Journal of Catalysis **187,** 285–297 (1999)
Article ID jcat.1999.2639, available online at http://www.idealibrary.com on IDEAL®

Synthetic Todorokite Produced by Microwave Heating: An Active Oxidation Catalyst

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Received November 9, 1998; revised July 14, 1999; accepted July 15, 1999

Microwave heating methods have been applied to the synthesis of a family of layered and tunnel-structured manganese oxide materials. These materials are known to interact strongly with microwave radiation, and thus pronounced effects on the microstucture might be expected. The work presented here is a study of the synthesis, characterization, and catalytic activity of a one-dimensional tunnel-structured manganese oxide catalyst known as OMS-1 (octahedral molecular sieve). The synthetic methods employed in the production of OMS-1 include constant temperature aging, ion exchange, *in situ* coprecipitation, and hydrothermal treatment. Heating was done using conventional convection methods and microwave radiation to probe the effect of microwave radiation on the material characteristics. The products were examined using X-ray diffraction, elemental analysis, determinations of the average manganese oxidation number, Auger spectroscopy, scanning electron microscopy, thermal stability studies, infrared spectroscopy, and surface area measurements. Catalytic activity was tested in the oxidative dehydrogenation reaction of ethylbenzene to styrene. The materials produced using microwave radiation were shown to have bulk characteristics similar to those prepared using conventional heating. However, the surface properties were shown to be different, resulting in different catalytic results. The differences in the properties and catalytic activity of the materials, as well as the implications of microwave heating as a synthetic tool, are discussed. © 1999 **Academic Press**

I. INTRODUCTION

Multivalent manganese oxide materials have recently gained attention for their catalytic and ion-exchange properties. Many different synthetic techniques such as sol–gel, coprecipitation, ion exchange, reflux, and hydrothermal treatment are employed in the production of these microporous minerals, and have been shown to highly influence the resultant properties. The specific reaction pathway to the manganese oxides produced in this work are dependent on solvent–solid interactions, i.e., precipitation, ion exchange, and hydrothermal treatment. It was thought that because microwave radiation interacts with the dipole moment of water it could affect the preceding reactions. Specifically, the effect would be most strong at the water–solid interfaces, leading to different surface structures and therefore different catalytic activity in microwave-prepared catalysts.

The growing interest in microwave processing can be attributed to several attractive factors. Significant savings in time and energy costs due to shorter processing times (2–6, 8, 9) and more homogeneous products (2, 6, 8, 9) is the most recognized reason. However, the synthesis of new materials (6), and improved microstructures have also been reported (1). For example, hexagonal MCM-41 was synthesized by heating the precursor gels in a microwave field for less than 1 h (2). The condensation reactions are accelerated, and lead to homogeneous products. The $YBa_2Cu_3O_{7-\gamma}$ superconductor was synthesized by two groups (3, 4) in which the processing times were drastically reduced.

Microwave processing of inorganic glasses (5) was shown to be automatically temperature controlled, with shorter processing times. As the material reaches its final product, it no longer absorbs microwave radiation and self-cools (except for ionically conductive glasses). Hydrothermal heating in a microwave field has led to simultaneous nucleation in the preparation of zeolites (6), resulting in a homogeneous product. It is thought that microwave radiation leads to better dissolution of precursor gels and resultant crystal growth. Microwave hydrothermal processing is used to prepare layered and network phosphates (7), large and homogenous $AlPO_4^{-5}$ crystals (8), and zeolite Y and ZSM-5 (in 10 min) (9).

In microwave heating the material absorbs microwaves and converts this electromagnetic energy to heat. In contrast with conventional heating, materials heated in a microwave furnace can be heated more evenly, with little or no temperature gradients from the surface to the inside. The absorption of microwaves and the extent of heating

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0021-9517/99 $30.00

depends on the material, its composition, and its phase, and, therefore, selective heating is possible. This is very desirable for such applications as removal of organics, ceramic joining, and drying.

The extent to which a material is influenced by microwave radiation can be defined by several different parameters. The equation

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad [1]$$

is used to describe the effect the electric component of an electromagnetic field has on a material. It is called the complex permittivity, ε^*, and it has a real part (the dielectric constant) and an imaginary part [the dielectric loss factor (where $j = (-1)^{1/2}$)] (10). The dielectric constant describes the ability of the material to be polarized by the electric field, and the loss factor is a measure of the efficiency with which the electromagnetic energy is converted to heat (by joule heating where free charge is found, and by rotational energy modes). One more useful parameter is the dielectric loss tangent, where $\tan\delta = \varepsilon''/\varepsilon'$, which describes the ability of a material to convert electromagnetic energy to heat energy at a given frequency and temperature (11).

Manganese oxides are known to absorb microwave radiation well (11, 12). The dielectric constant of MnO_2 is reported to be ~10,000 (13), which indicates that production of manganese oxides in a microwave field might lead to different microstructural products. Manganese oxides can form layered and one-dimensional tunnel structures in which the basic building block is the octahedral MnO_6 unit, which has edge- and corner-shared units. Several different manganese oxide minerals have been identified; among these are birnessite (a layered material) and todorokite (a one-dimensional tunnel material). They are both mixed valent systems, with an average oxidation number of Mn from 3.4 to 3.7.

The synthetically prepared layered material contains cations between the layers and is called OL-1 (octahedral layer). The cation located between the layers is reflected in the name; i.e., when Na is located between the layers, the material is called Na-OL-1 (see Fig. 1). To prepare synthetic todorokite (the tunnel-structured material called OMS-1, octahedral molecular sieve), the layered material is treated hydrothermally. The resultant tunnel size is 6.9 × 6.9 Å, and has three manganese oxide octahedra per side (see Fig. 2). Mg^{2+} is commonly found in the tunnels. Pore size distributions are broad in comparison to zeolites (23) perhaps due to the square pores.

The most common application of manganese oxides is in dry cell batteries. However, manganese oxide materials have been receiving more attention lately as oxidative catalytic materials (14). Recent studies have shown that OMS-1 converts methane (32.5%) selectively to higher hydrocarbons (15), ethylbenzene can be converted with high selectivity to styrene, and hexane is oxidized to hexanol, or 1-hexene (16). OMS materials are also being developed for use as sensors, photocatalytic materials, environmental catalysts, and other novel applications.

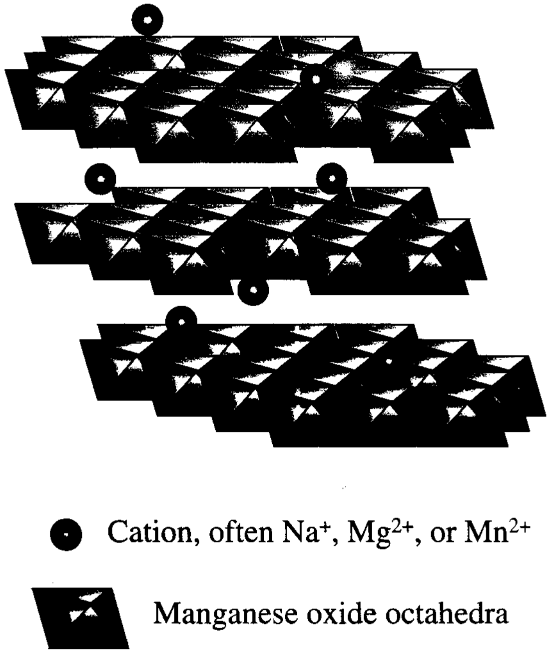

FIG. 1. Octahedral layers of manganese oxide, OL-1.

