Transformation of Cryptomelane-Type Manganese Oxides to Oxygen Deficient Systems by Microwave-Induced Oxygen Evolution

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Cryptomelane, a one-dimensional tunnel manganese oxide, is a good microwave absorber due to the effective coupling of MnO_2 with microwave irradiation. Transformations of cryptomelane were studied under microwave heating conditions at a frequency of 2.45 GHz. Microwave-induced oxygen evolution is fast and uniform, leading to the formation of oxygen deficient products. Microwave products in contrast to conventional heated products exhibited a strong tendency to adsorb water, and recombine with oxygen. The water adsorbed on the surface of materials is highly ordered. Oxygen recombination led to a recovery of the cryptomelane structure and a decrease in the level of the oxygen deficient phase. A reversible process during microwave-induced oxygen evolution and subsequent oxygen recombination is proposed.

Introduction

Microwave dielectric heating has been successfully used in the syntheses of many inorganic materials with considerable improvement in product quality and enhancement in processing rates.[1−14] In microwave irradiation, since heat is generated internally within materials, the heating is rapid and volumetric. The efficiency of coupling of materials with microwaves is determined by the dielectric properties (dielectric loss and dielectric constant) which are related to the compositions and structures of the materials. Therefore, selective heating is possible. The rapid, uniform, and selective heating by microwaves may not only accelerate the rates of reactions but also drive certain reactions to proceed in different ways. Therefore, different product distributions[3] or products with different phases and different properties may be produced.

Cryptomelane (α-MnO_2), a one-dimensional tunnel manganese oxide material consisting of 2 × 2 edge-shared MnO_6 units in which Mn^{4+} is dominant with minor amounts of Mn^{3+},[15−21] is a good microwave absorber due to the high efficiency of interaction between MnO_2 and microwaves.[22−24] In our previous study,[25] the formation of cryptomelane was accelerated by microwave heating, and a further phase transformation from cryptomelane to bixbyite (cubic Mn_2O_3), a CaF_2-type material with distorted edge-shared MnO_6 units,[26] was especially favored. Bixbyite emerged at a temperature (425 °C) that was much lower than that with conventional heating (above 600 °C), indicating that microwave-induced oxygen evolution is more rapid. In addition, the microwave products showed interesting properties in adsorption of water and oxygen.

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In this work, phase transformations of cryptomelane under microwave conditions have been studied. The main goal is to investigate microwave-induced oxygen evolution, oxygen recombination of microwave-prepared materials, and structural changes during oxygen release and recombination processes.

Experimental Section

Preparation. The procedure for preparing manganese oxides gel was the same as that described previously.[25] A solution of 0.15 M $KMnO_4$ was added to a solution of 0.05 M $C_4H_4O_4$ (maleic acid) while it was being stirred at room temperature. A dark brown gel was formed. The gel was exposed in air for 2 days, and then was heated at 110 °C for 2 days to remove water. Finally, calcination was carried out in either a microwave or a conventional furnace.

Microwave heating was carried out in a computerized microwave furnace (model 10-1300, MMT, Knoxville, TN) with a continuously variable power supply (maximum of 1.3 kW). A shielded K-type thermocouple with lead wire was used to measure and control the temperature. Inside the cavity, samples as fine black powders were put in alumina crucibles which were insulated by porous alumina brick. The thermocouple was inserted into the center of the sample through a hole drilled in the lid of the alumina brick enclosure. Each time, 15 g of manganese oxide gel was used in the microwave calcination.

Microwave samples MWT400, MWT600, and MWT650 were prepared by temperature-programmed microwave heating from room temperature to 400, 600, and 650 °C, respectively, at a heating rate of 10 °C/min without the samples being held at the final temperature. MWT425 was prepared under the same conditions except holding at 425 °C for 40 min. Sample MWP500 was prepared by power-programmed microwave heating from 0 to 500 W at a rate of 10 W/min, and holding at 500 W for 40 min. Conventional sample CVT750 was prepared by temperature-programmed heating from room temperature to 750 °C at a rate 10 °C/min and holding at 750 °C for 40 min. All samples were cooled to room temperature in air and then capped in glass bottles for analyses.

