

Unexpected Fe local order in iron oxide-coated nanocrystalline magnesium oxides with exceptional reactivities against environmental toxins

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Mg oxide nanoparticles are very reactive materials used to mitigate atmospheric pollution and to sequester polluting molecules. Using Fe K-edge XAFS, we have studied the structure of iron oxide-coated MgO nanoparticles before and after reaction with CCl₄. Before reaction, the local structure around Fe is totally different from that in iron oxide coatings on SrO and CaO nanoparticles, although these coated materials were prepared in the same way. In SrO and CaO, the iron oxide coating has been shown to be well separated from the bulk of the nanoparticle, whereas in MgO, Fe was found to mix with MgO. After reaction with CCl₄, Fe-Cl bonds can be detected when the coated nanoparticle is saturated. Such Fe-Cl EXAFS signals have not been observed in previously studied nanoparticles.

Keyword: nanoparticle, atmospheric pollution, EXAFS structure, coating surface

1 Introduction

Atmospheric pollution is a major worldwide environmental issue that should be addressed at the molecular level. Solutions to atmospheric pollution problems present some risk, including the creation of other pollutants from incomplete incineration. For several years we have been working on an alternative approach that involves separation of the toxic part of a polluting molecule by using a reactive solid material such as alkaline earth oxide nanoparticles. Nanoparticulate MgO, SrO, and CaO are very reactive materials used for the absorption of polluting molecules like chlorocarbon compounds (Li et al., 1992). The process is not catalytic but is based on the possibility that the metal oxide will remove the heteroatom (Cl) from the atmosphere and immobilize it in the solid.

An important parameter affecting the reactivity of this process are the surfaces of the metal oxide nanoparticles. Two different means of sample preparation have been performed to obtain the most reactive product. The first, called "AP" preparation, is a sol-gel process followed by an aerogel hypercritical drying procedure (Kopper et al., 1993). The second is termed a conventional preparation (CP) which generates oxides from ex-hydroxides.

It is possible to increase the reactivity of the nanoparticles by adding a small quantity of iron oxide as a surface coating. The specific surface area for [Fe]AP-MgO is about 460 m²/g, whereas for [Fe]CP-MgO it is 203 m²/g (Klabunde et al., 1996).

In previous papers (Decker et al., 1998; Moscovici et al., 1999) we proposed a model for reactions between iron oxide-coated SrO nanoparticles and CCl₄, which assumes that adsorbed CCl₄ readily reacts with the iron oxide (Fe₂O₃) to form FeCl₃. Calculated heats of

formation suggest that FeCl₃ can in turn react with strontium oxide to regenerate the Fe₂O₃ species and form a strontium chloride salt.

The aim of this work was to study the surface structure of iron oxide-coated AP-MgO nanoparticles before and after reaction. Due to the small quantity of iron oxide on the surface, powder X-ray diffraction and TEM were unsuccessful in determining the location of Fe ions, and only the EXAFS method can provide structural information about the surface.

EXAFS study of MgO nanocrystalline powders follows our previous studies on similar iron oxide-coated SrO and CaO. In these two compounds, the local coordination environment of Fe before reaction was found to be similar to that in very disordered iron oxides (Decker et al., 1998; Moscovici et al., 1999). However, iron oxide-coated MgO is less reactive than AP-SrO and AP-CaO. Comparative local structural information on [Fe]AP-MgO is required to explain these differences.

2 Experiment and data analysis

We have studied iron oxide-coated AP-MgO nanoparticles before and after reaction with CCl₄. We chose powdered commercial samples of Fe₂O₃ and FeCl₃ as model compounds. The experiments were done with the two types of samples prepared after reaction with CCl₄. First, the amount of CCl₄ pulsed over the samples was in stoichiometric excess for both AP and CP, assuming that 100% of the MgO reacts to form a chloride salt. The second preparation corresponds to a reaction with a smaller quantity of CCl₄. The pulse of CCl₄ over the sample was stopped just before saturation. The experimental conditions of these reactions are described elsewhere (Decker, 1998). The EXAFS spectra were recorded at the Fe K-edge at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique), Orsay, France on the EXAFS 2 and EXAFS 13 workstations in transmission and fluorescence modes. All the samples were prepared in a dry nitrogen atmosphere in a glove box and recorded in an atmosphere-controlled sample holder. EXAFS data analysis was performed with "EXAFS 98" and "EXAFS pour le mac" programs (Michalowicz, 1996 and 1998). After Fourier filtering, the 1st and the 2nd single shell Fe-O and Fe-X (X = Mg, Fe) were fitted to the standard EXAFS formula without multiple scattering. The amplitudes and phases were extracted from calculated spectra by the computer program FEFF7 (Rehr et al., 1992). Complete FEFF modeling of Fe₂O₃, FeCl₃, Fe₂MgO₄, and MgO was carried out, and no multiple-scattering paths were observed in the 1st two shells (R < 3.2 Å) except for the tetrahedral site of Fe₂MgO₄.

