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## Structural studies on colloidal tetraalkylammonium manganese oxides

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XAFS at the Mn K edge was employed to elucidate the structure of colloidal tetraalkylammonium (TAA) manganese oxides in sols and gels obtained by different preparation and heat treatment procedures. XANES analysis revealed an average valence of  $\sim 3.7$  for as-synthesized TAA colloids, whereas gelled TAA colloids showed a decreased average valence of  $\sim 3.5$ . XAFS analysis was carried out to distances of  $\sim 6.0$  Å around the central Mn atom employing theoretical backscattering phases and amplitudes calculated with the ab-initio code FEFF. A Birnessite layer  $\text{MnO}_x$  model structure was used which resulted in a good agreement with experimental data.

**Keywords:** XAFS, FEFF, multiple scattering, focusing effect, colloids

### 1. Introduction

Mixed valent manganese oxides are of interest due to their diverse range of electrical, magnetic, and catalytic properties. Recently, novel colloids of manganese oxide have been prepared using tetraalkylammonium cations (alkyl = methyl, ethyl, propyl, and butyl) to prevent agglomeration (Brock et al., 1998). These materials are of interest due to unique optical properties associated with quantum confinement and their potential as starting materials for novel manganese oxide materials. In this work Mn K-edge XAFS studies were performed on colloidal  $\text{MnO}_x$  samples prior and upon sol to gel transition and after different heat treatment procedures to reveal structural and electronic changes in the colloidal particles. Theoretical XAFS calculations known to yield reliable backscattering phases and amplitudes are applied in combination with suitable fitting routines to the analysis of colloidal manganese oxide systems.

### 2. Experimental section

#### 2.1 Preparation of colloidal manganese oxides

A detailed description of the synthesis of tetraalkylammonium (TAA) manganese oxide colloids appears elsewhere (Brock et al., 1999). The materials are prepared via reduction of tetraalkylammonium permanganate salts (alkyl = ethyl, propyl) with 2-butanol in aqueous solutions. XAFS measurements have been obtained on the colloids as-prepared (TAA-A), with the residual 2-butanol removed (TAA-H), and on the gels (TAA-G). Measurements have been made on both tetraethylammonium (TEA) and tetrapropylammonium (TPA) manganese oxide colloids and gels with manganese concentrations from 0.1–0.4 M.

#### 2.2 XAFS measurements

XAFS experiments were performed on the 31-pole-wiggler beam line 10-2 (Karpenko et al., 1989) at Stanford Synchrotron Radiation Laboratory (SSRL) with the storage ring operating at an energy of 3.0 GeV and injection current of  $\sim 100$  mA. A Si(220) double crystal monochromator was used and higher harmonics in the synchrotron beam were suppressed by detuning the monochromator to  $\sim 50\%$  of the maximum of the rocking curve. Colloidal manganese oxides samples were measured in a liquid cell with a fixed thickness of 1.0 mm. Reference compounds were prepared as a thin powder layer on kapton tape. About 6 layers of tape were stick together to improve sample homogeneity and to obtain an absorption edge jump of less than 1.0 absorption lengths. XAFS spectra were taken at a temperature of 300 K and in a photon energy range from 6.5 to 7.5 keV.

#### 2.3 Data reduction

Data reduction of experimental absorption spectra and XAFS fitting and simulation was carried out employing the XAFS analysis software package WinXAS97 version 1.1 (Ressler, 1998). Pre-edge background subtraction and normalization was carried out by fitting a linear polynomial to the pre-edge region and a cubic polynomial to the post-edge region of an absorption spectrum. The atomic background,  $\mu_0(k)$ , was determined using cubic splines and the radial distribution function  $\text{FT}(\chi(k))$  was obtained by Fourier transforming the  $k^3$  weighted experimental XAFS  $\chi(k)$  function, multiplied by a Bessel window, into the R space.

### 3. Results and discussion

In order to determine the average valence (AV) of the systems studied, a calibration curve (Fig. 1) was assembled from least-squares fit results of an arctangent step function to the Mn K XANES of various manganese oxide references of different valence (i.e.  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ ). A linear regression fit is found to give a very good match to the set of four experimental edge positions versus valence. Subsequently, the resulting linear fit was used to determine the valence of the colloidal  $\text{MnO}_x$  samples from their Mn K edge position. It is noted from Fig. 1 that a difference in valence of  $\sim 2.0$  corresponds to an absorption edge shift in photon energy of  $\sim 7$  eV. The magnitude of this shift is comparable to experimental energy shifts in the pre-edge peak and previously reported Mn K pre-edge shifts (Manceau et al., 1992a). Arctangent positions and corresponding valence of the systems studied can be found in Table 1.

