

## Conversion of hausmanite ( $\text{Mn}_3\text{O}_4$ ) particles to nano-fibrous manganite ( $\text{MnOOH}$ ) at ambient conditions

S. RABIEI\*, D. E. MISER, J. A. LIPSCOMB, K. SAOUD, S. GEDEVANISHVILI, F. RASOULI  
*Research Center, Philip Morris USA, Richmond, Virginia 23234, USA*

$\text{Mn}_3\text{O}_4$  has been implemented as catalysts for combustion and CO oxidation, and also used in molecular sieves [1–5].  $\text{MnOOH}$  has been used for adsorption of chemical and radioactive wastes [6] and for oxidation of non-biodegradable materials [7, 8]. However, less attention has been paid to the effect of the history of these materials on their performance. The history is meant to include the duration and conditions of storage or chemical and physical treatments. Manganese oxides have several oxidation states and the corresponding redox mechanisms are explained in various references [9, 10]. To accurately understand their catalytic behavior, the chemical and physical changes that the material has gone through must be known. It can not be assumed that materials remain unchanged during storage. To do so may lead to inaccurate conclusions. Knowing the changes that may occur in the material structure, lack of attention to these changes may lead to inaccurate conclusions based on incorrect presumed structures. For example, it may not be correct to compare a newly synthesized  $\text{Mn}_3\text{O}_4$  sample with one that has been stored at ambient conditions for some period of time because of the reasons to be explained later. In this paper it is shown that even exposure to open air at room temperature can alter both the physical and the chemical structures of manganese oxides, resulting in the transformation from hausmanite ( $\text{Mn}_3\text{O}_4$ ) to manganite ( $\text{MnOOH}$ ) and on heat treatment to  $400^\circ\text{C}$ , manganite transformed to pyrolusite ( $\text{MnO}_2$ ).

Manganese oxide was synthesized by a precipitation method at  $65^\circ\text{C}$  from a 0.1 M aqueous solution of manganese(II) nitrate by adjusting the pH to 11 using a 1 M aqueous solution of sodium hydroxide and aging for 1 hr. The precipitate was dried in ambient air, crushed with a mortar and pestle, and sieved to below  $45\ \mu\text{m}$  using a sieve-shaker system. This material will be referred to as “fresh manganese oxide” throughout the rest of this paper. To study the effect of moisture, “fresh manganese oxide” samples were placed in a humidity chamber with temperature control capability.

The surface area of various samples was measured using an AutoSorb-1 (Quanta Chrome) machine and by using the Brunauer–Emmett–Teller (BET) method at the normal boiling point of liquid  $\text{N}_2$ . The morphology and structure of the samples were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), high-

resolution transmission electron microscopy (HRTEM) and fourier transform infrared spectroscopy (FTIR).

Fig. 1a is an SEM image of the “fresh manganese oxide” consisting of small agglomerated particles in the range of about 100–600 nm. EDS analysis of the particles indicated the presence of manganese and oxygen. Powder X-ray diffraction revealed a pattern consistent with hausmanite ( $\text{Mn}_3\text{O}_4$ ). This is also consistent with the results reported by other authors who used similar synthesis procedures [9, 11].

A “fresh manganese oxide” sample was exposed to room temperature  $25(\pm 3)^\circ\text{C}$  at a relative humidity (RH) of 60% for 1 week. A number of fibers grew in the sample due to this treatment as shown in Fig. 1b.

Fig. 1c and d are SEM images of the “fresh manganese oxide” after exposure to 100% (RH) for 3 days at 44 and  $92^\circ\text{C}$ , respectively. The amount of the “fresh manganese oxide” agglomerates is lower in the sample treated at higher temperature (Fig. 1d) as compared to the sample treated at lower temperature (Fig. 1c) suggesting a higher rate of the transformation from the “fresh manganese oxide” agglomerates to the fibers.

The partial morphological transformation shown in Fig. 1b, c and d indicates a change in the material structure; however, the new fibrous material could not be distinctively characterized by the X-ray diffraction technique. The inefficacy of the X-ray diffraction method for the analysis of some manganese oxides is addressed in the literature [12]; therefore, FTIR and HRTEM techniques were used for further characterization of the fibrous material.