3 Results and discussion

3.1 Before reaction with CCl₄

In spite of the non-reducing conditions of its preparation, we cannot rule out the presence of some Fe(II) ions in [Fe]AP-MgO. The Fe K-edge spectrum of [Fe]AP-MgO is close to that of Fe₂O₃ and is typical of Fe(III) in an octahedral site coordinated by oxygens (Fig. 1).

Figure 2 presents the EXAFS spectra of [Fe]AP-MgO, [Fe]AP-SrO, and Fe₂O₃. The spectrum of [Fe]AP-MgO is completely different from that of Fe₂O₃, indicating that the local structure around Fe in [Fe]AP-MgO doesn't correspond to that in Fe₂O₃. It is also different from the Fe local structure of the AP-SrO coating.

This difference is confirmed by the imaginary parts of the FT (Fig. 3). The 1st peak of the Fe EXAFS signal FT in AP-MgO coating corresponds to a Fe-O signal as for Fe₂O₃. The 2nd peak is out of phase with the 2nd peak of Fe₂O₃. Thus, it does not correspond to the same Fe-Fe signal as in Fe₂O₃.

In order to characterize quantitatively the Fe local order in [Fe]AP-MgO, we used two structural models – Fe₂O₃ and Fe₂MgO₄, which is a

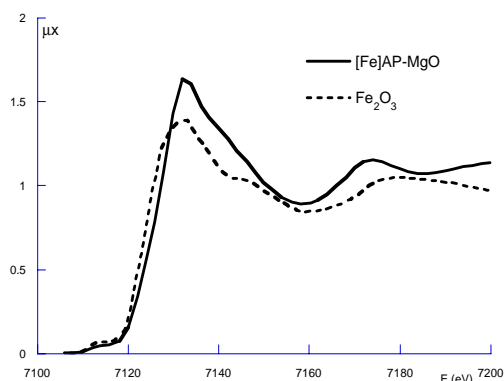


Figure 1
Edge spectra of [Fe]AP-MgO and Fe₂O₃

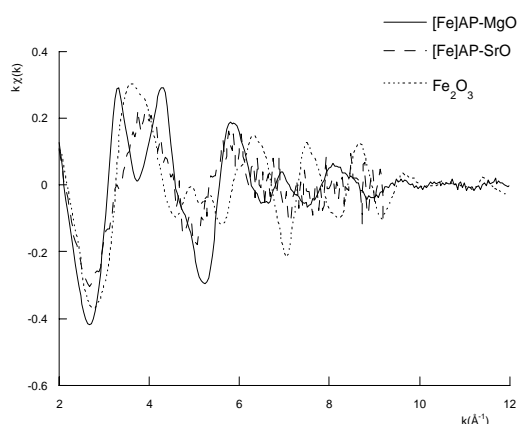


Figure 2
Fe K-edge EXAFS spectra of iron oxide-coated AP-MgO and AP-SrO and commercial Fe₂O₃ before reaction with CCl₄.

mixed Fe/Mg oxide with an inverse spinel structure (Wyckoff, 1963). In the later compound, Fe ions occupy both tetrahedral (T_d, Fe-O = 1.92 Å, Fe-Fe = 3.48 Å) and octahedral (O_h, Fe-O = 2.04 Å, Fe-Fe = 2.97 Å) sites. The fit of the 1st shell gives 6.8 O at 2.015 Å, which is compatible with an octahedral site.