Experimental FT XAFS  $\chi(k)$  functions of references and manganese colloids studied are displayed in Fig. 2. Peak distances in this plot are not phase corrected for the phase shift associated with the photoelectron scattering process and hence are shifted to lower R values by about 0.4 Å. Besides the Mn-O peak at  $\sim 1.5$  Å to more distinct peaks can be seen at  $\sim 2.4$  Å (npc) and  $\sim 5.2$  Å. The former (*Mn*, *ES* in Fig. 2) corresponds to a Mn-Mn distance across the edge of two edge sharing  $\text{MnO}_6$  octahedra, whereas the latter (*F* in Fig. 2) corresponds to a Mn-Mn distance along the centerline of three edge-sharing octahedra (Manceau et al. 1992b). In addition, a dashed line at  $\sim 3.1$  Å in Fig. 2 indicates a hypothetical peak position that would correspond to a Mn-Mn distance across the corner of two corner-shared  $\text{MnO}_6$  octahedra. As can be noticed from Fig. 2, only the gelled samples TPA-G and TEA-G exhibit small peaks at this position indicating a certain amount of corner-shared

octahedra in these systems. The references, the TAA-A, and the TAA-H samples show no discernable amount of corner shared octahedra in their structures. Furthermore, a low FT peak can be observed at  $\sim 8.2$  Å that belongs to a Mn-Mn distance along the centerline of four edge shared  $\text{MnO}_6$  units. Of all measured systems, this peak appears to be most pronounced in the Birnessite experimental data.

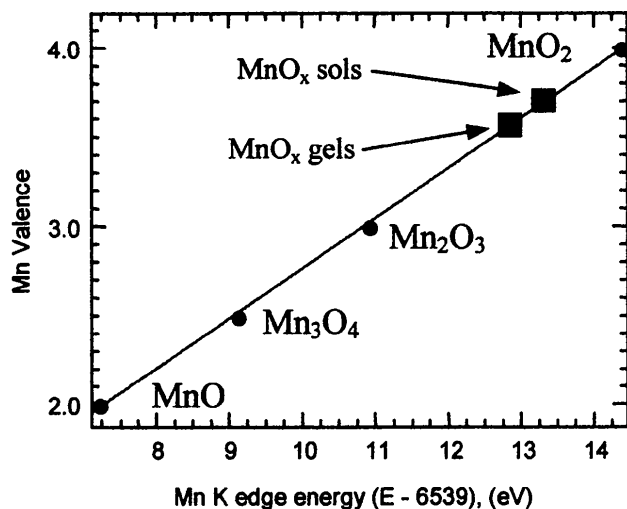


Fig. 1. Mn K edge position of various Mn reference compounds as a function of Mn valence. Solid line represents linear regression fit to the four data points.

Table 1. Arc tangent position obtained from refinement of an ATAN step function to the XANES region and the average valence based on linear curve in Fig.1. Fit errors were estimated from the least-squares covariance matrix to be  $\sim 0.01$ .

Sample	Arc tangent Pos., (eV)	Valence
TPA-A	12.79	3.55
TPA-H	13.55	3.68
TPA-G	12.61	3.50
TEA-A	13.19	3.66
TEA-H	13.30	3.69
TEA-G	12.85	3.56
Birnessite	12.73	3.53
Feitknechtide	11.58	3.22

In order to extract more quantitative information about the  $\text{MnO}_x$  layer structure in the colloidal systems studied, a multiple-shell multiple-scattering XAFS analysis was carried out to  $\sim 6.0$  Å around the central Mn atom. XAFS fitting was done using theoretical backscattering phases and amplitudes calculated with the ab-initio multiple-scattering code FEFF7 (Rehr et al., 1994). A Birnessite layer  $\text{MnO}_x$  model structure was used which resulted in a good agreement with experimental data. All significant multiple-scattering paths with a weight of 2 % and more with respect to the main Fourier transform peak were included in the refinement, resulting in a total of 13 single scattering paths and 44 multiple scattering paths. Although collinear scattering paths (focusing effect) showed the strongest MS contribution to the entire XAFS function, other triangular

and higher scattering paths had to be taken into account to obtain a good agreement with experiment.