The FTIR experiments revealed a change in the sample's chemical structure from hausmanite ( $\text{Mn}_3\text{O}_4$ ) to mainly manganite ( $\text{MnOOH}$ ) resulting from the exposure of “fresh manganese oxide” to ambient conditions, as is shown in Fig. 2. Referring to Fig. 2, the “interim Mn-oxide” is a “fresh manganese oxide” ( $\text{Mn}_3\text{O}_4$ ) sample after exposure to 60% RH at room temperature for about 2 weeks. The presence of a prominent shoulder in the  $600\text{--}750\ \text{cm}^{-1}$  region can be observed in the reference hausmanite spectrum and also in the “interim Mn-oxide” spectrum. Other similarities between the hausmanite and the “interim Mn-oxide” spectra are the peak height ratio of the 500 and  $600\ \text{cm}^{-1}$  bands, the shift of the  $500\ \text{cm}^{-1}$  band to a slightly lower energy, and the absence of a prominent band below  $475\ \text{cm}^{-1}$ . The rest of the “interim Mn-oxide” spectrum is consistent

\* Author to whom all correspondence should be addressed.

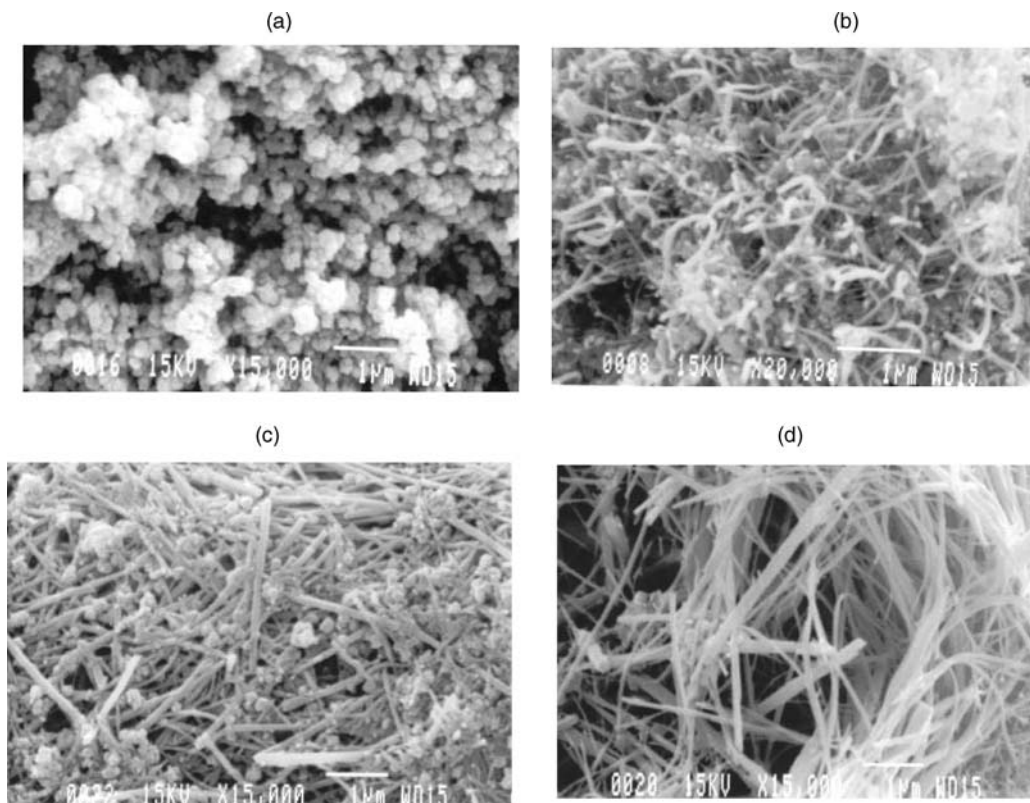


Figure 1 (a) “Fresh  $Mn_3O_4$ ”, (b) same after exposure to 60% RH at 25 °C for 1 week (c) same after exposure to 100% RH at 44 °C for 3 days (d) same after exposure to 100% RH at 92 °C for 3 days.