In this study three related materials are prepared both with microwave radiation and with conventional heating. The layered manganese oxide, Na-OL-1, is first synthesized, then ion-exchanged to form Mg-OL-1. This is treated hydrothermally to produce the 3 × 3 tunnel structure, OMS-1. The preparation of OMS-1 using microwave heating for all steps (including precipitation) has been previously reported, and is termed the total microwave heating method here (17). In this study the aging, ion-exchange, and

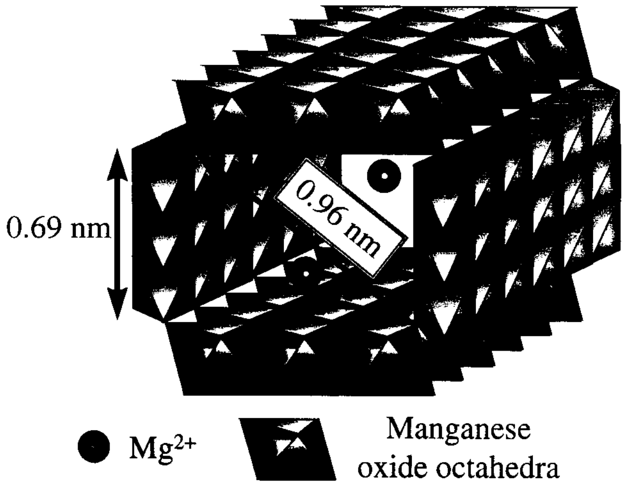

FIG. 2. Octahedral molecular sieve (OMS-1) made of 3 × 3 blocks of manganese oxide octahedra.

hydrothermal treatment steps using microwave heating are compared with the data from the previous report.

The materials are characterized by X-ray powder diffraction (XRD), elemental analysis, titrations for the determination of the average oxidation number of manganese, thermal analysis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), surface area measurements, and Auger spectroscopy. The OMS-1 materials are used to catalyze the reaction of ethylbenzene to styrene.

II. EXPERIMENTAL

A. Synthesis

1. Microwave apparatus. A microwave oven, purchased from Microwave Materials Technology in Knoxville, Tennessee (Model 10-1300), was used to prepare the samples. It has a variable power output from 0 to 1300 W, uses a frequency of 2.45 GHz, and is temperature controlled using a Pt resistance thermometer in intimate contact with the sample. The microwave autoclaves are transparent to microwave radiation, and were purchased from CEM, Matthews, North Carolina, and are designed for *in situ* temperature measurements. The microwave setup is shown in Fig. 3.

2. Synthesis procedures. The conventionally and microwave-synthesized manganese oxides were prepared under similar conditions involving three steps. Na-OL-1 is prepared, ion-exchanged to make Mg-OL-1, and then treated hydrothermally to prepare OMS-1. Alternatively, the ion-exchange step and the hydrothermal treatment can be combined into one step. The synthetic details are as follows. First the layered manganese oxide, Na-OL-1, is prepared by the reduction of potassium permanganate in sodium hydroxide with a solution of manganese chloride and magnesium chloride. The Mn^{7+}-to-Mn^{2+} salt ratio is set so that the theoretical final average oxidation number (which will be referred to as the TAON) of manganese is 3.3 or 3.45 and the Mn^{7+}-to-Mg^{2+} ratio is 2 : 1. For example, to make Na-OL-1 with a TAON of 3.45, 1.5928 g of $MnCl_2 \cdot 4H_2O$ and 0.3166 g of $MgCl_2 \cdot 6H_2O$ were dissolved in 35 mL of H_2O and added over a period of 5–7 min with vigorous stirring at 50°C to a solution of 35 mL of 3 M NaOH solution containing 0.5056 g of $KMnO_4$. After the solutions are added together they are stirred for a total of 20 min, covered with Parafilm, and then aged in either a water bath or the microwave oven at 50°C for 24 h. The layered phase thus obtained (Na-OL-1) is washed and filtered immediately five times with 300 mL of H_2O.

The Na-OL-1 is transferred to 70 mL of a 1.5 M $MgCl_2$ solution and stirred for 10 min, covered with Parafilm, and aged in either a water bath or the microwave oven at 50°C for 20 h. The resultant Mg-OL-1 is washed and placed in 70 mL water in an autoclave at 160°C for 35 h to prepare OMS-1. Alternatively, the Na-OL-1 was transferred to 70 mL of a 1.5 M $MgCl_2$ solution in an autoclave, stirred for 10 min, and placed in a convection oven or the microwave oven at 160°C for 35 h. The resultant OMS-1 is washed five times with water and dried overnight at 110°C.

These materials are compared with those prepared by a total microwave heating method in which the precipitation takes place while the sample is irradiated with microwaves. The details of this method and the characterization of the products have been published (17).

B. Characterization

1. X-ray diffraction. XRD samples were prepared both by suspensions in water with subsequent drying and by

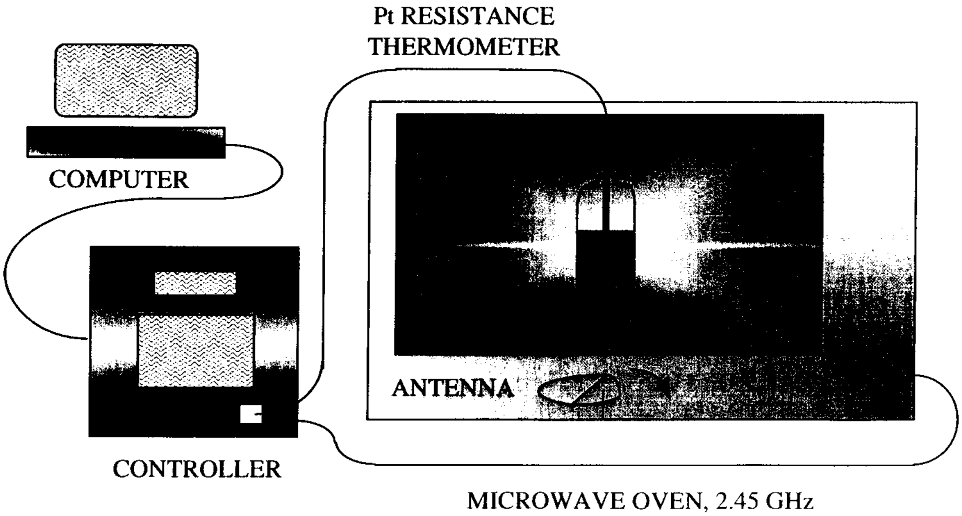

FIG. 3. Microwave oven setup.

grinding the powder and side mounting the sample in a holder to eliminate preferred orientation. Side mounting is done by using a 2.5 × 5-cm piece of aluminum with a semicircular depression machined out so that when a glass slide is placed on top, the side is open. Powder is then sifted into the opening, the glass slide is removed, and the sample is ready for analysis. XRDs patterns were recorded at 0, 1, 2, and 3 h of the forming Na-OL-1 as well as fully aged Na-OL-1, Mg-OL-1, and OMS-1. The instrument used is a Scintag XDS-2000 theta–theta diffractometer with a Cu$K\alpha$ radiation source.

2. Elemental analysis. Samples were analyzed for elemental analysis using flame atomic absorption (AA) with a Perkin–Elmer Model 2380 AA, and by inductively coupled plasma (ICP) with an atomic emission spectrometer (ICP-AES), Perkin–Elmer Model P40. Approximately 15 mg of sample was dissolved in 5 mL of aqua regia, then diluted to 100 mL. All samples were analyzed for K, Na, Mg, and Mn.

3. Determination of the average oxidation number of manganese. Two different titration methods were performed on the Na-OL-1 and OMS-1 samples to determine the average oxidation number of the manganese (18). The total manganese content was determined by dissolving the sample in concentrated HCl and titrating with a standardized permanganate solution to a potentiometric endpoint according to the equation

$$\mathrm{Mn}^{7+} + 4\mathrm{Mn}^{2+} \Rightarrow 5\mathrm{Mn}^{3+}, \qquad [2]$$

where Mn^{3+} is stabilized as a pyrophosphate complex. The measurement of available oxygen in the manganese sample was determined by reduction to Mn^{2+} with measured and excess Fe^{2+} and subsequent titration of the excess Fe^{2+} using standardized permanganate solutions. From these titrations it is also possible to calculate the mass per mole of Mn in the sample.

