JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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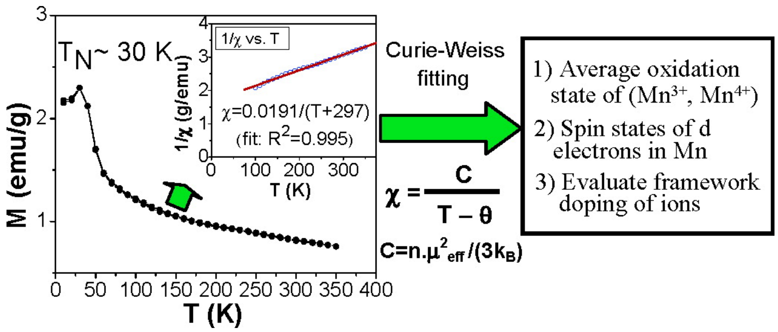
J. Am. Chem. Soc., **2005**, 127 (17), 6166-6167• DOI: 10.1021/ja043406a • Publication Date (Web): 06 April 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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A Magnetic Route to Measure the Average Oxidation State of Mixed-Valent Manganese in Manganese Oxide Octahedral Molecular Sieves (OMS)

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Porous manganese oxide octahedral molecular sieves (OMS) have drawn significant research interest due to their applications in catalysis, ion storage and separation, battery electrodes, chemical sensors, and patterning.[1] In addition to the various nanoscale tunnel structures, one very important feature that makes manganese oxide OMS a unique group of functional materials is the mixed-valent framework manganese (Mn), usually 3^+ and 4^+ or 2^+, 3^+, and 4^+.[2] The importance of mixed-valent Mn is also demonstrated by the enhanced ferromagnetism and colossal magneto-resistance effects in the $La_{1-x}A_xMnO_3$ (A = Ca, Ba, or Sr) perovskite systems[3] and Mn-doped semiconductors, such as GaAs and ZnO for spintronics (spin-carrier electronics), where mixed-valent Mn plays an important role as the hole carrier.[4] The ratio of different valent Mn in OMS is usually characterized by the average oxidation state (AOS) of Mn.

Until now, chemical titration methods, such as thiosulfate titrations or the potential voltametric titrations, are the only major methods that chemists can rely on to measure AOS of mixed-valent Mn.[5] Here, we report another method to determine the AOS of Mn for mixed-valent manganese oxides by magnetic measurements.

An example is demonstrated using the synthetic potassium manganese dioxide, KOMS-2, which has nanoscale 2 × 2 tunnel structures constructed by edge and corner sharing of MnO_6 octahedra. The KOMS-2 was synthesized by the sol−gel combustion method.[6] X-ray diffraction (XRD) was used to identify a pure phase of cryptomelane (JCPDS: 29-1020). In addition, field emission scanning electron microscope images showed a nanorod morphology with a typical diameter of 30 nm and length of 200−500 nm. Magnetic measurements were carried out using a Quantum Design MPMS SQUID magnetometer for temperatures $10\ \text{K} \le T \le 350\ \text{K}$ and applied fields $-50\ \text{kOe} \le \text{H} \le +50\ \text{kOe}$. EPR data suggest that the possible mixed-valence states of Mn in KOMS-2 here are 3^+ and 4^+ (see Supporting Information).

Figure 1a shows the response of magnetization M (in emu/g) with applied magnetic field H (in kOe) at various temperatures T (in K) for KOMS-2. For temperature $T \ge 100$ K, the $M-H$ curves are completely linear and pass through the origin. This linear response of M to H justifies the calculation of a susceptibility χ (in emu/g) by $\chi = M/H$ to describe the paramagnetic behavior of KOMS-2. Figure 1b shows the magnetization as a function of temperature in a magnetic field $H = 25$ kOe. There is a weak magnetic transition at $T_1 \approx 225$ K and a clear transition at $T_2 \approx 50$ K, which are discussed below. Figure 1c shows the Curie−Weiss fit ($1/\chi$ versus T) for KOMS-2.

