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Manganese speciation in exhaust particulates of automobiles using MMT-containing gasoline

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XAFS spectroscopy is used to speciate Mn-containing auto exhaust particulates emitted from MMT-added gasoline engines and collected in a controlled manner. A series of Mn compounds was also measured to model and aid quantification of the unknown species in the particulates. XANES results show that the average Mn valence in these particulates is ~2.2 and that MnO, Mn_3O_4, $MnSO_4{\cdot}H_2O$ and a Mn phosphate are the predominant phases present. The amount of each component varies depending on engine history and test cycle. The XAFS analysis was found to corroborate the XANES results.

Keywords: Mn Speciation, MMT-gasoline, exhaust particulates

1. Introduction

Methylcyclopentadienyl manganese tricarbonyl (MMT) is a promising gasoline additive for enhancing fuel efficiency and decreasing emissions in automobiles. Environmental concerns about airborne manganese particulates and their potential health hazards require intensive studies regarding the form and distribution of manganese emitted from the automotive engine (McKinsey, 1998). As a part of these investigations we employed Mn K-edge XAFS spectroscopy to characterize exhaust particulates sampled in a controlled manner from different automobiles running MMT-containing gasoline. Using a set of Mn model compounds, manganese species in the exhaust particulates were determined and quantified using a XANES fitting procedure. In addition, XAFS results on exhaust particulate were found to corroborate the XANES analysis.

2. Experimental section

2.1 Model compounds - these include oxides: MnO, Mn_2O_3 Mn_3O_4 and MnO_2; selected divalent salts: MnS, $MnSO_4{\cdot}H_2O$, $Mn_2P_2O_7$, $Mn_5(PO_4)_2$ $[PO_3(OH)]_2{\cdot}4H_2O$; and trivalent $MnPO_4$.

2.2 Particulate samples - these are collected on teflon coated fiberglass filters from two automobiles (a '97 and a '98 Ford Taurus) with two different mileage histories (4000 and 40,000 miles) and four test cycles given in Table 1.

2.3 XAFS measurements were performed on beamline 10-2 (Karpenko et al., 1989) at SSRL with SPEAR operating at an electron energy of 3.0 GeV and injection current at ~100 mA. For bulk model compounds, a conventional transmission mode was used to collect the absorption spectra. For the dilute filter specimens, a fluorescence detection mode utilizing a Lytle detector was used. A 2 mm high x 20 mm wide beam was incident to the samples at 45 deg. A Si(220) double-crystal monochromator, 50% detuned, was used. Multiple scans varying from 4 sweeps for XANES and 8 sweeps for EXAFS were performed to yield optimal S/N ratios. All spectra were collected in the QEXAFS mode (Frahm, 1988). A manganese metal standard foil located in front of a reference ion chamber was measured simultaneously with each sample for in-situ energy calibration.

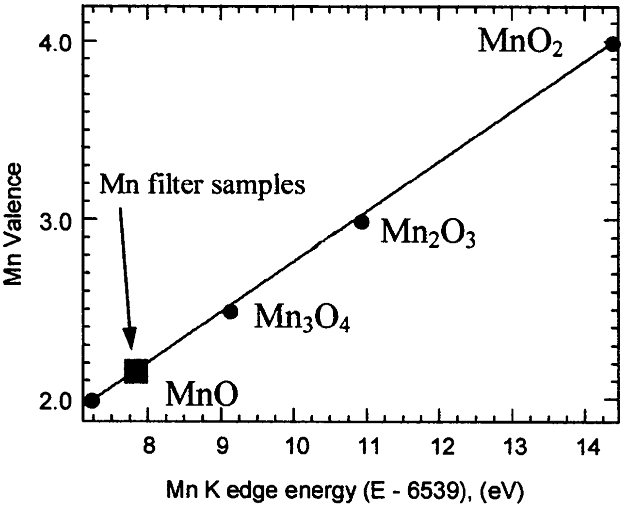

Fig. 1. Mn K edge position of Mn oxide reference compounds as a function of Mn valence. Solid line represents linear regression fit to the four data points.

3. Results and discussion

Fig. 1 shows a linear relationship of Mn valence vs. K-edge position in the chosen series of Mn oxide model compounds. The edge positions were obtained from the maxima in the first derivatives of the corresponding (fitted) arctangent functions. The experimental edge shifts for all filter samples are in the range of ~8 eV, indicating an overall Mn valence of ~2.2 in the exhaust particulates.

Visual examination reveals two distinct XANES patterns emerging from the exhaust particulates: Group 1 with a single absorption feature in the whiteline and Group 2 with a doublet feature. Their normalized XANES spectra are shown in Fig. 2 together with those of MnO, Mn_3O_4, $MnSO_4{\cdot}H_2O$ and $Mn_5(PO_4)_2[PO_3(OH)]_2{\cdot}4H_2O$ which have been chosen for quantitative simulation based on valence consideration and the presence of sulfur and phosphorus from ESCA analysis.