4. Thermal analysis. Thermogravimetric analysis was performed using a TA Instrument Model 2950-TGA with a scan rate of 10°C/min. Samples were loaded using an automatic sampling attachment. Differential scanning calorimetry was performed using a TA Instrument (Model 2920) with a heating rate of 20°C/min in N_2.

5. Scanning electron microscopy. An Amray 1645 scanning electron microscope using a tungsten filament and an acceleration potential of 20 kV was used to examine samples mounted by suspension in water onto an aluminum peg, dried overnight, then gold-coated to minimize charging.

6. Fourier transform infrared. A Nicolet Magna-IR Model 750 was used to investigate the manganese environment. The mid-IR range was detected using a mercury–cadmium–telluride (MCT) detector and for the far-IR range a DTGS-PE detector was used. Resolution of the instrument is up to 0.125 cm^{-1}. The background of the spectrometer before data collection was checked with the maximum and minimum intensities at zero path difference of the interferogram. The samples were analyzed using the reflectance attachment of the instrument.

7. BET surface area analysis. The surface areas of the OMS-1 samples were measured using BET. The instrument used is a NOVA 1000 for BET surface area measurements, purchased from Quantachrome. Five point measurements were taken.

8. Auger spectroscopy. Auger electron spectroscopy was used to look at surface species of the OMS-1 prepared by microwave aging, conventional heating, and total microwave synthesis. The instrument used is a PHI 610, and scans were run from 30 to 2000 eV with a resolution setting of 6%. A beam energy of 3.0 keV and a beam current of 150 nA were used.

C. Catalytic Activity

OMS-1 samples with a TAON of 3.45 were tested for catalytic activity in the conversion of ethylbenzene to styrene. Twenty milligrams of sample with particle sizes of 300 to 590 μm was mounted on the far side of a U-shaped quartz reactor. The samples were pretreated in He at 300°C for 1 h. The temperature was monitored using a thermocouple placed outside the reactor next to the bed, and maintained at 300°C during the reaction. Two different O_2 gas mixtures (used as the carrier gas) were bubbled through ethylbenzene. The first had a stoichiometric amount of O_2 (0.5 mol of O_2 to 1.0 mol of ethylbenzene, balance helium), and the second was air (roughly 25 times excess of O_2). Both were made to flow through the reactor at 20 (or 30) mL/min, resulting in a 1.03*e*-5 (or 1.54*e*-5) mol/min reactant flow. A gas chromatograph equipped with a TCD online and a gas chromatograph/mass spectrometer (Hewlett–Packard Model 5890 Series II chromatograph with a Hewlett–Packard Model 5971 mass selective detector) with a sample loop were used to analyze the products. Each reaction was run for 12 to 16 h.

III. RESULTS

A. Structural Studies

The XRD data from the initial stages of Na-OL-1 formation are shown in Fig. 4 for the microwave sample and Fig. 5 for the conventional sample. The peaks at 7.0 and 3.5 Å are due to Na-OL-1, and the peak at 4.6 Å is due to a layered manganese oxide hydroxide, feitknechtite. Percentages of relative intensity of the main peak of feitknechtite (4.6 Å) to Na-OL-1 (7.0 Å) are shown in Table 1 for samples taken at 1, 2, and 3 h (the zero-hour sample has no Na-OL-1 peak). It can be seen that much less feitknechtite is produced in the microwave-irradiated samples.

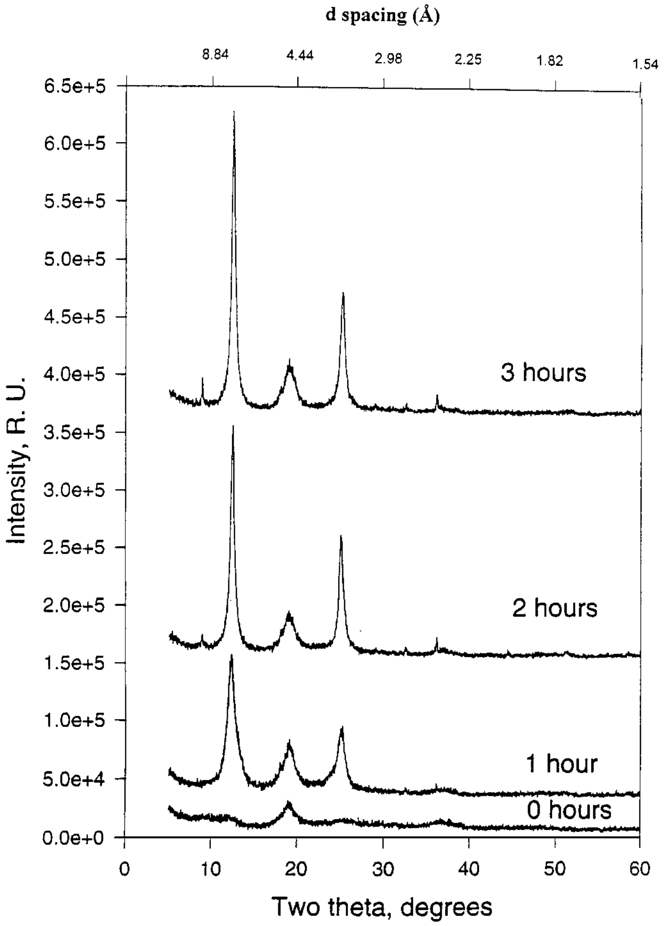

FIG. 4. X-ray diffraction data for the initial formation of Na-OL-1 at 0, 1, 2, and 3 h with microwave heating.

Typical XRD data for fully formed Na-OL-1, Mg-OL-1, and OMS-1 samples prepared by microwave or conventional heating are shown in Fig. 6 (where the TAON, theoretical average oxidation number, is 3.45). Both methods of heating produce similar results when the TAON is 3.45. However, when the synthesis was performed with a TAON of 3.3 there were reduced manganese oxide phases in the final product of the conventionally heated material, and when a TAON of greater than 3.45 was used crystallization of the Na-OL-1 was poor for all samples. A high-resolution, long-term scan of OMS-1 prepared with a TAON of 3.45 for all methods of heating (including the results from the total microwave synthesis) can be found in Fig. 7. Other variables of this synthesis were explored, and have been previously discussed (17).

TABLE 1

Formation of Na-OL-1: Percentage Intensity of the Main Peak of Feitknechtite (F) (4.6 Å) to the Main Peak of Na-OL-1 (O) (7.0 Å) during Aging

	Relative intensity (% F/O)	
Time (h)	Microwave sample	Conventional sample
1	33	61
2	16	68
3	15	65

B. *Elemental Analysis and Average Oxidation Number of Manganese*

The results of the AA, ICP, and titration experiments for the Na-OL-1 and OMS-1 samples with a TAON of 3.3 are shown in Table 2, and those for the OMS-1 samples with a TAON of 3.45 (including the material synthesized by the total microwave synthesis) are shown in Table 3. Proposed formulas (based on approximate molar masses of 115 g/mol Mn for the Na-OL-1 samples, and 105 g/mol Mn for the OMS-1 samples), Mg : Mn ratios, Na : Mn ratios, and average oxidation number for manganese are all presented. The approximate masses per mole of Mn all fall between 105 and 120, by titration and AA, with Na-OL-1 being closer to 115 and the OMS-1 being about 107. It