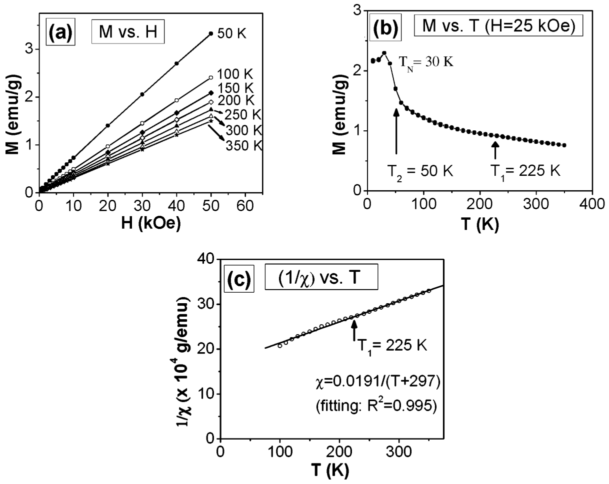

Figure 1. Magnetic measurements of KOMS-2. (a) Magnetization M versus applied magnetic field H for various temperatures; (b) M versus T for H = 25 kOe; (c) Curie−Weiss fit. The temperatures T_1 and T_2 represent magnetic transitions. For $T \ge T_1$, a very good fit to the Curie−Weiss law yields 3.74 μ_B for the effective Mn magnetic moment.

To explore the applicability of the Curie−Weiss law, χ is expressed as eq 1.

$$\chi = \frac{C}{T-\theta} + \chi_o \qquad (1)$$

where θ is the Curie−Weiss temperature; C is the Curie−Weiss constant, and χ_o represents any temperature-independent contribution(s) to the susceptibility, such as diamagnetism of ionic cores. By both calculation and linear fitting, it was determined that here $\chi_o \le 1\%\chi$ and, hence, is negligible.[7] As shown in Figure 1c, the Curie−Weiss law best describes the paramagnetic behavior for KOMS-2 when $T \ge T_1 = 225$ K, as indicated by the linear behavior of $1/\chi$ versus T. This fit yields a value of $\theta = -297$ K from the intercept and $C = 0.0191$ emu·K/g from the slope ($^1/_C$). Using eq 2, the Curie−Weiss constant can be related to the effective magnetic moment

$$C = \frac{n{\mu_{\text{eff}}}^2}{3k_B} \qquad (2)$$

where k_B is the Boltzmann constant; μ_{eff} is the effective magnetic moment (magnitude in Bohr magneton, μ_B), and n is the number of magnetic atoms per unit sample mass. A value of $\mu_{\text{eff}} = 3.74\ \mu_B$ is obtained for the effective magnetic moment of mixed-valent Mn (Mn^{4+} and Mn^{3+}) in KOMS-2 from eq 2. (For the calculation, the standard formula for cryptomelane, KMn_8O_{16}, was used.)

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10.1021/ja043406a CCC: $30.25

Table 1. AOS Determination by the Magnetic Method

sample[a]	ref value AOS[b]	measured AOS[c]	difference	deviation error
KOMS-2 (600 °C)	3.85	3.88	+0.03	+0.8%
MnO	2.00	1.95	−0.05	−2.5%
Mn_2O_3	3.00	3.01	+0.01	+0.3%
Mn_3O_4	2.67	2.49	−0.18	−6.7%
γ-MnO_2	3.98	4.04	+0.06	+1.5%
β-MnO_2	4.00	4.23	+0.23	+5.8%
OMS-5	3.85	3.93	+0.08	+2.0%
OMS-6	3.84	3.83	−0.01	−0.3%
KOMS-2 (reflux 100 °C)	3.87	3.83	−0.04	−1.0%
KOMS-2 (80 °C)	3.72	3.78	+0.06	+1.6%

[a] Details of sample information are provided in the Supporting Information. [b] Reference values of titration/theoretic AOS. [c] Measured AOS values by the magnetic method.

