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MANGANESE EMISSIONS FROM COMBUSTORS*

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Introduction. Undesirable emissions from aircraft, automotive and stationary gas turbine engines are produced in the combustion chamber with no significant change during subsequent flow through the turbine. These emissions can therefore be characterized by studying model combustion chamber¹ exhaust. The apparatus used has previously been described in detail^{2,3}. Emphasis is therefore placed on results obtained using X-ray photoelectron spectroscopy to analyze particulate exhaust collected from a model combustor burning JP-4 with 2-methyl cyclopentadienyl manganese tricarbonyl (MMT) added in concentrations ranging from 0 to 0.25% by volume. It is desired to determine the oxidation state and physical form of the manganese after combustion as well as its effect on other particulate emissions.

Method. X-ray photoelectron spectroscopy (XPS) consists of determining the binding energy of photoelectrons expelled from a sample irradiated with monoenergetic X-rays⁴. Applications of the

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technique to particulate analysis have been reported⁵. The electron binding energies obtained are characteristic of the element observed, with the precise value of these energies being modified by the valence electron distribution of the molecule in which the observed atom exists. The difference in electron binding energy between the elemental and molecular forms of an atom is known as the chemical shift. These shifts are correlated to the effective charge an atom possesses in a molecule and are used to establish oxidation states. The oxidation states of manganese, however, have such small chemical shifts that it is difficult to unambiguously assign an effective charge from a measurement of the chemical shift alone.

Because of this difficulty, the multiplet splitting effect was employed here to determine the oxidation state. Multiplet splitting of core electron binding energies has been observed in the photoelectron spectra of transition metal compounds and other paramagnetic species⁶. In any atomic or molecular system with unpaired valence electrons the 3s-3d exchange interaction effects the core electrons differently, according to the orientation of their spin. This causes the 3s core level to be split into two components. For an Mn^{2+} ion whose ground state configuration is $3d^5 4s^0$ the two multiplet states will be 7S and 5S . In an Mn^{4+} ion having the ground state configuration $3d^3 4s^0$ the two spectroscopic states will be 5F and 3F . The magnitude of the multiplet splittings should in first approximation be proportional to the number of unpaired 3d electrons. Hence the Mn(3s) splitting will be greatest for Mn^{2+} ions, and least for Mn^{4+} .

Results. A photoelectron spectrum of the exhaust particles in the binding energy range 0 to 670 eV is shown in Figure 1. The major constituents are manganese, carbon and oxygen, with

Fig. 1 X-ray photoelectron spectrum of particles emitted by a model combustor burning JP-4 with 0.25% (vol.) MIT and collected on a Nuclepore filter.

trace amounts of nitrogen and sulfur. The Mn(3p) level was used for the chemical shift measurements while the Mn(3s) level provided the multiplet splitting data. Mn(3p) binding energies have been determined for the exhaust particle samples and for the compounds MnO, Mn₂O₃, Mn₃O₄ and MnO₂. These values, corrected for sample charging using the hydrocarbon contaminant with a C(1s) binding energy of 285.0 eV, are listed in Table I. Clearly it cannot be determined on the basis of chemical shift alone whether the oxidation state is MnO, Mn₃O₄ or Mn₂O₃.

Table I. Measured Mn(3p) Electron Binding Energies

Sample	Exhaust	MnO*	Mn ₃ O ₄	Mn ₂ O ₃	MnO ₂
Binding energy, (eV)	48.9 ± 0.2	48.8 ± 0.2	48.9 ± 0.2	49.0 ± 0.2	49.9 ± 0.2

* powered reagent grade MnO which undergoes rapid surface oxidation at ambient conditions was used⁷.