For the 2nd shell, we tried either Fe or Mg. The results for these fits are given in Table 1. With only Fe neighbors at about 3 Å, the fit is unsatisfying, whereas for a shell of Mg, we obtain a significantly better fit (Fig. 4). The difference is due to the phase shift between Fe-Mg and Fe-Fe signals. The statistical F-test of this fit (Michalowicz et al, 1998) gives a probability of 86% in favor of a Mg shell at 3.03 Å. Fits with a mixing of Mg and Fe can also be done. Due to the increase in number of variable parameters and correlation effects, these fits are not reliable. If there is some Fe in the 2nd shell, the Mg contribution is clearly dominant. In [Fe]SrO and [Fe]CaO nanoparticles, the Fe local structures were found to be very disordered and weakly bound to the bulk (Moscovici et al, 1999 and Decker, 1998). In [Fe]MgO, we found an Fe local environment totally different from that of [Fe]SrO or [Fe]CaO. The Fe EXAFS spectrum is well ordered with a clear Fe-Mg correlations. Although the iron oxide coatings of the MgO, CaO, and SrO nanoparticles were deposited under exactly the same chemical conditions, insertion of Fe in MgO was found in the MgO nanoparticles. The Fe-O and Fe-Mg distances and number of neighbors

are close to those for the octahedral sites of Fe₂MgO₄, but a simple substitution of Mg by some Fe in MgO is also possible. It is impossible to characterize more precisely the location of iron at the surface or in the bulk of the MgO nanoparticles in this study.

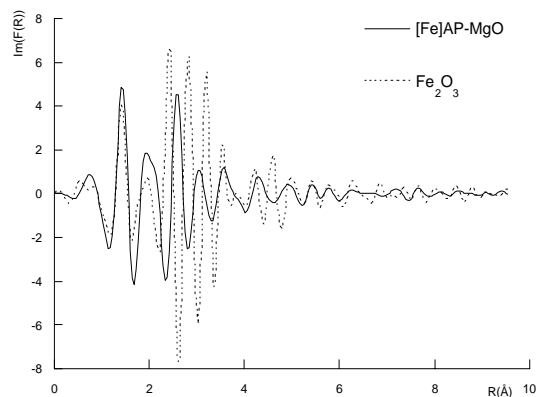


Figure 3
FT spectra of iron oxide-coated AP-MgO and commercial Fe₂O₃ at the Fe K-edge before reaction with CCl₄.

Table 1
Fitting results for 1st and 2nd shells of iron oxide-coated AP-MgO nanoparticles before reaction: N_{ind}=17, N_{par}=3, Δχ²=14 for Fe-Mg and Δχ²=27 for Fe-Fe.

	N	σ(Å)	R(Å)	ΔE ₀ (eV)
Fe-O	6.8 (6)	0.110(5)	2.015(12)	-3.31 (1.1)
Fe-Mg	7.6(1.8)	0.10(1)	3.031(14)	-0.32 (1.0)
Fe-Fe	14.36(2.0)	0.148(5)	3.172(11)	-3.01(1.0)

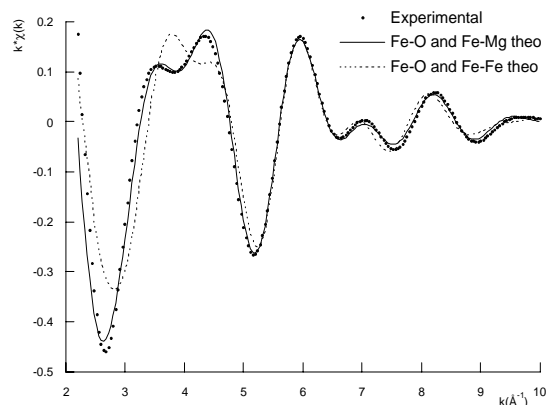


Figure 4
AP-MgO filtered experimental spectrum and theoretical best fit with Fe-O (1st shell) and Fe-Mg or Fe-Fe (2nd shell).

1.2 After reaction with CCl₄

Figures 5a and 5b present, respectively, the FT modulus of the Fe K-edge EXAFS spectra of [Fe]AP-MgO after CCl₄ reaction in the unsaturated and saturated modes. For the unsaturated compound, the only change is a slight disorder, which is represented by the small decrease of both Fe-O and Fe-Mg amplitudes (Fig. 5a).

For the saturated compound (Fig. 5b), the Fe-O and Fe-Mg peaks remain, but with a strong decrease in their amplitudes. In addition, a new peak appears just between the previous ones. Since the reaction of these nanoparticles with CCl₄ implies storage of chlorine, this peak is

assigned to a Fe-Cl pair correlation. This hypothesis is qualitatively verified in Figure 6 where the [Fe]AP-MgO and FeCl₃ FT spectra are compared. The position and the phase of this 3rd peak matches quite well with the FeCl₃ signal (Fe-Cl = 2.30 Å). Fitting this feature as a Fe-O pair correlation would lead to an abnormal distance (about 2.3 Å) for such oxides and a phase inversion impossible to correct with a reasonable E₀ shift.