Characterization. X-ray diffraction (XRD) was carried out on a Scintag XDS 2000 diffractometer with CuKα radiation. The tube voltage was 45 kV with a current of 40 mA.

Thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 thermogravimetric analyzer (TA instrument). The heating rate was 10 °C/min with a carrier gas of N_2 or O_2. H_2O and O_2 during temperature-programmed desorption (TPD) in He at a rate of 10 °C/min were analyzed on a MKS-UTI PPT mass spectrometer.

Infrared (IR) spectra were recorded on a Nicolet Magna-IR System 750FT-IR spectrometer. Diffuse reflectance methods were employed with an MCT-B detector and a KBr beam splitter. For each sample, 200 scans and a resolution of 4 cm^{-1} were used.

Oxygen Recombination Reactions of As-Prepared Samples. Samples prepared by either microwave or conventional methods were treated in an O_2/N_2 mixture (partial O_2 pressure of 0.58 atm) at required temperatures on the TGA equipment. The amount of oxygen taken up was calculated by the weight increases of the TGA curves. The resultant products were determined by XRD, TGA, and IR.

Results

Characterization. Cryptomelane was synthesized by heating the amorphous gel at 425 °C for 40 min by both methods with identical XRD patterns (Figure 1a). On the basis of ICP-AES elemental analysis and oxidation state determination,[27] the composition of cryptomelane is given as $K_{0.1}MnO_{1.94}$. By conventional heating at 640 °C for 3 h, a new peak at 2.72 Å, the strongest peak of bixbyite, emerged and its intensity increased with prolonged calcination times or elevated temperatures. Traces b and c of Figure 1 are the XRD patterns of the conventional product prepared at 750 °C for 40 min (CVT750) and a pure bixbyite sample, respectively. This peak can also be observed in the product by microwave heating at 425 °C for 3 h.[25] As the microwave heating temperature was increased, products were formed with the relative intensities of two other peaks at 6.92 and 3.49 Å in addition to the intensity of the peak at 2.72 Å also increasing in contrast to the XRD pattern of cryptomelane. Traces d and e of Figure 1 are the XRD patterns of the microwave products prepared at 600 (MWT600) and 650 °C (MWT650), respectively. By further decomposition of cryptomelane by heating at a power of 500 W for 40 min, a product (MWP500) was obtained, whose three strongest XRD peaks were at 6.92, 3.49, and 2.72 Å with small peaks at 3.11 and 2.39 Å. The latter two are characteristic peaks for cryptomelane. Products of conventional heating at 640 °C for 14 h and 750 °C for 40 min, respectively, exhibited an increase in the intensity of the peak at 2.72 Å for bixbyite and a decrease in the intensity of the peaks for cryptomelane, however, without a consistent increase in the intensity of the peaks at 6.92 and 3.49 Å.