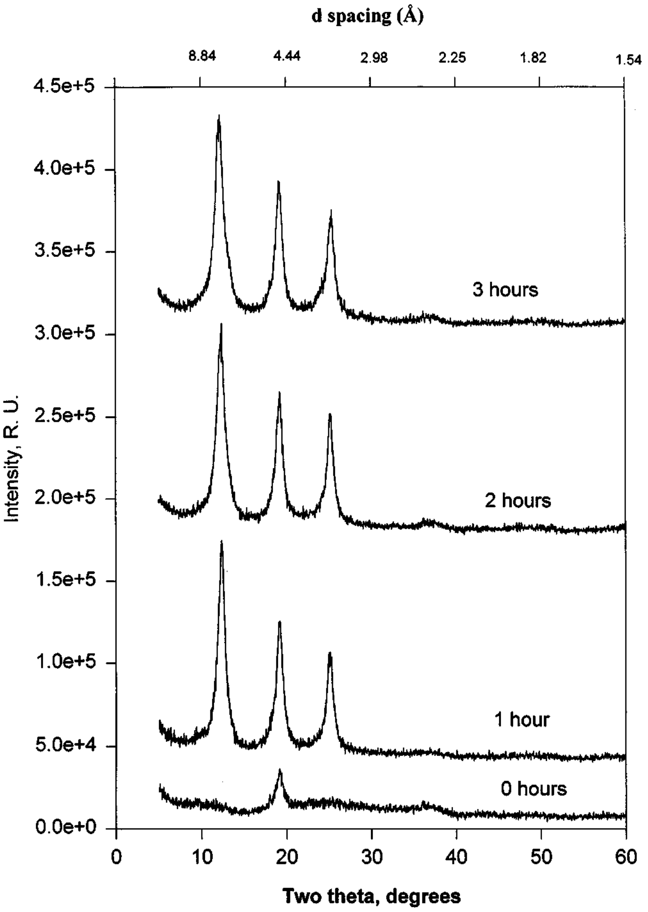

FIG. 5. X-ray diffraction data for the initial formation of Na-OL-1 at 0, 1, 2, and 3 h with conventional heating.

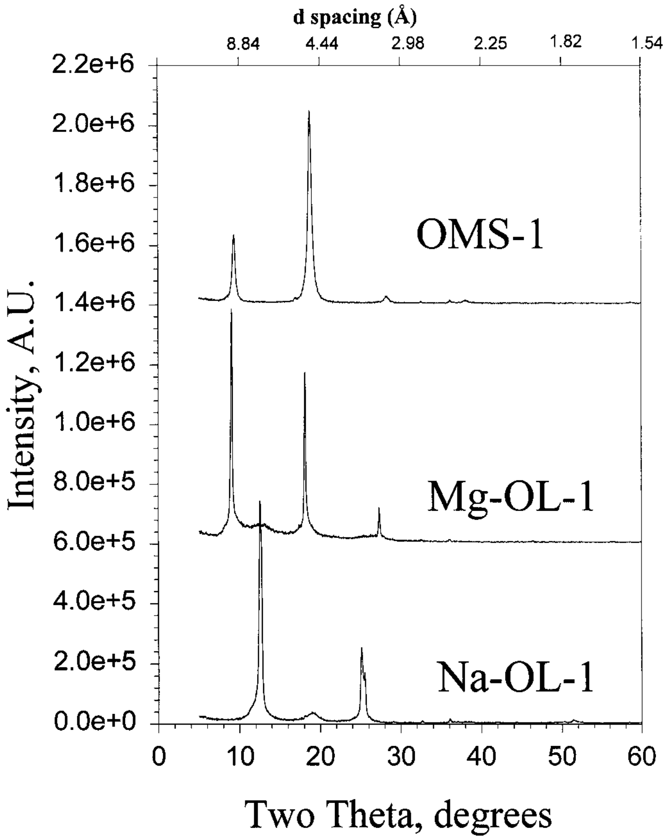

FIG. 6. Typical X-ray diffraction patterns of Na-OL-1, Mg-OL-1, and OMS-1.

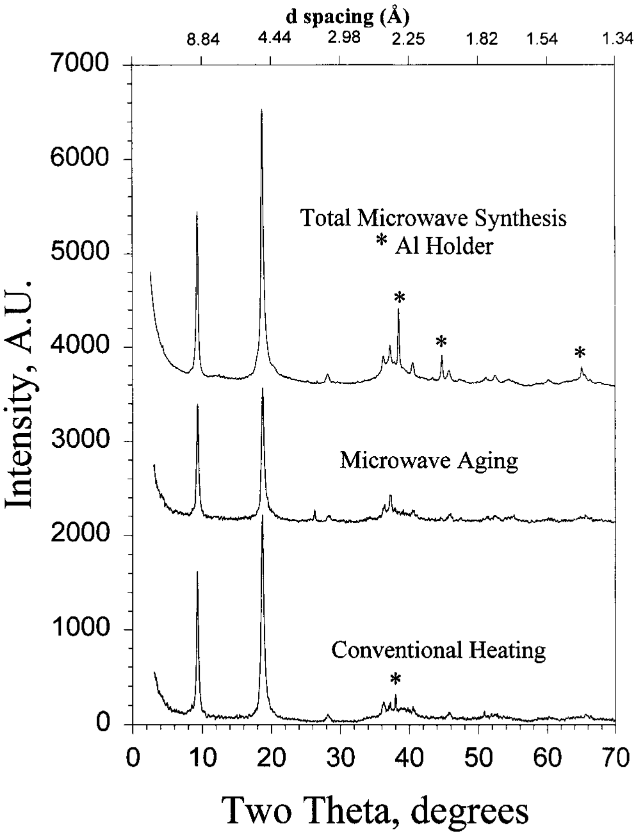

FIG. 7. Long-scan X-ray diffraction data for OMS-1 prepared using conventional heating, microwave aging, and the total microwave synthesis.

is expected that the samples contain varying amounts of water of hydration. The average oxidation number for the microwave-aged sample with a TAON of 3.3 was calculated to be an average of 0.20 unit higher than those of the conventionally prepared samples (3.46 and 3.66 for conventional heating and microwave aging), and the samples with a TAON of 3.45 were seen to all be about the same (3.58, 3.61, 3.57 for conventional heating, microwave aging, and total microwave heating respectively). The Mg : Mn ratio is higher in the microwave-aged samples with a TAON of 3.3 than in the conventionally heated samples. When the samples are prepared with a TAON of 3.45, the Mg : Mn ratios of the conventionally heated samples are higher than those of the microwave-aged material.

C. Thermal Analysis

Samples were subjected to thermal analysis by TGA. The results for the microwave and conventionally prepared samples show similar trends. See Figs. 8, 9, and 10 for the results of the analysis on Na-OL-1, Mg-OL-1, and OMS-1 samples,

TABLE 2

Elemental Analysis of Samples Prepared with a TAON of 3.3 for Mn: Average Oxidation Number of Manganese (AON), Mg : Mn and Mn : Na Molar Ratios, and Proposed Formula[a]

Sample	AON for Mn (±0.02)	Mg : Mn (ICP)	Na : Mn (AA)	Proposed formula[b]
OL-1, CV	3.41	0.206	0.23	$Na_{0.33}Mg_{0.30}Mn^{II}_{0.43}Mn^{IV}_{1.0}O_{2.86} \cdot xH_2O$
OL-1, MW	3.62	0.231	0.21	$Na_{0.26}Mg_{0.28}Mn^{II}_{0.23}Mn^{IV}_{1.0}O_{2.64} \cdot xH_2O$
OMS-1, CV	3.46	0.262	9.7*e*-3	$Mg_{0.36}Mn^{II}_{0.37}Mn^{IV}_{1.0}O_{2.74} \cdot xH_2O$
OMS-1, MW	3.66	0.283	5.9*e*-3	$Mg_{0.34}Mn^{II}_{0.20}Mn^{IV}_{1.0}O_{2.53} \cdot xH_2O$

[a] MW = microwave-aged samples, CV = conventionally heated samples, TAON = theoretical average oxidation number, ICP = inductively coupled plasma, AA = atomic absorption.

[b] $x = 1.0$ to 2.0.