A least squares procedure with the WinXAS program (Ressler, 1998) utilizing a linear combination of the four chosen Mn model compounds was employed to simulate and quantify the unknown Mn XANES of the particulates. Results for the Group I and II particulates are given in Figs. 3(a) and 3(b) respectively. The doublet observed in the whiteline of the Group II materials may now be rationalized in terms of the high concentration of Mn3O4. The simulated concentrations of (model) components in each exhaust particulates are given in Table 1, showing that the Group II particulates contain 33% Mn_3O_4 and higher and a corresponding lower combined sulfate and phosphate content with respect to the Group I particulates.

Table 1 Particulate sample history, test cycle, and simulated composition.

Vehicle	Mileage	Test Cycle	Mn_3O_4, (%)	MnO, (%)	$MnSO_4$, (%)	MnPhos, (%)	Group
'97	4.000	FTP extended.	6	9	51	34	I
'97	4.000	UDC	12	10	46	32	I
'97	40.000	FTP extended	12	10	50	28	I
'97	40.000	UDC	12	7	46	35	I
'98	4.000	FTP	24	10	42	24	I
'98	4.000	FTP inactive catalyst	8	10	48	34	I
'98	4.000	FTP extended	34	8	28	30	II
'98	4.000	UDC	33	9	31	27	II
'98	40.000	FTP	47	11	28	14	II
'98	40.000	FTP inactive catalyst	21	11	42	27	I
'98	40.000	FTP extended	18	6	50	28	I
'98	40.000	UDC	46	7	32	15	II

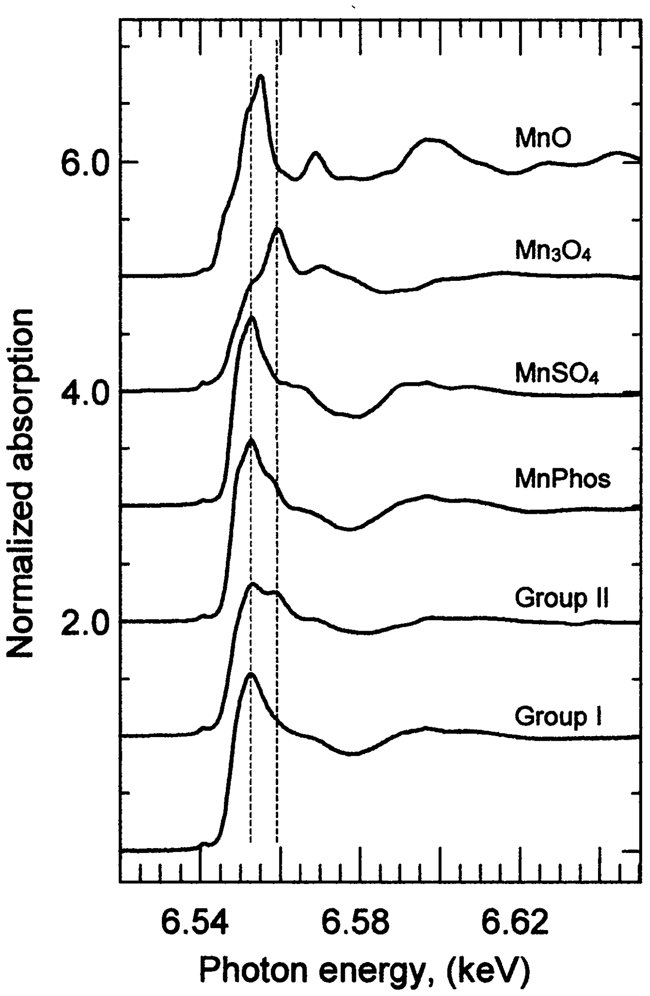

Fig. 2. Normalized Mn K-edge XANES spectra of manganese model compounds and Group I and II particulates.

Fourier transforms of the measured EXAFS signals are also revealing. The results are plotted in Fig. 4. Fourier transforms of Group II particulates exhibit a strong peak in the 3.0 Å region, which is also prominent in that for Mn_3O_4, but not in those of the Group I materials. This corroborates well with the XANES simulations.

4. Concluding remarks

XAFS spectroscopy is a powerful diagnostic tool to speciate environmental materials as demonstrated in this study. Further details of this work are described in a forthcoming publication (Ressler et al., 1998).