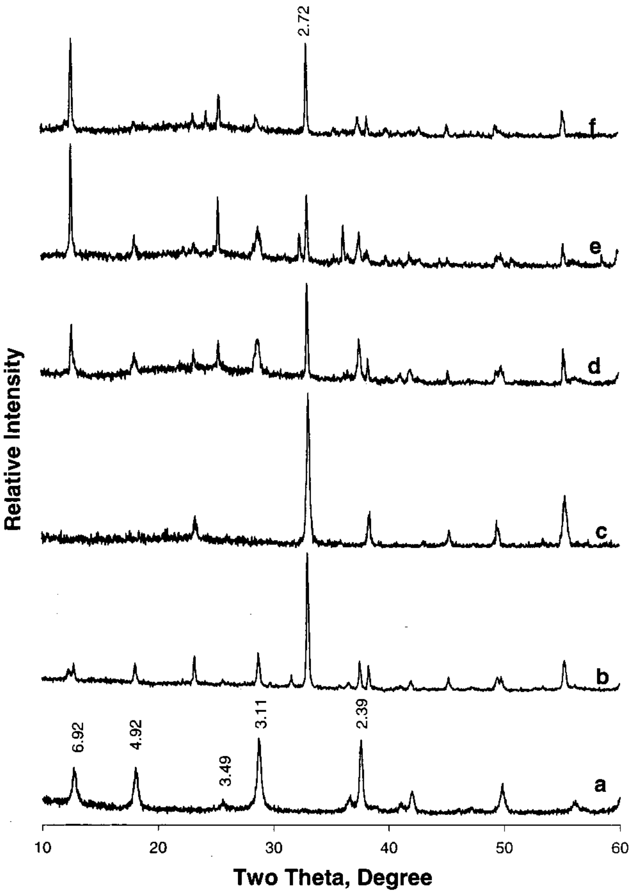

Figure 1. XRD patterns of (a) cryptomelane, (b) CVT750, (c) bixbyite, (d) MWT600, (e) MWT650, and (f) MWP500.

Four stepwise weight losses were observed in the TGA curve of cryptomelane in the temperature range of 100−900 °C when the reactions were performed in N_2 (Figure 2a). TPD-MS analysis demonstrated that water desorp-

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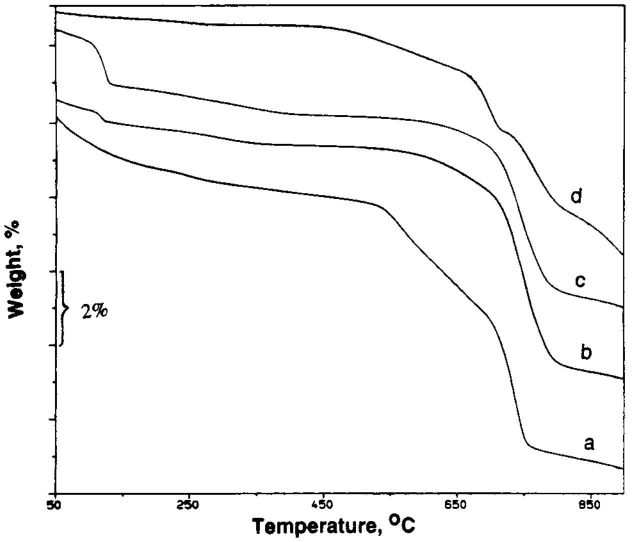

Figure 2. TGA results in N_2 for (a) cryptomelane, (b) MWT600, (c) MWT650, and (d) CVT750.

tion was finished below 350 °C. The three weight losses above 350 °C were due to oxygen evolution. The first step of oxygen loss occurred at 528−694 °C (2.8%), the second at 694−758 °C (3.4%), and the third at 758−900 °C (0.6%). In the TGA curve of sample MW600 (Figure 2b), the first step of oxygen loss was reduced to 1.6%, and the starting temperature increased to 544 °C in comparison to data for cryptomelane. As the microwave heating temperature was increased to 650 °C, the product (MWT650) exhibited a further reduced first oxygen loss (0.7%) and a higher starting temperature (615 °C) (Figure 2c).

The water loss for microwave products exhibited an interesting variation. The initial gel had the largest weight loss, occurring between 100 and 350 °C. As the microwave heating temperature was raised, the water loss in the TGA for these products was first reduced, and then increased for preparation temperatures above 600 °C. This indicated water in these samples was from different sources. The water content decrease was due to the removal of water from the initial gel, and the increase of the content of water for products prepared at temperatures above 600 °C was due to adsorption of water from the atmosphere. In addition, the amount of water loss for high-temperature products (>600 °C) increased with increases of the preparation temperature (MWT650, 1.2%; MWT600, 0.3%), occurring in a narrow temperature range from 100 to 130 °C.