TABLE 3

Elemental Analysis of Samples Prepared with a TAON of 3.45 for Mn: Average Oxidation Number of Manganese (AON), Mg : Mn for Bulk and Surface, and Proposed Formula

Sample	AON for Mn (±0.02)	Mg : Mn (ICP)	Mg : Mn (Auger)	Proposed formula[a]
OMS-1, CV	3.58	0.342	0.49	$Mg_{0.44}Mn^{II}_{0.266}Mn^{IV}_{1.00}O_{2.70} \cdot xH_2O$
OMS-1, MW aged	3.61	0.260	0.20	$Mg_{0.32}Mn^{II}_{0.242}Mn^{IV}_{1.00}O_{2.57} \cdot xH_2O$
OMS-1, total MW synthesis (17)	3.57	0.285	0.27	$Mg_{0.36}Mn^{II}_{0.274}Mn^{IV}_{1.00}O_{2.64} \cdot xH_2O$

[a] $x = 1.0$ to 2.0.

respectively. The Na-OL-1 samples lose approximately 8% of their mass at 30–110°C. There is a second loss of weight from 250 to 300°C, which accounts for about 5% percent in mass, then a minor weight loss at 525°C (less than 2%), and more at 750°C undetermined amount). The conventionally heated Mg-OL-1 sample shows a similar trend, with a decrease in mass at 100°C of 8%, then a second more gradual decrease of about 9% from 120 to 375°C. There then is a sharp loss at 535°C (of about 4%) and another transition at 700°C. The microwave-aged Mg-OL-1 has the same trend, but the mass losses are broader, as seen from the derivative peaks in Fig. 9. The OMS-1 samples show an initial loss of water from room temperature to 100°C of less than 3%, then two much sharper transitions centered at 275 and 325°C with a loss of 10% mass. At 550°C both samples have a sharp mass loss of about 3%, and then start losing mass again at 700°C.

Differential scanning calorimetry studies of the OMS-1 samples heated either conventionally or with microwaves show the same heat flow patterns (see Fig. 11). There is one major endotherm centered at 370°C for both of the samples, with the onset of heat flow starting at 350°C. There is also an exotherm with an onset at 631°C for both samples.

D. *Microscopy*

SEM images revealed platelike morphology for the Na-OL-1 samples and a mixture of platelike and fibrous morphology for the OMS-1 samples. Figure 12 shows the results of the SEM studies of the microwave-aged, conventionally heated, and total microwave-synthesized OMS-1 samples.

E. *Diffuse Reflectance Infrared Spectroscopy*

Reflectance IR spectra of the OMS-1 samples prepared using conventional and microwave methods showed no differences. Figure 13 shows the results of the far-IR experiments, and compares the microwave-aged, conventionally heated, and total microwave-synthesized OMS-1 samples. There are absorbance peaks at 546, 500, and 460 cm^{-1}.

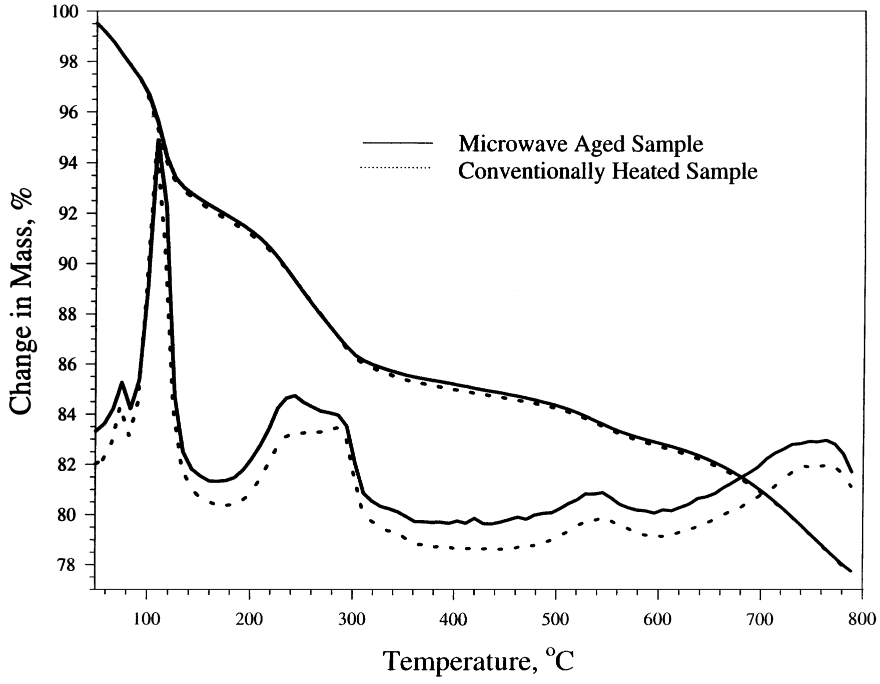

FIG. 8. TGA data and derivatives for Na-OL-1 prepared using microwave and conventional synthesis.

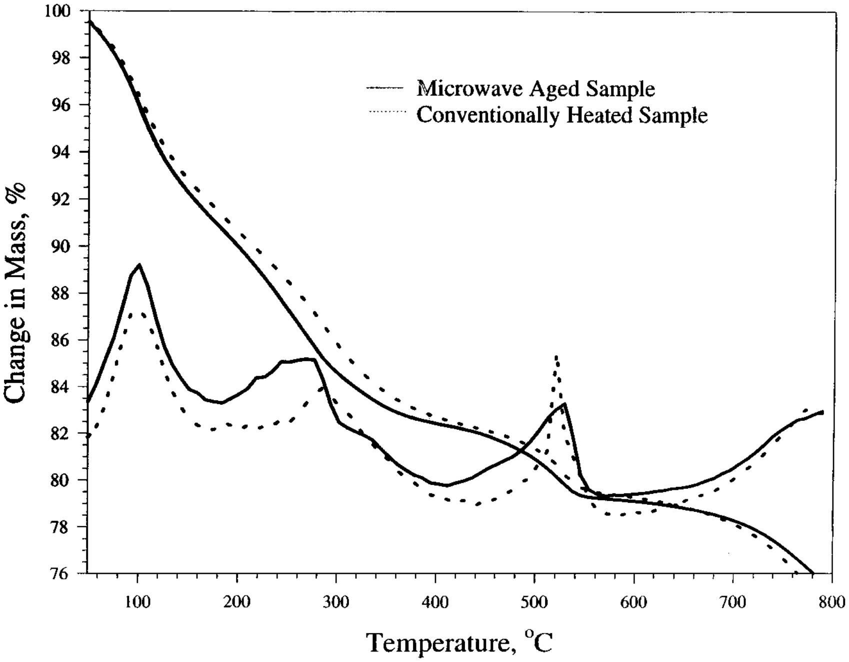

FIG. 9. TGA data and derivatives for Mg-OL-1 prepared using microwave and conventional synthesis.

F. Surface Area Measurements

The surface areas of the OMS-1 samples were measured and compared with those of the sample prepared by total microwave synthesis methods. The conventionally heated material has a surface area of 27 m^2/g and the microwave-aged material has a surface area of 40 m^2/g. These results are summarized later in Table 5.

G. Auger Spectroscopy

Auger electron spectrometry was used to look at surface species. For the microwave-aged OMS-1 samples the following elements and their corresponding atomic percentages were detected: Mn (37.2%), O (55.2%), Mg (7.5%), K (0.1%). For the conventionally synthesized OMS-1 samples the following elements and their corresponding atomic

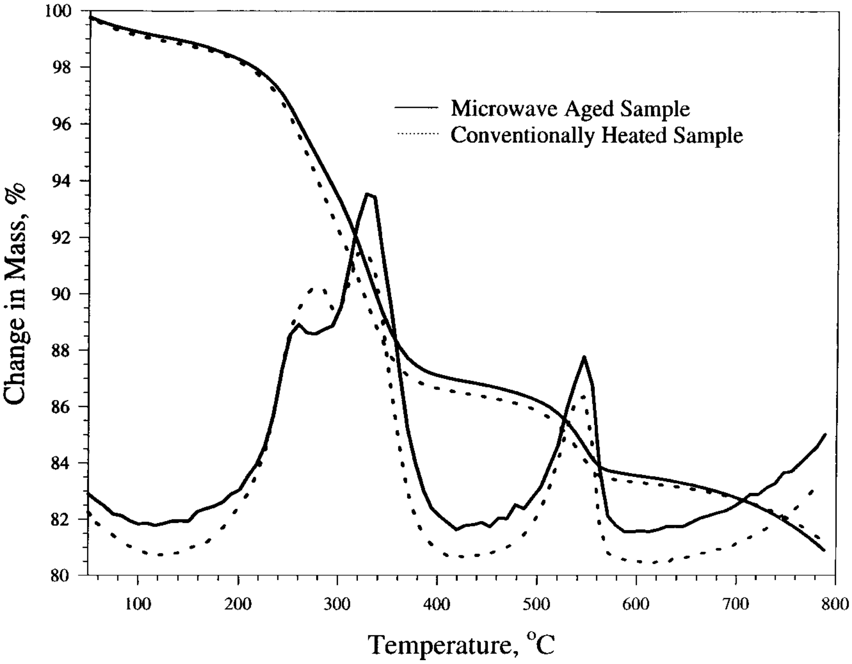

FIG. 10. TGA data and derivatives for OMS-1 prepared using microwave and conventional synthesis.