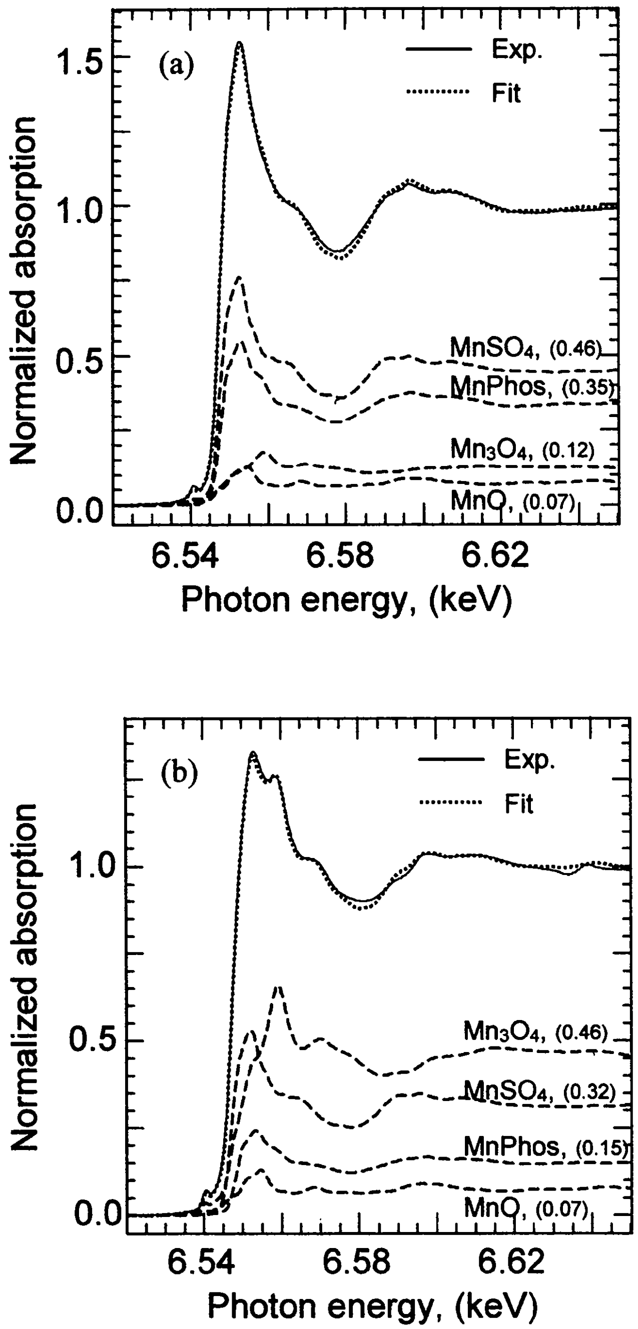

Fig. 3. Experimental (___) and simulated (----) XANES spectra for Group I (a) and Group II (b) particulates. The fractions of model components making up the simulated spectra are also plotted.

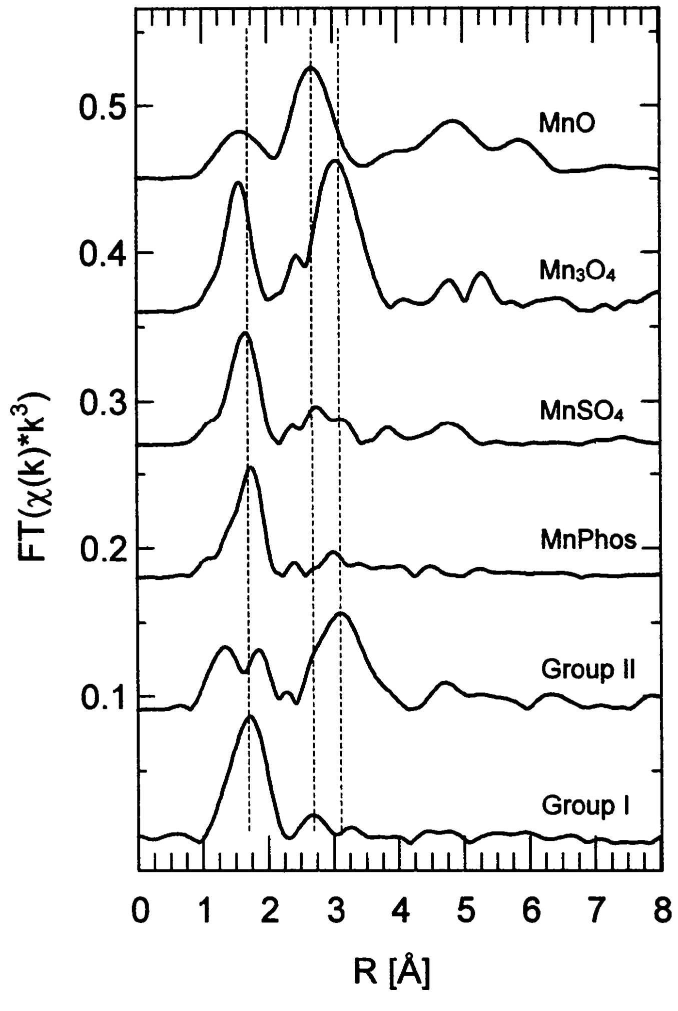

Fig. 4. k3-weighted Fourier transforms of EXAFS signals from Group I and II particulates, and the four Mn model compounds.

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