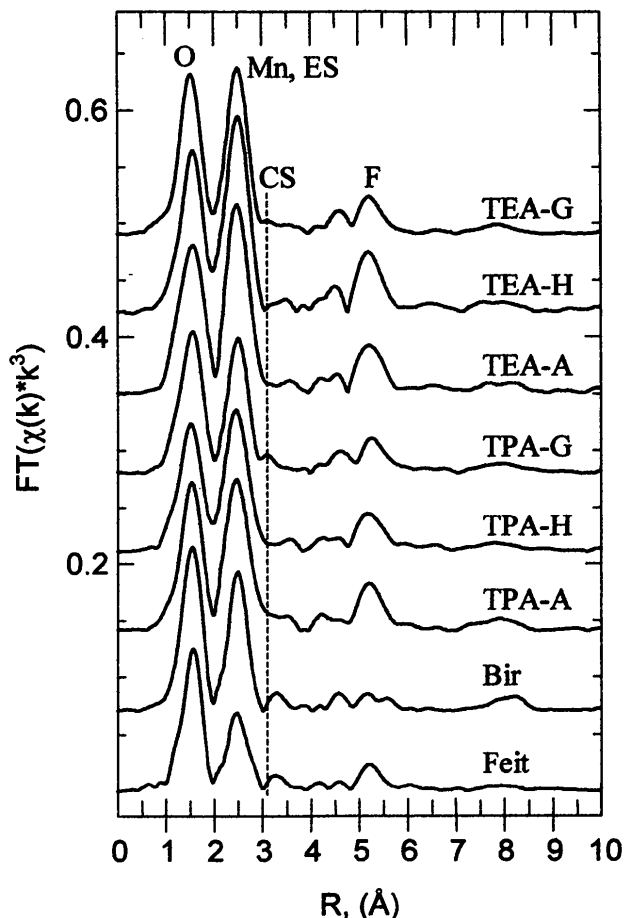


Fig. 2. Fourier transformed Mn K edge experimental  $\chi(k)$  functions of colloidal manganese oxides and reference compounds (not phase shift corrected). Prominent FT peaks as indicated are O: 1<sup>st</sup> shell = Mn-O distance in  $\text{MnO}_6$  octahedron, Mn, ES: 2<sup>nd</sup> shell = Mn-Mn distance between two edge-shared  $\text{MnO}_6$  units, CS: Mn-Mn distance between two corner-shared  $\text{MnO}_6$  units, F: „focusing„ peak corresponds to collinear arrangement of three edge-shared  $\text{MnO}_6$  units.

The approach taken in the current XAFS analysis is to determine SS shell distances in a structure known to contain sets of slightly varying bond lengths within one shell owing to (i) Jahn-Teller distortions in an octahedral coordination geometry at  $\text{Mn(III)}$  sites and (ii) different bond length between  $\text{Mn}^{\text{III}}\text{O}_6$  and  $\text{Mn}^{\text{IV}}\text{O}_6$  units. Therefore, in order to reduce the number of free running parameters in the XAFS fit and to make the determination of slightly varying bond lengths more reliable, the following constraints were applied in the XAFS refinement of colloidal manganese oxides.

- (i) The same basic  $\text{MnO}_x$  layer structure was assumed in all cases based on the resemblance of XANES spectra and  $\text{FT}(\chi(k))$  peak positions and amplitude observed experimentally.
- (ii) All coordination numbers (SS and MS) were fixed and were not refined in the fit. This assumption neglects vacancies in the structure as well as finite size effects.
- (iii) SS path distances were allowed to run free in the refinement; MS path distances

were calculated from the constituent SS paths distances assuming the dieder bond angle between SS paths to be the same as in the Birnessite model structure. (iv) Debye Waller factors,  $\sigma$ , were calculated from the correlated Debye model assuming two different Debye temperatures for Mn and oxygen backscatterers, respectively. (v) Two energy corrections  $E_0$  were fitted for Mn and oxygen backscatterers, respectively. In total, the employed refinement constrains allowed the number of free running parameters in the fit to be reduced from 228 to 18. This turned out to result in reliably converging XAFS fit and reasonable structural and scattering parameters. As an example, XAFS fit results for TPA-A are given in Table 2. The good agreement between experimental XAFS function and theoretical calculation can be seen from Fig. 3. Further details on the XAFS analysis procedure together with the results on all colloidal systems studied will be presented in a forthcoming paper (Ressler, 1999).