The oxidation state assignment is made by examining the multiplet splittings of the 3s electron level in spectra such as shown in Fig. 2. MnF₂ is included since it is the most ionic

Fig. 2 Comparative X-ray photoelectron spectra of 3s core levels for MnF₂, exhaust particles and MnO₂ showing the multiplet splitting of the 3s level. It is concluded that MnO is the principal manganese oxide in the emitted particles.

compound of divalent manganese and therefore its Mn^{2+} ion must exhibit the largest possible 3s multiplet splitting. Mn(3s) spectra were also obtained for Mn_3O_4 and Mn_2O_3 . A summary of the measured multiplet splittings along with values from the literature is given in Table II.

Table II. Multiplet Splitting of Mn(3s)

Compound	Splitting (eV)			
	This Work	Wertheim et al. (Ref. 7)	Fadley et al. (Ref. 8)	Carver et al. (Ref. 9)
MnF_2 (2+)	6.4 ± 0.2	6.50 ± 0.02	6.5	6.3
Exhaust Particulate	6.1 ± 0.2	-----	-----	-----
MnO (2+)	-----	6.05 ± 0.04	5.7*	5.5*
Mn_3O_4 (2+ and 3+)	5.5 ± 0.2	-----	-----	-----
Mn_2O_3 (3+)	5.5 ± 0.2	5.50 ± 0.10	-----	5.4
MnO_2 (4+)	4.6 ± 0.2	4.58 ± 0.06	4.6	-----

* Earlier lower values for MnO (including Ref. 3) were due to surface oxidation of available analytical grade MnO. The MnO reference compound used in Ref. 7 was produced by oxidation of clean Mn in vacuo.

Based on the excellent agreement between the exhaust particulate and MnO multiplet splitting magnitudes, it is concluded that the oxidation state of the manganese in the combustor exhaust is +2 as MnO. Other Mn^{2+} compounds are eliminated by the fact that oxygen is the only negatively charged species present in sufficient concentration to stoichiometrically balance the manganese. XPS measurements of atomic ratios in the exhaust sample showed that the ratio of sulfur to carbon atoms increased from 0.047 for pure JP-4 fuel to 0.145 when the additive was used. It has been demonstrated¹⁰ that MMT strongly influences the size distribution in the exhaust, producing many more small particles. The resulting increase in the surface area available for heterogeneous reactions could explain the increase in the sulfur to carbon ratio¹¹.

It is interesting to note that the manganese oxide in the exhaust particles was stable over long periods of time in the ambient atmosphere, whereas the reagent grade powdered MnO is readily oxidized. Only when heated to 500°C for 10 min. in O_2 at 100 μ Hg total pressure, was the monoxide in the exhaust sample observed to form higher oxides. The stability of the particulate manganese suggests that the MnO is intimately associated with other components of

the exhaust particles. Since carbon is by far the most abundant constituent of the particles it is likely that the manganese monoxide is trapped in carbonaceous material which may form a barrier against further oxidation.

A neutron activation analysis of the exhaust samples was also obtained¹² which indicated that all the manganese added to the fuel was emitted. Knowing the amount of manganese emitted and the oxidation state as MnO , the mass of manganese monoxide emitted can be calculated. Since the total mass of particulate emissions is also measured, the mass of carbon emitted is immediately obtained. The resulting emission indices are shown in Fig. 3 as a function of additive concentration. Small amounts of the additive, less than 0.01% (vol.), decrease the

Fig. 3 Typical experimental results for the total particulate emission index. The solid line is an averaged total particulate EI. The carbonaceous EI is the difference between the total EI and the MnO EI.

emitted mass. However, at additive concentrations greater than 0.01% (vol.) both the total mass and the mass of carbon emitted increase. The carbon emission index reaches a plateau as additive concentration increases at ~ 1.7 gm/kgm fuel above the no additive level. A carbon deposition rate of ~ 1.6 gm/kgm of fuel has been reported for a similar combustor¹³. This leads to the conclusion that prohibition of carbon deposition within the combustion is the cause of the increased mass emission. Similar minimums in mass emissions at low additive concentrations have been observed for oil burning furnaces¹⁴ and power generating turbines¹⁵.

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