TABLE 4

Catalytic Data: Conversion of Ethylbenzene (EB) to Styrene (ST) Using OMS-1 Samples Prepared by Different Synthetic Methods[a]

Sample	Using stoichiometric O_2 Conversion of EB (%)	Selectivity to ST (%)	Yield (%)	Using excess O_2 Conversion of EB (%)	Selectivity to ST (%)	Yield (%)
Conventional heating	29	29	8.4	14	60[b]	8[b]
Microwave aging	27	41	11	24	47	11
Total microwave heating	16	62	9.9	48	23	11
Total microwave heating (30 mL/min)	28	42	12	35	28	9.8

[a] Flow rate is 20 mL/min unless noted. Conversion is ±5%, selectivity ±9%.

[b] Erratic selectivity (±20%).

percentages were detected: Mn (30.9%), O (52.6%), Mg (15.6%), C (0.9%). This compares to the sample prepared using the total microwave synthesis of OMS-1 with the following elements and their corresponding atomic percentages: Mn (34.3%), O (53.6%), Mg (9.3%), C (2.6%), and Cl (0.2%).

H. Catalytic Activity

The OMS-1 samples prepared to have a TAON of 3.45 were used to convert ethylbenzene to styrene. Samples prepared using conventional heating, microwave aging, and total microwave heating were used. Experiments were conducted at 300°C, under both stoichiometric and excess oxygen (air) conditions. The oxygen/ethylbenzene gas mixture was passed through the system using no catalyst and with only glass-wool plugs. In both cases there was no conversion of the ethylbenzene. There may have been condensation of styrene or polystyrene in the lines to the gas chromatograph due to adsorption even though the line was heated yielding lower selectivities than true values. The conversion data after steady state was reached (less than 90 min for stoichiometric experiments and 5 h for experiments using excess oxygen in which CO_2 is the primary product) for all the experiments can be found in Table 4. The conversion of ethylbenzene and the yield of styrene, normalized to the surface area, can be found in Table 5.

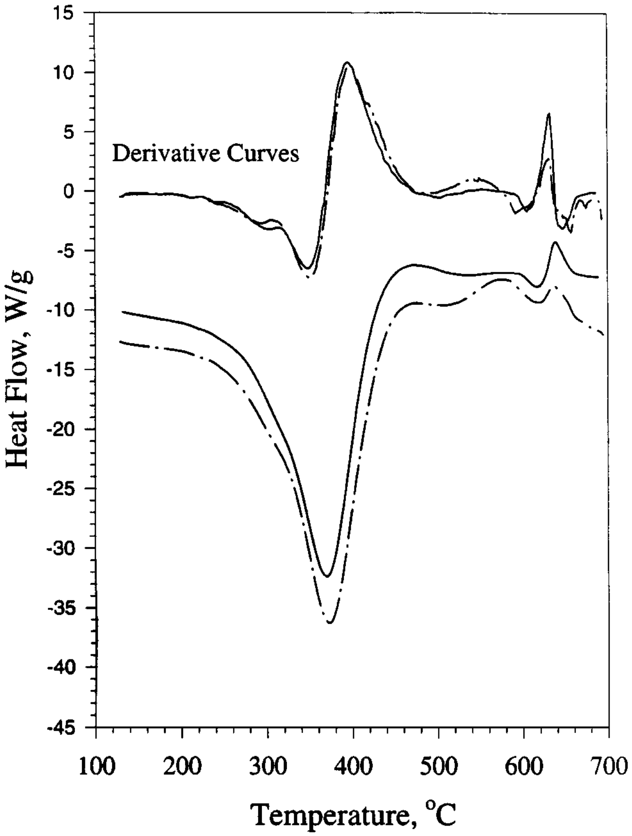

FIG. 11. DSC data and derivatives for OMS-1 prepared using microwave (solid line) and conventional synthesis (dashed line).

Using a flow rate of 20 mL/min of the ethylbenzene gas mixture with stoichiometric oxygen, the conventionally

TABLE 5

Surface Areas and Aereal Rates: Conversion of Ethylbenzene (EB) to Styrene (ST) Using OMS-1 Samples Normalized to Surface Area[a]

Sample	Surface area (m^2/g)	Aereal rate (× *e*-6 mol min^{-1} m^{-2}) Using stoichiometric O_2 Aereal rate of EB	Yield of ST	Using excess O_2 Aereal rate of EB	Yield of ST
Conventional heating	27	5.6	0.87	2.7	0.87
Microwave aging	40	3.5	1.4	3.1	1.5
Total microwave heating	48	1.7	1.1	5.2	1.2
Total microwave heating (30 mL/min)	48	4.5	1.9	5.6	1.6

[a] Twenty milligrams of sample was used in each run, and the flow rate was 20 mL/min unless noted.