The sample prepared conventionally at 750 °C (CVT750) exhibited a total amount of oxygen loss of about 5.5%. The TGA curve was complicated, in which weight losses due to oxygen evolution occurred from 450 to 900 °C with no distinguishable steps of oxygen loss. No increase in the amount of water loss between 100 and 130 °C was observed.

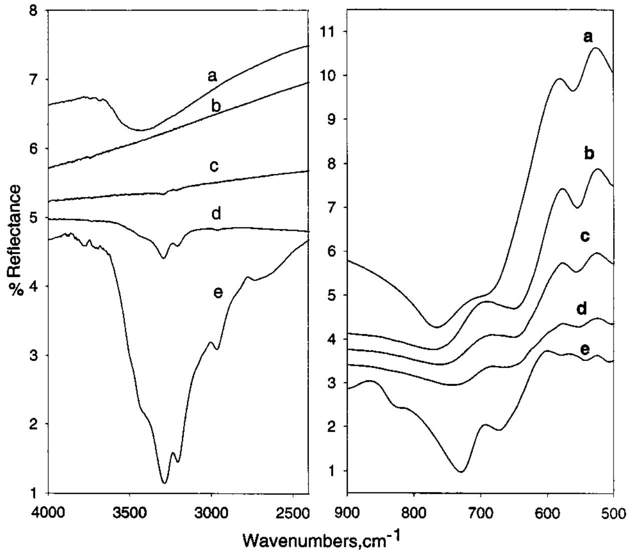

Figure 3. FTIR spectra of (a) MWT400, (b) cryptomelane, (c) MWT600, (d) MWT650, and (e) MWT500.

The trend for water content was further supported by IR results shown in Figure 3 (left). The initial gel (not shown in Figure 3) showed a large broad band in the region of 3500−2500 cm^{-1} and a strong band at 1600 cm^{-1}, because of the stretching vibration and bending vibration of hydroxyl groups in water.[25] When the preparation temperature was increased to 400 and 425 °C (Figure 3a,b), the intensity of this band was lowered and the band disappeared, respectively. When the microwave temperature was raised to 600 °C (Figure 3c), two small bands at 3293 and 3206 cm^{-1} appeared in the spectra of the products. The relative intensity of these bands increased with increases of the preparation temperature, which is consistent with the TGA results which show that more water was adsorbed by MWT650 than by MWT600. The shape of the water absorption bands was different from those of water in amorphous gels and poorly crystallized cryptomelane prepared at 400 °C (MWT400), indicating that the nature of these water molecules was different. No hydroxyl bands were observed for conventional products prepared at 750 °C (CVT750).

The right panel of Figure 3 shows the FTIR spectra in the diagnostic region of manganese oxide groups. A strong absorption band existed in the spectra of all samples in the region of 800−700 cm^{-1}, but with different peak positions and widths. For cryptomelane, MWT600, MWT650, and MWP500, this band appeared at 773, 763, 744, and 730 cm^{-1}, respectively.

Oxygen Treatment and Characterization of Resultant Products. The above samples were heated in a mixture of O_2 and N_2 (partial O_2 pressure of 0.58 atm) on the TGA instrument from 100 to 900 °C. The first parts of TGA curves were similar to those obtained in N_2 in the range of 100−420 °C, where weight loss of water was observed. After 425 °C, a weight increase occurred. Figure 4 shows that MWT650 achieved its maximum weight increase (1.3%) at 690 °C, and a quick weight loss due to evolution of oxygen subsequently started at 710 °C. Sample MWT650 had a weight gain that was larger than that of MWT600. Cryptomelane did not exhibit any weight increase during oxygen TGA; only weight losses of water and oxygen were observed. Conventional product CVT750 exhibited an oxygen gain of 0.2%.