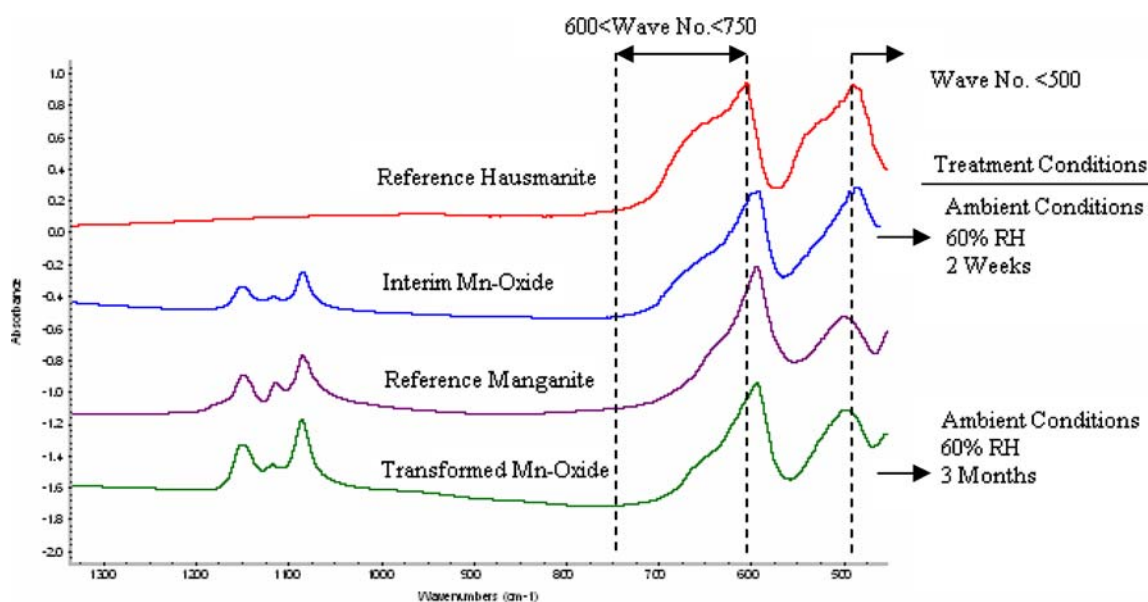


Figure 2 FTIR spectra of manganese oxide in different stages during transformation from hausmanite to mainly manganite.

with the manganite reference spectrum and therefore, the “interim Mn-Oxide” is likely a mixture of hausmanite and manganite. The SEM observations revealed the presence of two types of particle morphologies in the “interim Mn-oxide”: equant particles similar to the “fresh manganese oxide” particles and fibrous particles. Fig. 3 is an HRTEM image from one of the equant particles in the partially transformed sample. Interplanar spacings and angles of these grains were consistent with hausmanite. The inset in Fig. 3 is a fast fourier transform (FFT) of the high-resolution image. The intensities of the inset show this to be a [0 2 0] pole of hausmanite.

The “transformed material” in Fig. 2 is obtained from the “interim material” after a prolonged exposure to 60% RH at room temperature for a total period of 3 months. A near complete transformation of this material to manganite ( $MnOOH$ ) is concluded. The FTIR spectrum of a “reference manganite” sample is shown in the same figure for comparison.

The major part of the original  $Mn_3O_4$  material is transformed to manganite ( $MnOOH$ ) as shown by the FTIR spectra in Fig. 2. However, careful examinations of the fibers using the HRTEM also revealed the presence of some amount of groutite, another phase of  $MnOOH$  (Fig. 4). The largest  $d$  spacing observed,

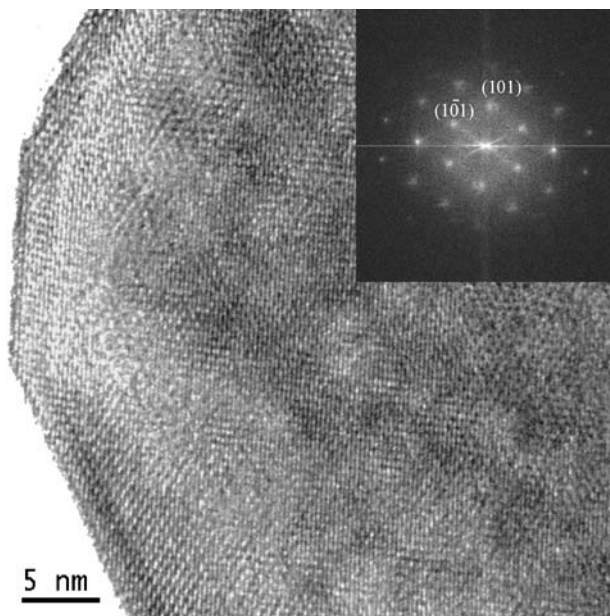


Figure 3 HRTEM image and the corresponding FFT's of the equant grains in a partially transformed manganese oxide sample.