The negative value for the Curie−Weiss temperature $\Theta = -297$ K indicates the strong antiferromagnetic interactions between the Mn moments. The weak magnetic transition at $T_1 = 225$ K agrees with the results by Sato, which is sensitive to the synthesis conditions.[8] Sato also suggested that weak ferromagnetism occurs at T_2, which then disappears at lower temperatures. An alternative explanation is that the cusp-like behavior shown in Figure 1b might indicate an antiferromagnetic transition where the Néel temperature is $T_N \approx 30$ K.

The summation of the magnetic moment from each ion (Mn^{3+} and Mn^{4+}) produces an effective magnetic moment in the system. If the atomic fraction of Mn^{4+} out of the total Mn is y, then

$$(\mu_{\mathrm{eff}})_{\mathrm{Mn}} = y \times (\mu)_{\mathrm{Mn4+}} + (1 - y) \times (\mu)_{\mathrm{Mn3+}} \qquad (3)$$

If Mn^{3+} is in the high spin state, the effective magnetic moment of Mn^{4+} and Mn^{3+} will be larger than 3.87 μ_B, which is apparently higher than the one observed here (3.74 μ_B). Therefore, this suggests that Mn^{3+} is in the low spin state for KOMS-2. Indeed, for Mn^{3+}-(d^4) under octahedral fields, Jahn−Teller (JT) distortion usually occurs to lower the system's ground state, resulting in a high spin state of Mn^{3+} ($t^3_{2g}e^1_g$).[9] However, the presence of higher valence state ions, such as Mn^{4+}, can suppress the JT distortion on Mn^{3+}.[10] When the ratio of Mn^{4+}/Mn^{3+} is higher than some critical point, such as 0.4−0.5, the JT distortion on Mn^{3+} is negligible.[10a]

Therefore, the ratio of Mn^{4+} to Mn^{3+} can be resolved from eq 3, which is 87.5−12.5%. This gives an AOS of 3.88 for manganese in the KOMS-2, which is in good agreement with the titration results (AOS = 3.85 ± 0.05).[5b,11]

This magnetic method has also been applied to other samples such as 2 × 4 (OMS-5) and 2 × 3 (OMS-6) tunnel structure manganese oxides and commercial MnO, Mn_2O_3, and Mn_3O_4. As shown in Table 1, the magnetic method produces AOS results in excellent agreement with the titration/theoretical reference AOS values. A maximum deviation error of ±7% is obtained for the 10 different examples.

A magnetic route has been successfully applied to determine the AOS of both mixed-valent framework Mn and single oxidation states of Mn in manganese oxide OMS. The general procedure includes (1) obtaining Curie−Weiss constant C by the Curie−Weiss fit of $1/\chi$ to T, (2) calculating μ_{eff} using eq 2, and (3) calculating AOS using eq 3. The results from the magnetic method are in good agreement with titration results. The magnetic route confirms that framework manganese in KOMS-2 and OMS-6 is mixed-valent, consisting of 3^+ and 4^+ with Mn^{3+} in the low spin state. As stated before, the titration method is interfered by any dopant redoxable ions leading to imprecise AOS evaluation. For the magnetic method, if the dopant redoxable ions are "diamagnetic" (no unpaired electrons), such as V^{5+} ($3d^0$), then they will not possess any magnetic moments, and thus, the AOS analyses will not be affected. Therefore, the magnetic method may be extended for the AOS measurements of ion-doped manganese oxide OMS, which is inappropriate for the titration method. If the dopant ions are not diamagnetic, this method may not be used to determine AOS of Mn. However, by comparing the magnetic behavior of OMS before and after doping, this method may be used to determine if the dopant ions are present as individual clusters or are doped into the framework of OMS, which is very difficult to characterize even with HRTEM and EXAFS techniques. That is, magnetic methods can be used for identification of minor/impurity phases in paramagnetic or ferromagnetic samples as also pointed out by Wold.[12] The requirements are that (1) the systems should show Curie−Weiss behavior over a temperature range and (2) there are no more than two paramagnetic ions present.

Acknowledgment. We thank the Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy for financial support, and Dr. Francis S. Galasso for helpful discussions and comments.

Supporting Information Available: XRD, EPR, and FESEM of KOMS-2, possible temperature-independent contributions (χ_o) to the magnetic susceptibility, and magnetic measurements of AOS for examples in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA043406A