As in [Fe]AP-MgO before reaction with CCl₄, the Fe local structure after reaction of [Fe]AP-MgO differs from those of [Fe]AP-CaO and [Fe]AP-SrO. In these cases, we have previously shown that the surface disordered structure is converted to ordered Fe₂O₃ upon CCl₄ reaction. No Fe-Cl bond was detected. In the present work, in contrast, we see a weak disorder effect or the presence of a Fe-Cl signal.

We have seen that the EXAFS spectrum at the Fe K-edge of [Fe]AP-MgO before reaction is unable to clarify where the Fe ions migrate inside the MgO nanoparticle. After CCl₄ reaction, the Fe local environment is not modified by the presence of chlorine until total saturation. A model with the Fe ions near the surface would explain this behavior more likely than a homogeneous Fe-MgO solid solution.

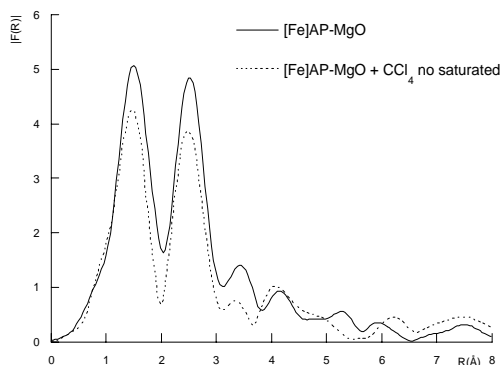


Figure 5a

FT Modulus spectra of coated AP-MgO before and after reaction with CCl₄ without saturation.

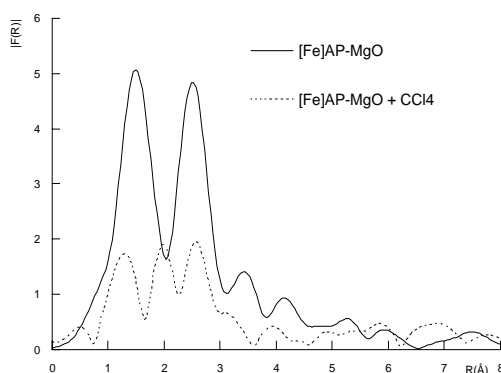


Figure 5b

FT Modulus spectra of iron oxide-coated AP-MgO before and after reaction with CCl₄ with saturation.

This model can be used to explain the differences observed in the reactivities of iron oxide-coated CaO and MgO nanoparticles for the

destruction of CCl₄, although their chemical preparations were identical (Table 2).

Table 2

Reaction ratio for destructive absorption of CCl₄ with Fe coated MgO and CaO

Sample	Reaction ratio (Mole CCl ₄ /Mole MO)
AP-MgO	0.17
AP-CaO	0.31
[Fe]AP-MgO	0.36
[Fe]AP-CaO	0.51

For CaO, the iron oxide coating leads to the maximum reactivity ratio (0.5 mol CCl₄/mol MO). The AP-MgO nanoparticles are less reactive (0.36). This difference may be due to the fact that Fe in MgO is a less efficient surface catalyst than the disordered Fe₂O₃ on the surface of [Fe]SrO and [Fe]CaO.

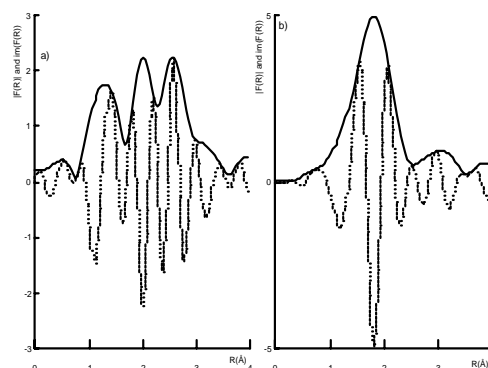


Figure 6

Complete FT spectrum of a) iron oxide-coated AP-MgO after reaction with CCl₄ in saturation and b) complete FT spectrum of the model compound FeCl₃

4 Conclusion

We have shown that the structural environment of Fe in iron oxide-coated MgO nanoparticles is different from that in coated SrO and CaO nanoparticles. In the case of [Fe]AP-MgO, it was possible to show that Fe occupies octahedral sites with a 1st shell of oxygens and a 2nd shell of Mg. We propose that Fe occupies sites near the surface of the nanoparticles. After reaction with CCl₄, chlorine does not coordinate Fe until saturation.

The particular Fe local structure found in these MgO nanoparticles is probably the reason for the less efficient reactivity for dechlorinating CCl₄. This result suggests that new coating methods are needed to obtain a better reactivity.

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