted conditions and procedures. A conversion of 30.9% and 100% selectivity were obtained for this catalyst.

Table 2. Conversion and Selectivity of Cinnamyl Alcohol to Cinnamyl Aldehyde with Use of As-Prepared OMS-2 Nanomaterials[a]

catalyst name	conversion ±1 (%)	selectivity ±1 (%)
OMS-2: 100 °C, 5 min	31.4	100
OMS-2: 120 °C, 5 min	31.8	100
OMS-2: 200 °C, 5 min	29.3	100
OMS-2: 200 °C, 30 min	32.5	100
OMS-2: 200 °C, 30 s	32.3	100

[a] Reaction condition: 1 mmol cinnamyl alcohol, 3 mL of toluene solvent, 50 mg of OMS-2, 200 °C, 10 min MW heating. Conversion and selectivity determined and confirmed by GC-MS.



Equation 1

4. Discussion

4.1. Crystallization of OMS-2 Nanomaterials. In this work, microwave-assisted hydrothermal synthesis of OMS-2 materials was complete in 10 s at 200 °C. Different oxidants, such as $K_2Cr_2O_7$, $KMnO_4$, and $K_2S_2O_8$ can be used to oxidize manganese(II) salts to prepare OMS-2 materials.[26,27,35] Among these oxidants, $K_2S_2O_8$ possesses the highest electrical potential (2.01 eV) for $S_2O_8^{2-}$/SO_4^{2-} in the half reaction, indicating a very strong tendency for the reaction to occur. The high redox potential (0.74 eV) between $S_2O_8^{2-}$ and SO_4^{-} and MnO_2/Mn^{2+} is the driving force of the reaction and is in response to the rapid nucleation reaction, especially with the assistance of microwave irradiation. The choice of solvent was also very important. Water possesses a medium dielectric loss ($\tan \delta = 0.123$) and is an excellent solvent for microwave-assisted synthesis. The rapid nucleation rate was obtained when water was heated by microwave irradiation. The excess use of templates offered by both cationic parts of potassium persulfate and potassium sulfate favored the growth of OMS-2 nanowires.

The reaction temperature (T), pressure (P), and power (W) were monitored and profiled when the reactions proceed. Figure 9 shows the T, P, and p profiles when the reaction was conducted at 200 °C for 5 min. The reaction temperature in the reactor vial was well maintained at 200 °C, the pressure was maintained at 15 bar, and the power was maintained at 50 W for 5 min. Table 3 shows the T, P, and W parameters when the reaction was conducted under different conditions. Obviously, for the

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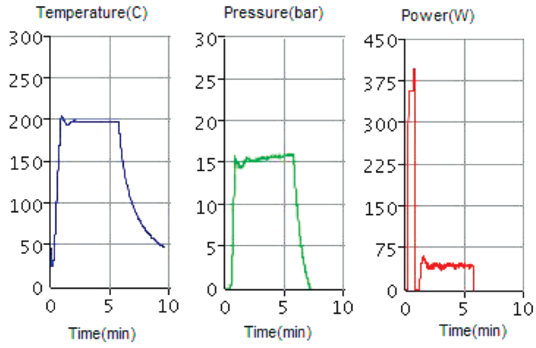

Figure 9. Representative profile of *T*, *P*, and *p* monitored when the reaction was performed at 200 °C, 5 min.

Table 3. Observed Reaction Temperature, Pressure, and Power under Different Reaction Conditions

sample name	temperature ±5 (T/°C)	pressure ±1 (P/bar)	power ±5 (p/W)
AMO: 80 °C, 5 min	75	1	20
OMS-2: 100 °C, 5 min	100	2	30
OMS-2: 120 °C, 5 min	120	3	35
OMS-2: 160 °C, 5 min	160	8	40
OMS-2: 200 °C, 5 min	200	15	50
OMS-2: 200 °C, 30 min	200	18	350

same reaction time, higher pressures were obtained with increased reaction temperature, which leads to the formation of longer OMS-2 nanowires as shown in Figure 5. Such direct observation of reaction temperature and pressure in the hydrothermal reaction was unprecedented. A longer reaction time resulted in a higher pressure in the reactor vial when using the same reaction temperature.

4.2. Shape Evolution of OMS-2 Fibers. Based on the temperature-dependent and time-dependent studies, the OMS-2 nanowires may evolve from a "nucleation—flake—fiber" process. At the beginning of the redox reaction between $S_2O_8^{2-}$ and Mn^{2+}, manganese oxide units were produced in solution.[36] The high electrical potentials between $S_2O_8^{2-}$ and SO_4^- and MnO_2/Mn^{2+} in the redox reaction made reactions proceed very easily and rapidly, especially with the microwave irradiation. When reaction temperature increased, the concentrations of manganese oxide units (MnO_6) in solution increased. Aggregation of the manganese oxide units then occurred to form small particles.[36] These particles may serve as nuclei for self-assembly of the flower-like morphology. With an increased reaction time, the flakes were destroyed and form fibrous shape materials due to the stress-induced splitting. Increased reaction temperature leads to increased pressure in the reaction system, which resulted in a faster destructive process and thus formed more nanowires.

4.3. Catalytic Property of OMS-2. OMS-2 materials prepared with MW-HT methods showed 29—32% conversion with 100% selectivity to cinnamyl aldehyde under microwave heating conditions. The materials prepared by the conventional method and microwave assisted method show no significant differences in catalytic activity. The mixed-valent manganese species on the surface of OMS-2 materials contribute to the heterogeneous catalytic activity. The high-temperature resistant properties of OMS-2 materials as determined with TR-XRD (Figure 7) studies allow these materials to be used in the 200 °C microwave assisted catalysis. The surface area of as-prepared OMS-2 materials varied from 78.6 to 129.4 m^2/g. The selectivity of cinnamyl alcohol to cinnamyl aldehyde with the use of all OMS-2 catalysts prepared by microwave assisted and conventional methods is the same and the conversions are very close (percent error 9%). There is no correlation of activity and surface area. In fact, larger surface area OMS-2 prepared at 100 °C was slightly less (1.1%) active than OMS-2 prepared at 200 °C with the same reaction time.[4]

5. Conclusions

The MW-HT technique is a rapid process for preparation of OMS-2 nanomaterials. With this technique, direct observation of reaction temperature and pressure in a hydrothermal reaction can be easily achieved. Reaction temperatures higher than 100 °C resulted in crystalline phase OMS-2 materials while reaction temperatures below 80 °C resulted in the formation of an amorphous manganese oxide material. The OMS-2 nanowires evolved from thin nanoflakes with increased reaction temperature. This technique could also be used to fabricate other types of OMS materials and doped OMS-2 materials, which is now under investigation in our lab.

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