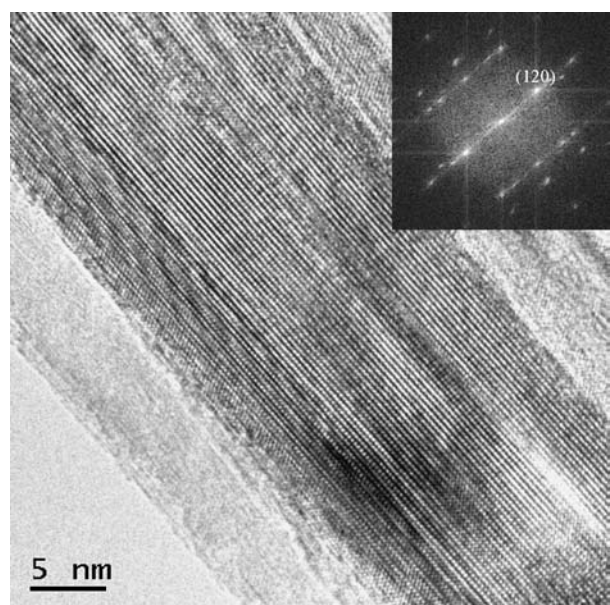


Figure 4 HRTEM image and the corresponding FFT of the fibers.

though rarely, was about 5.3 Å, placing a constraint on the size of the largest unit cell parameter. Defects appear in the image shown in Fig. 4 parallel to  $\langle 1\ 2\ 0 \rangle$  and are represented in the FFT by streaking in  $\langle 1\ 2\ 0 \rangle$ . The difference between the first and the second-order levels in directions normal to  $\langle 1\ 2\ 0 \rangle$  is about 10 Å, indicating that unit cell parameters must be at least that large. Given the apparent cell size, the size of the observed  $d$  spacing and measured angles between the assigned lattice directions, the most likely assignment of manganese oxides or hydroxides (or hydrates) found in the 2001 ICDD database is groutite (card 75–1199).

The BET measurements did not show a considerable difference between the specific surface area of the fresh manganese oxide and the completely transformed manganite sample, both with a BET measurement of  $32(\pm 3)$  m<sup>2</sup>/g.

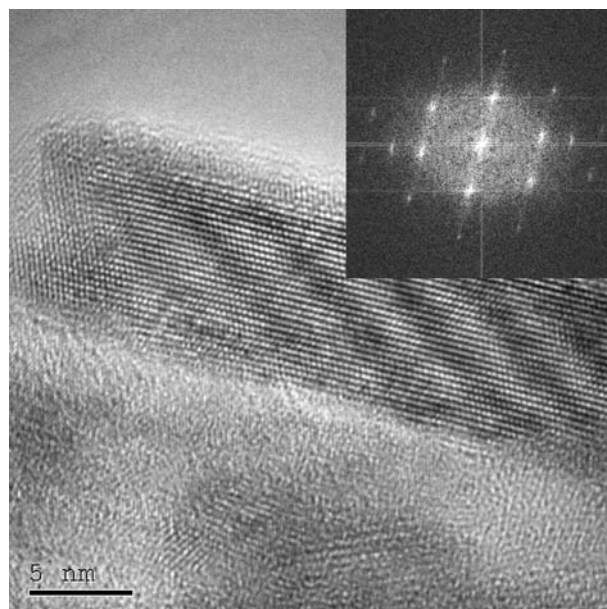


Figure 5 Pyrolusite, MnO<sub>2</sub>, after heat treatment at 400 °C for 30 minutes.

The attempts to measure the rate of transformation from hausmanite to manganite at different temperatures and humidities *via* gravimetric methods were unsuccessful due to the affinity of the manganese oxide to adsorb high amounts of moisture on its surface. This affinity overshadowed the weight change due to the hausmanite/manganite transformation.

To investigate the effect of heat, a fibrous sample from the “transformed material” in Fig. 1d was placed in pure helium at 400 °C for 30 min. Fig. 5 is an HRTEM image of a fiber after this treatment. The inset in Fig. 5 shows the FFT of the image and may be indexed using a pyrolusite (MnO<sub>2</sub>) unit cell. Fibers could still be detected in the heat-exposed sample by SEM. Many of them were smaller than the average size found in the unheated sample.

To conclude, the synthesized Mn<sub>3</sub>O<sub>4</sub> is shown to change its chemical identity and morphology from irregularly shaped particles of hausmanite Mn<sub>3</sub>O<sub>4</sub> to mainly manganite MnOOH with a fibrous morphology as a result of exposure to 60% RH at room temperature. The fibers convert to pyrolusite MnO<sub>2</sub> on heat treatment. These transformations from hausmanite to manganite and/or pyrolusite could alter the properties of the material and should be considered when appropriate. Transformation to the fibrous structure could be induced systematically as a technique to combine the advantages of a highly porous material with the nanometer-size material characteristics, offering a potential solution for applications where resistance to mass transfer plays a vital role in parallel with other desired properties [13].

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