The calcined samples were treated in oxygen (partial O_2 pressure of 0.58 atm) at 550 °C so oxygen recombination and corresponding structural changes could be studied. For sample MWT650, weight increases of 0.4 and 1.0% were achieved due to recombination of oxygen during a period of time of 10 min and 1 h, respectively.

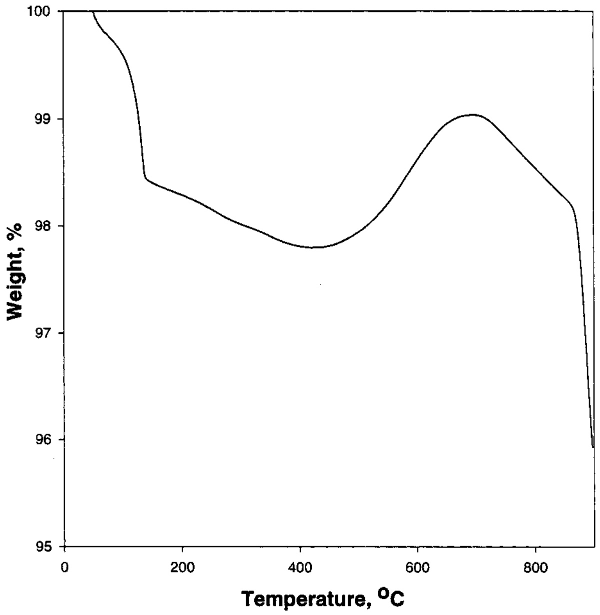

Figure 4. TGA curve of MWT650 in a mixture of O_2 and N_2 (partial O_2 pressure of 0.58 atm).

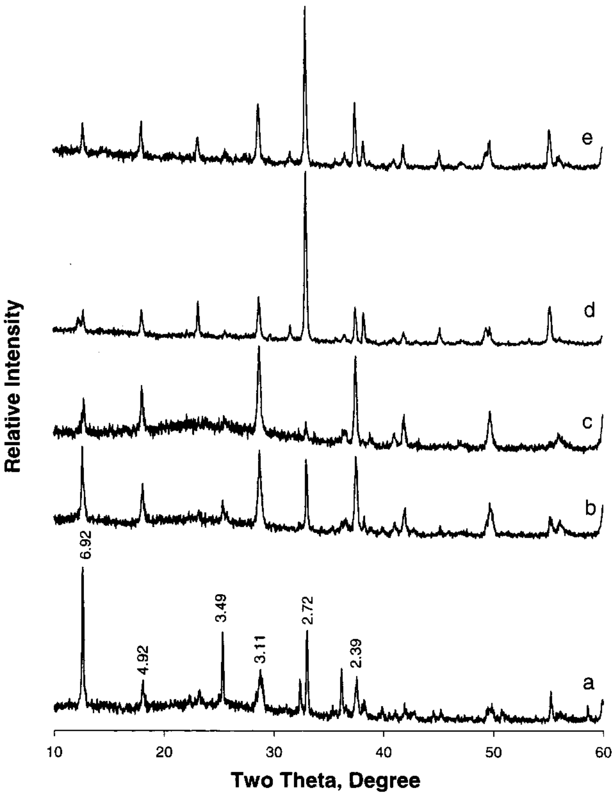

Figure 5. XRD patterns before and after oxygen treatment (partial O_2 pressure of 0.58 atm) at 550 °C: (a) MWT650 before treatment, (b) MWT650 after 10 min, (c) MWT650 after 1 h, (d) CVT750 before treatment, and (e) CVT750 after 1 h.

The corresponding XRD patterns are shown in traces b and c of Figure 5. The intensities of XRD peaks at 6.92, 3.49, and 2.72 Å, which had increased by microwave calcination at 650 °C, decreased after the oxygen treatment. The relative intensity and sharpness of the peaks at 3.11 and 2.39 Å (two of the basal XRD peaks for cryptomelane) were remarkably increased. A similar trend was observed with oxygen treatment of samples MWT600 and MWP500.