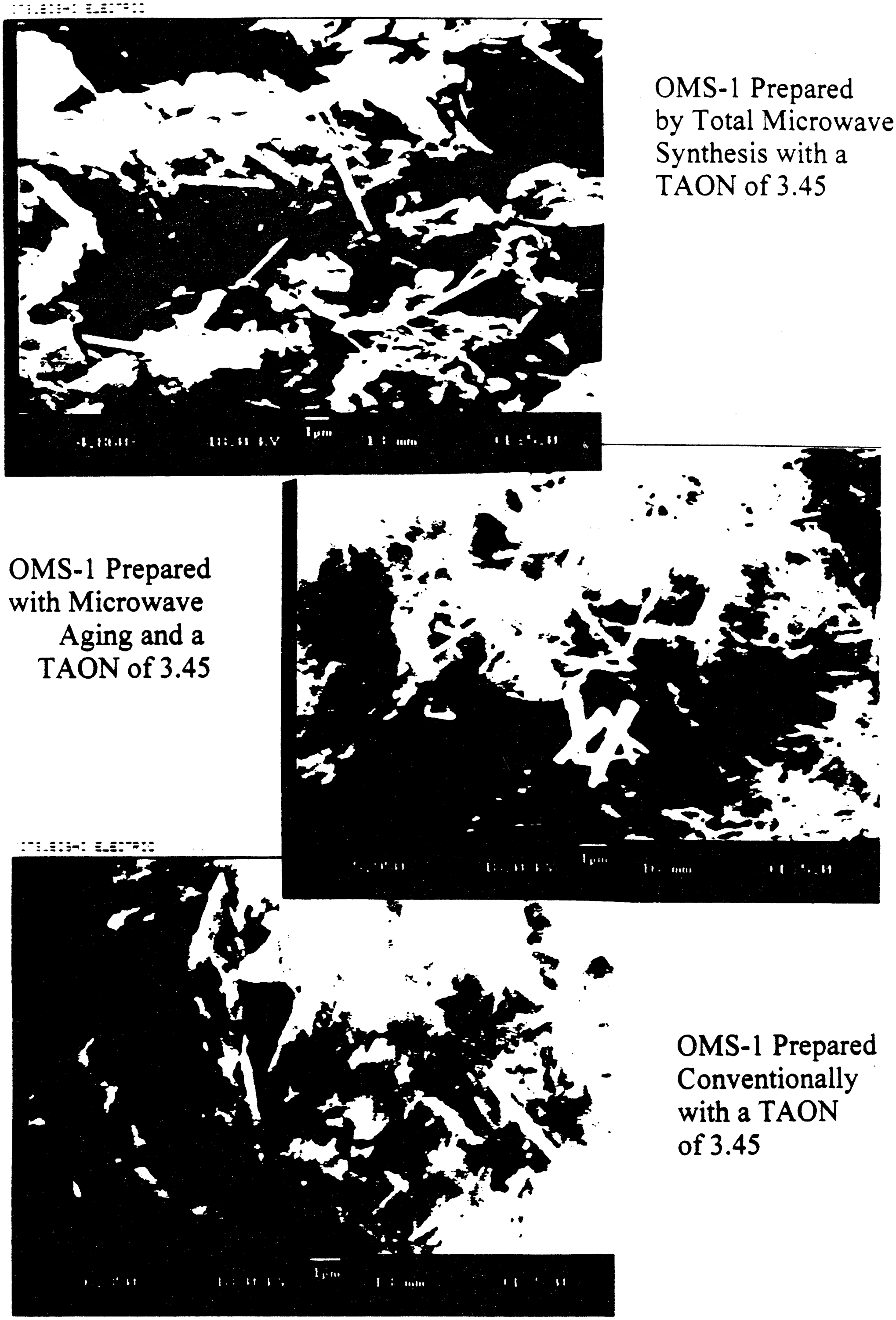

FIG. 12. SEM images for OMS-1 prepared using conventional heating, microwave aging, and the total microwave synthesis.

heated OMS-1 converted 29% of the ethylbenzene, with a selectivity of 29% to styrene, and an aereal rate of 5.6*e*-6 mol min^{-1} m^{-2}. The OMS-1 prepared using the microwave aging method showed a conversion of 27%, a selectivity to styrene of 41%, and an aereal rate of 3.5*e*-6 mol min^{-1} m^{-2}. The OMS-1 prepared using the total microwave heating method showed a conversion of 16%, a selectivity to styrene of 62%, and an aereal rate of 1.7*e*-6 mol min^{-1} m^{-2}.

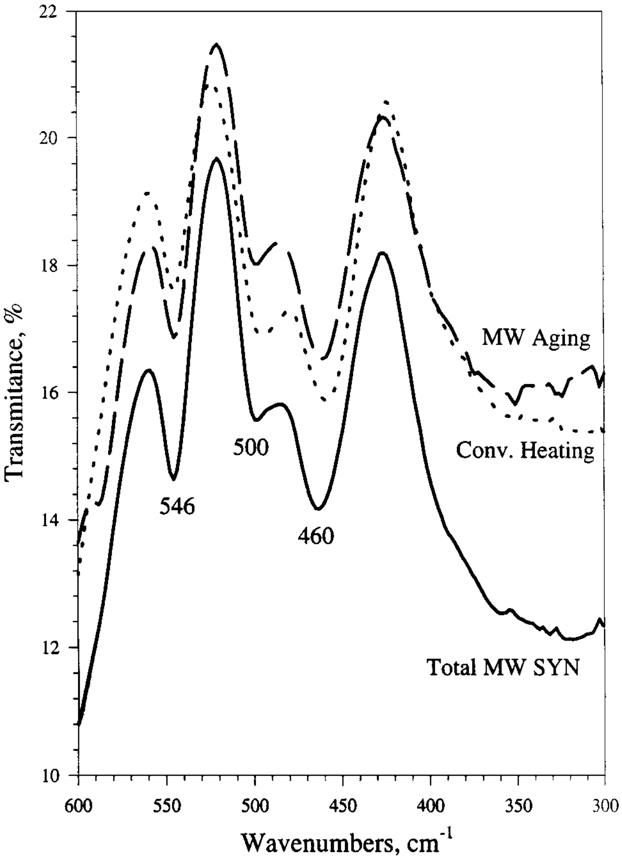

FIG. 13. Reflectance IR data for OMS-1 prepared using conventional heating, microwave aging, and the total microwave synthesis.

For the OMS-1 prepared using the total microwave heating method with a flow rate of 30 mL/min, the conversion of ethylbenzene is 28%, the selectivity to styrene is 42% and an aereal rate of 4.5*e*-6 mol min^{-1} m^{-2} was obtained.

For the experiments using excess oxygen the following results were obtained. The conventionally heated OMS-1 converted 14% of the ethylbenzene, with an erratic selectivity of 40–70% to styrene and an areal rate of 2.7*e*-6 mol min^{-1} m^{-2}. The OMS-1 prepared using the microwave aging method showed a conversion of 24%, a selectivity to styrene of 47%, and an areal rate of 3.1*e*-6 mol min^{-1} m^{-2}. The OMS-1 prepared using the total microwave heating method showed a conversion of 48%, a selectivity to styrene of 23% and an areal rate of 5.2e-6 mol min^{-1} m^{-2}.

IV. DISCUSSION

A. Structural Analysis

The manner in which Na-OL-1 is initially formed in the microwave oven suggests that the development of the layered structure proceeds along the same pathway, but faster in a microwave field than in the conventionally heated system. Much less feitknechtite appears in the X-ray patterns of the microwave samples (Fig. 4) than in the conventionally prepared samples (Fig. 5), while Mg-OL-1 starts to form at this stage, as opposed to none being formed when using conventional heating. The small sharp peak at $2\theta = 9.5°$ in Fig. 4 shows that Mg-OL-1 forms in the microwave-heated sample before ion exchange. This peak is missing in the conventionally heated sample. It could be that microwaves allow more dissolution of reagents (manganese and magnesium hydroxides), inhibiting the formation of feitknechtite and hydroxides of Mg and Mn. In fact, the presence of Mg-OL-1 in the initial stages of the synthesis strongly suggests that Mg^{2+} exists in solution, even under these very basic conditions. Supporting this is the elemental analysis, which shows more Mg and less Na in the Na-OL-1 sample prepared using microwave aging. Microwave heating has been researched extensively to digest metal oxide samples because of the fast rate of digestion and the efficiency at which it occurs (19). This effect on the solubility of reagents suggests that coprecipitation reactions would proceed differently in the presence of a microwave field.

We have recently reported details of Mg^{2+} substitution in the framework of OMS-1 (24). It is possible from analytical data of Table 2 that enhanced Mg^{2+} content for the microwave materials leads to more framework Mg^{2+} incorporation. More experiments would be needed to determine whether this Mg^{2+} incorporation is aided by microwave heating.

Figure 6 shows typical XRD patterns for fully developed Na-OL-1, Mg-OL-1, and OMS-1. The Na-OL-1 interlayer distance is assigned to the peak at 7.0 Å, and, after ion exchange to Mg-OL-1, the layers open up to 10.1 Å. After hydrothermal treatment, the layers contract slightly to 9.8 Å for the tunnel formation. The XRD results of the OMS-1 prepared by microwave aging and conventional heating are similar when the synthesis uses a TAON of 3.45. However, when the TAON is reduced to 3.3, the conventionally heated material shows minor amounts of the crystallized reduced spinel phase. It is unclear if this is Mn_3O_4 or $MgMn_2O_4$, but is most likely a combination of the two.