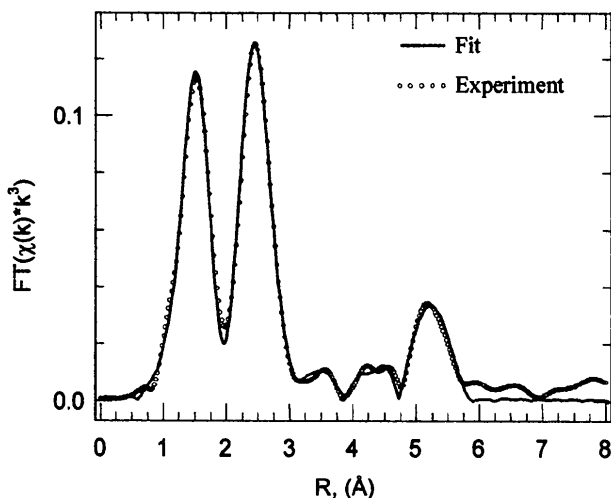


Fig. 3. XAFS refinement (solid) using theoretical phases and amplitudes to experimental TPA-A Fourier transformed  $\chi(k)$  (dots). Fit results can be found in Table 2.

Table 2. XAFS fit: coordination number CN (fixed), distance R, and Debye-Waller factor  $\sigma$  (calculated from correlated Debye model) of the 1<sup>st</sup>, 2<sup>nd</sup>, 5<sup>th</sup>, and 6<sup>th</sup> shell in the structure of TPA-A colloid (k range [2.2 - 14.4] Å<sup>-1</sup>; fit range [0.9 - 6.0] Å; R=6.3 %; N<sub>idp</sub> = 42; N<sub>free</sub> = 18; Θ<sub>O</sub> = 927±2 K; Θ<sub>Mn</sub> = 457±1 K; S<sub>0</sub><sup>2</sup> = 0.75; E<sub>0</sub>(O) = 1.8 eV; E<sub>0</sub>(Mn) = -3.6 eV).

Shell	CN	R, (Å)	σ, (Å)
1 <sup>st</sup>	4	1.87	0.06
Mn - O	2	1.93	0.06
2 <sup>nd</sup>	2	2.83	0.08
Mn - Mn	4	2.87	0.08
5 <sup>th</sup>	4	4.92	0.08
Mn - Mn	2	5.03	0.08
6 <sup>th</sup>	2	5.65	0.08
Mn - Mn	4	5.74	0.08

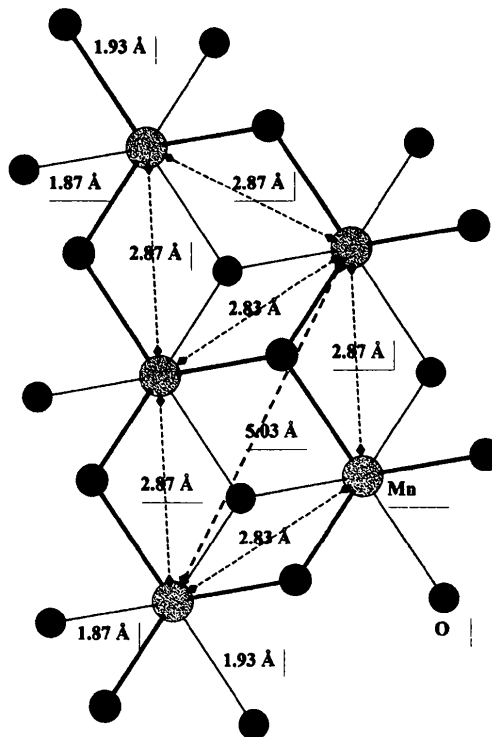


Fig. 4. Top view on a section of a MnO<sub>x</sub> layer model structure used. Bond length based on XAFS fit results for sample TPA-A (Table 2).

#### 4. Concluding remarks

In this work x-ray absorption spectroscopy at the Mn K edge was successfully employed to elucidate the structure of colloidal tetraalkylammonium manganese oxides XAFS analysis was carried out to distances of ~ 6.0 Å employing theoretical backscattering phases and amplitudes calculated with the ab-initio code FEFF. Good agreement with experiment could be achieved. In a future work (Ressler, 1998), analysis of a collinear scattering path in the MnO<sub>x</sub> layer structure by virtue of the corresponding multiple-scattering amplitude will be described which reveals further medium-range structural information on the colloidal systems. As a result, medium-range 2D structures for colloids samples and references are proposed.

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