For the oxygen treatment products, a decrease in the amount of water loss in the temperature range of 100−130 °C was detected by TGA in N_2 atmosphere, as well as a decrease in the intensity of the hydroxyl absorption bands in the range of 3000−3300 cm^{-1} in the IR spectra. On the other hand, the amount of the first oxygen loss gradually increased with increases in the rate of oxygen uptake, and the starting temperature for oxygen loss was correspondingly decreased. By multiple step oxygen treatment, the product exhibited XRD patterns and TGA curves similar to those of cryptomelane originally synthesized at 425 °C.

Conventional samples CVT750 showed a small decrease in the relative intensity of the XRD peak at 2.72 Å for bixbyite under the same oxygen treatment conditions with less weight gain (<0.4%) (Figure 5e). Pure bixbyite exhibited almost no oxygen recombination even after prolonged oxygen treatment. No structural change of bixbyite was found by XRD or IR analyses.

Discussion

Properties of Microwave Heating Products. Oxygen evolution occurs with reduction of Mn^{4+}, leading to the formation of oxygen deficient products such as bixbyite (Mn_2O_3) and hausmannite (Mn_3O_4), when cryptomelane is heated at high temperatures.[15,28,29] Usually, cryptomelane is converted to bixbyite with heating in air at temperatures between 600 and 900 °C.[15,28,29] In our experiments, bixbyite was obtained by conventional heating at 640 °C for 3 h, and the amount increased with prolonged calcination times and elevated temperatures, which is consistent with literature results. In microwave calcination, oxygen deficient products were also obtained, recognized by the emergence of an additional XRD peak at 2.72 Å (the basal XRD peak of bixbyite). The average oxidation state of manganese decreased to 3.65 and 3.54 with microwave heating at 600 and 650 °C, respectively. The relative intensities of the other two peaks at 6.92 and 3.48 Å, which belong to the cryptomelane phase, were also increased along with that of the peak at 2.72 Å when the microwave calcination temperature was raised, and decreased during subsequent oxygen treatment. The basal XRD peaks at 3.11 and 2.39 Å for cryptomelane exhibited the reverse trend, concurrently. The consistent changes of these peaks suggest that bixbyite and cryptomelane exist in metastable states. The oxygen deficient phase is used to specifically refer to the microwave products in contrast to bixbyite which was formed in conventional syntheses.

The behavior of the microwave products in water adsorption and oxygen recombination is directly related to the oxygen deficient phase. The variation of the water content in these samples has been shown in Figure 3 (left). The nature of water can be resolved from the shapes and positions of hydroxyl stretching vibrational bands. The broad continuous band covering the 3500−2500 cm^{-1} region for the initial gel suggests a large variety of water types. The water can be removed by microwave heating at elevated temperatures. No hy-

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droxyl band was observed in the spectrum of cryptomelane synthesized at 425 °C. The reappearance of hydroxyl bands at 3293 and 3206 cm^{-1} for microwave products MWT600 and MWT650 is due to adsorption of water from the atmosphere as samples were exposed to air. The sharpness of these bands indicates that water molecules are uniformly distributed, located on single, crystallographic ordered sites, as suggested by Potter et al.[30] The equivalency of these water molecules can be further supported by the TGA results which show that water loss for microwave products MWT600 and MWT650 occurred in a temperature range (100−130 °C) that was much narrower than that of the initial gel (100−350 °C). The lower frequencies of these sharp bands in contrast to the isolated hydroxyl groups (usually above 3500 cm^{-1}) could be due to a decrease in the O−H bond strength by the interaction between water molecules and the surface of these materials.