From the elemental analysis and oxidation number data, it can be seen that the microwave-aged samples with a TAON of 3.3 have a higher average oxidation number than do the conventionally heated samples (3.66 as compared with 3.46 for the conventionally heated material). The high AON of the microwave-aged samples is related to the absence of the formation of the stable lower oxidation states, Mn_3O_4 and Mn_2O_3, whereas the presence of reduced phases in the conventionally heated samples lowers its AON. That the microwave-aged samples do not show evidence of a reduced phase even at lower TAON (3.3) is probably related to the increased dissolution of manganese hydroxide phases in the initial formation of Na-OL-1, where less

MnO(OH) (feitknechtite) is seen in the microwave-aged sample. With less MnO(OH) formed, the lower oxidation impurities can be avoided. Also, it is known that microwave heating causes the rapid dissolution of mineral ores (19). In fact, microwave digestion of mineral samples has long been used in analytical laboratories because of the quantitative, fast dissolution of normally difficult-to-dissolve materials. When synthesized to have a TAON of 3.45, the average oxidation numbers of the microwave-aged (3.61) and conventionally heated (3.58) OMS-1 samples have approximately the same average oxidation number.

The results from the IR experiments show the expected pattern for synthetic todorokite (OMS-1) (20). There have been three absorption bands associated with this manganese oxide at 546, 500, and 460 cm^{-1}.

B. Thermal Stability

The TGA data of both the microwave-aged and conventionally heated samples showed the same trends. The Na-OL-1 samples sustain a mass loss from 100 to 130°C of about 8%. This is also true for the Mg-OL-1 samples. The OL-1 materials (both Mg and Na) show mass losses at 200–290°C, with the Mg-OL-1 mass loss being a slower one. From 300 to 400°C both layered materials are fairly stable. The first weight loss is attributed to physisorbed water, and the second is most likely chemisorbed water inside or outside the tunnels, probably in the form of magnesium and manganese hydroxides. A subsequent mass loss of 2–5% can be attributed to the loss of oxygen. Studies performed earlier (17) showed that this mass loss is delayed by 100°C in an O_2 atmosphere. At $>700°\text{C}$ there is another mass loss also associated with oxygen. At this temperature the material has been reduced to MnO.

The OMS-1 samples show a major loss from 210 to 350°C in the TGA experiments. Samples heated in air at 420°C for 8 h showed XRD reflections corresponding to OMS-1. The first reflection at 9.5-Å *d* spacing is barely detectable, the second reflection at 4.7 Å is still strong and sharp, and the other reflections are broad, but have retained their original intensity and appear to have shifted slightly to lower *d* spacings. Although there needs to be a careful investigation of the lattice parameters, it would appear that the tunnel structure has collapsed, but sheets of manganese octahedra are still intact. After heating to 545°C in N_2, the microwave-aged sample loses about 4% mass and is reduced to Mn_3O_4 as seen from the XRD pattern, as is appropriate for its mass loss. The same process occurs for the conventionally heated material. The losses are the same in O_2, but delayed to 639°C for the microwave sample, and 638°C for the conventionally prepared sample, indicating that it is oxygen lost at 545°C and that there is subsequent reduction to the spinel. At 700°C a second oxygen loss is noted, and when the sample is heated to 900°C for 4 h, crystalline MnO is observed.

C. Surface Characteristics

The surface characteristics of the OMS-1 materials synthesized with a TAON of 3.45 were investigated, and will be compared with that which was synthesized using total microwave synthesis. The morphologies of the materials were observed using SEM, and there were increasing amounts of fibrous material when the material was treated with microwave radiation. SEM data clearly show a mixture of plate and fibrous morphologies in all of the OMS-1 samples that were studied. However, the degree to which each of the two types was present increased with increasing exposure to microwave radiation. Previous SEM studies of conventionally heated Mg-OMS-1 have shown that plate morphologies were dominant in conventionally prepared material (21). The material synthesized by Golden *et al.* (22) was reported to have single fibers growing from a central plate, as seen by TEM. From the SEM data alone it would appear that there is not complete conversion of Mg-OL-1, presumably the platelike material, to OMS-1, the fibrous material. However, the XRD patterns do show a shift in the main peak from 10.1 to 9.5 for both conventionally and microwave-prepared samples. One possible explanation is that as the tunnels are formed, the layers contract as they link together, and with complete formation of the three-dimensional linkage the crystals become able to free themselves from the surface of the mother layers, and then appear as free fibers. This happens to a greater extent in the microwave-radiated samples.

As the tunnel formation increases, it also appears that the surface area increases. The BET surface area was measured to be 27 m^2/g for the conventionally heated sample, 40 m^2/g for the microwave-aged material, and 48 m^2/g for the OMS-1 prepared using total microwave synthesis. Auger data provide the most important indicator of the changes that can be affected using microwave radiation. Very different amounts of surface species were encountered on the surface of the OMS-1 catalysts (refer to Table 3). With a Mg : Mn atomic ratio of 0.49, the conventionally heated catalyst surface is strikingly different from that of the microwave-radiated samples. The microwave-irradiated samples had surface concentrations of Mg that were very similar to the bulk measurements done using ICP. This could be related to the increased crystallinity of the microwave-irradiated samples. With the microwave/material interaction, there could be a dissolution solution mechanism that allows “cleaner” precipitation and crystal growth of materials, leading to a surface that is different from that of the material prepared via conventional heating.

D. Catalysis Studies

Many significant trends are noted in the reaction of ethylbenzene to styrene. The deactivation periods of the experiments conducted with excess oxygen were all much longer than those of experiments conducted using stoichiometric oxygen. Stoichiometric samples reached steady state after an average of 30 min, except for the sample whose flow rate was 30 mL/min, in which case steady state was reached at an average of 90 min. For the samples using excess O_2, steady state was reached at an average of 5 h (conventional heating, microwave aging, and total microwave synthesis), and at 7 h for the sample run at 30 mL/min. During the deactivation period, the conversion of ethylbenzene is 100% while the selectivity to styrene is 0%, due to total oxidation of CO_2. The catalyst is reduced during this period.

Previous catalytic studies have shown a reversible loss of oxygen from 300 to 550°C. The oxidative properties of these catalysts are attributed to such reversible losses of oxygen. When excess oxygen is added, the system does not reach equilibrium to the preferred lower oxidation state as quickly, resulting in oxidation of ethylbenzene. The loss of the tunnel structure is prolonged in excess oxygen.

When stoichiometric oxygen is used, the conversion of ethylbenzene was highest for the samples produced using conventional heating (5.6), decreasing with microwave aging (3.5), and lowest with the samples produced using the total microwave heating method (1.7). This trend was reversed when an excess amount of air was used; i.e., the conventional heating had the lowest conversion (2.7), microwave aging was intermediate (3.1), and the total microwave heating method had the highest conversion (5.2). Other data suggest that the crystal formation of the OMS-1 prepared using the total microwave method is more advanced than in the other preparations. Adding extra oxygen probably promotes total oxidation. The conventionally prepared sample shows a reverse situation. With increased availability of oxygen the reversible oxygen sites cannot take advantage of the excess oxygen and conversion decreases. This leads to a selective, however low, conversion of ethylbenzene to styrene.

The lowest yields of styrene are from the samples prepared using conventional heating; the highest are from the sample run at 30 mL/min. Our data indicate that surface oxygen is important in the selective oxidation whereas excess oxygen promotes combustion.

V. CONCLUSIONS

From this study, it is evident that the crystallization kinetics of OMS-1 and OL-1 are faster in a microwave field, leading to better-formed crystals. This faster reaction also helps to avoid the formation of reduced phases, such as Mn_3O_4 and Mn_2O_3, and the microwave radiation has the effect of inhibiting the formation of magnesium hydroxide deposits on the surface. This leads to different catalytic properties that could possibly be tailored to suit the requirements of the reaction. Microwave heating can be a useful synthetic tool, because of time saved in normally lengthy reaction processes and in opening new pathways to novel surface structures.

ACKNOWLEDGMENTS

We are thankful to Mr. Guan-guang Xia for his assistance with the titration experiments, to Dr. Sang Hyun Park for help with the IR analysis, and to Dr. Francis Galasso, Dr. Jin Yun Wang, and Mr. Guan Guang Xia for helpful discussions. We thank the Joint NSF/EPRI Initiative on Microwave Induced Reactions, CTS 9413394, and E. I. DuPont de Nemours for support of this research.

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