Products with more oxygen deficient phase show a strong band in the Mn−O diagnostic region with increased sharpness and lowered frequency (Figure 3b, right) with respect to those of cryptomelane. Cryptomelane contains a broad distribution of Mn−O groups, due to the complexity of this structure. With microwave treatment, some type of oxygen species is uniformly released, as illustrated by TGA results (Figure 2), accompanied by a conversion of some manganese oxide species. This may contribute to the shifting and sharpening of the Mn−O band in the 800−700 cm^{-1} region.

The oxygen deficient phase has a strong tendency to trap oxygen and recover the cryptomelane structure. The weak broad peak at 3.11 Å present in the XRD pattern of the microwave product prepared at 650 °C (MWT650) clearly shows that the cryptomelane structure had partly collapsed. But after this sample was exposed to air at room temperature for 3 months, some changes were detected by XRD, IR, and TGA. The XRD peak at 3.11 Å grew sharper with an increased relative intensity. The amount of the first step of oxygen loss by TGA was increased with lower starting temperatures. This indicates that sample MWT650 had gained oxygen from air and partly recovered the precursor structure of cryptomelane even at room temperature. When the temperature or oxygen partial pressure is increased, the oxygen recombination process is accelerated. Larger amounts of oxygen are recombined; larger amounts of cryptomelane are recovered, and the more oxygen deficient phase decreased under such conditions. Microwave evolution of oxygen and the subsequent oxygen recombination are reversible. This process is shown in eq 1:

$$\text{cryptomelane} \underset{+\mathrm{O}}{\overset{-\mathrm{O}}{\rightleftarrows}} \text{oxygen deficient phase} \qquad (1)$$

Formation of Oxygen Deficient Products by Microwaves. The above results and analyses suggest that products with defect structures have been formed by microwave evolution of oxygen. For some metal oxides at high temperatures or low oxygen pressures, oxygen can escape from oxide surfaces into the atmosphere, leaving oxygen vacancies that are filled by electrons.[31] In the oxygen evolution of cryptomelane, electrons are captured by high-oxidation state manganese, forming lower-oxidation state products. This process is shown in eq 2:

$$\mathrm{Mn^{4+}} + \underset{\text{(lattice)}}{\mathrm{O^{2-}}} \xrightarrow{\text{MW oxygen evolution}} \mathrm{Mn^{3+}} + {}^{1}/_{2}\mathrm{O} + \underset{\text{(oxygen vacancy)}}{\mathrm{V_o}} \qquad (2)$$

Oxygen release from the cryptomelane lattice and oxygen uptake from the atmosphere may happen at the same time during both microwave heating and conventional heating in phase transformations of cryptomelane. During microwave heating, the microwave radiation interacts with materials immediately. The energy provided by microwaves enables evolution of certain oxygen species. Uptake of oxygen as an opposing process may not be favored. This may explain the rapid emergence of low-oxidation state products.

As the microwave heating temperature goes up, oxygen species in cryptomelane are released in a sequence from low-temperature oxygen to high-temperature oxygen. This is supported by our TGA results which show that the starting temperature for the first step of oxygen loss increased with the decrease of the amount of the first oxygen loss. These data suggest that certain oxygen species in cryptomelane have been uniformly released. The rapid and uniform evolution of oxygen possibly leads to the formation of oxygen vacancies in the products, but without destroying the basic skeleton of the parent cryptomelane structure. Thus, oxygen can be easily captured by the oxygen vacancies in the lattices, leading to the recovery of the cryptomelane structure. In this process, electrons transfer from manganese to oxygen atoms which have been trapped by oxygen vacancies from the atmosphere. This redox process is shown in eq 3:

$$\mathrm{Mn^{3+}} + \mathrm{O} + \underset{\text{(oxygen vacancy)}}{\mathrm{V_o}} \xrightarrow{\text{CV oxygen recombination}} \mathrm{Mn^{4+}} + \underset{\text{(lattice)}}{\mathrm{O^{2-}}} \qquad (3)$$

But during conventional (CV) heating, energy is transferred from an external source to the material, which is slower and less uniform than the direct interaction between material components and microwaves. In this case, the process of combination of oxygen from the atmosphere is more competitive with the process of releasing oxygen from the framework under conventional heating conditions than that under microwave irradiation. On the other hand, oxygen released from certain manganese oxide species can be accepted by others; i.e., oxygen can be transferred among manganese oxide species. These two factors could be responsible for the slow formation of bixbyite due to the retarded oxygen evolution. Higher calcination temperatures and longer times are required to obtain comparable amounts of released oxygen. Under these conditions, rearrangement of the framework structure may take place, leading to the formation of bixbyite, the more

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stable phase, with less oxygen vacancies. Thus, products prepared by conventional heating at 640 °C for 14 h and 750 °C for 40 min have a smaller tendency to adsorb water and recombine oxygen and a lower degree of recovery of cryptomelane.

Oxygen Variation and Phase Transformations. During transformations from an amorphous manganese oxide (AMO) gel to cryptomelane and from cryptomelane to bixbyite, oxygen combination and oxygen evolution exist as two competitive processes. AMO has more surface oxygen, which can be released from the gel at low temperatures (below 300 °C), as well as the decomposition of organic residues and removal of water. This is a weight decrease process.[25] Then with increases in temperature, a weight increase begins due to oxygen uptake from the atmosphere, along with oxygen rearrangement, leading to the formation of crystalline product (cryptomelane) in which almost all oxygen atoms are located in the lattice.[32] As the heating temperature continues to increase, the amounts of oxygen reach an equilibrium. This equilibrium can be retained in a certain temperature range with no obvious weight change, where products exhibit the cryptomelane structure.[25] After that, oxygen release from cryptomelane becomes dominant over oxygen combination, gradually forming lower oxidation state products (Mn_2O_3 bixbyite).

According to XRD, IR, and TGA results, we propose that phase transformations under microwave conditions are similar to the process described above which involves oxygen evolution, oxygen combination, and oxygen rearrangement. However, oxygen evolution is more uniform and faster, while oxygen combination and rearrangement steps are limited. This may account for the rapid formation of the metastable oxygen deficient products, showing a high affinity for H_2O, a strong tendency to recombine oxygen, and a great probability of recovering the cryptomelane structure. When these products were treated with oxygen, a weight increase is observed. Finally, equilibrium will be achieved with no obvious weight change when the cryptomelane structure is recovered.

Conclusions

Phase transformations of cryptomelane were accelerated by microwave heating. Microwave products, in contrast to conventionally heated products, exhibit interesting properties such as a high affinity for H_2O, a strong tendency to recombine oxygen, and easy recovery of the cryptomelane structure. Under microwave conditions, certain types of oxygen species are rapidly and uniformly released, leaving oxygen vacancies which are responsible for H_2O adsorption and oxygen recombination. With oxygen treatment, this part of oxygen can be recovered with recovery of the cryptomelane structure. Resultant products exhibit less water adsorption and oxygen recombination. The reversible process has been shown in eq 1:

$$\text{cryptomelane} \xrightleftharpoons[\text{(2) CV, }+\text{O}]{\text{(1) MW, }-\text{O}} \text{oxygen deficient phase}$$

In processes 1 and 2, oxidation and reduction reactions are involved, leading to a conversion between Mn^{4+} and Mn^{3+}, as summarized in eq 4:

$$\mathrm{Mn^{4+}} + \underset{\text{(lattice)}}{\mathrm{O^{2-}}} \xrightleftharpoons[\text{oxygen recombination}]{\text{oxygen evolution}} \mathrm{Mn^{3+}} + {}^{1}\!/_{2}\mathrm{O} + \underset{\text{(oxygen vacancy)}}{\mathrm{V_o}} \qquad (4)$$

Such transformations and regeneration of oxygen deficient materials obtained by microwave-induced oxygen evolution may be important in catalytic, adsorptive, and electrochemical applications.

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