

J. Synchrotron Rad. (1999). **6**, 604–606

Alkaline earth oxide nanoparticles as destructive absorbents for environmental toxins

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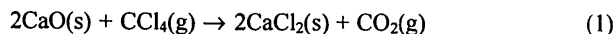
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Sr and Ca oxide nanoparticles are very reactive materials used to mitigate atmospheric pollution and to sequester polluting molecules. We have studied the structure of SrO nanoparticles, using Sr K-edge and Fe K-edge XAFS, that were prepared with various reactivities, with or without a Fe₂O₃ coating, and before and after reaction with CCl₄ or SO₂. For CCl₄, the polluting fraction of the reagent is totally absorbed in the bulk particle. For SO₂, the results show a total reaction for the Aerogel Preparation (AP) compound. For the coated particles before reaction, the iron oxide has a very disordered structure, and it is mixed with small metallic iron clusters for Conventional Preparation (CP) compounds.

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

1. Introduction

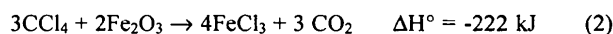
The principal method used to destroy atmospheric pollution particles and molecules is their incineration. Unfortunately, this method presents some risk of increasing pollution. One alternative process consists of destroying and sequestering the polluting species using a reactive solid material. Alkaline earth oxide nanoparticles have been chosen to be efficient materials for this purpose. These nanoparticles (MgO, CaO or SrO) are very reactive materials used for the storage of polluting molecules like organophosphor, sulfur or chlorocarbon compounds (Li et al., 1992). The process is non-catalytic but is based on the possibility of the metal oxide removing the heteroatom (Cl, P, S) from the atmosphere and immobilizing it in the solid as a nontoxic substance. As an example, equation 1 shows the reaction between the nanoparticles CaO and the toxic molecule CCl₄.



This reaction depends on the high reactivity and reaction capacity of the surface of the metal oxide nanoparticles. Two different ways of preparation have been performed to obtain the most reactive product. The first particle preparation method is a sol-gel process followed by an aerogel hypercritical drying procedure which we denote as AP nanoparticles (Aerogel Preparation) (Koper et al., 1993). The second method involves conventional preparation, denoted as CP. The specific surface area for the AP is between 140 and 500 m²/g whereas that for the CP is between 90 and 170 m²/g. For the commercial metal

oxide (SrO) the specific surface area is about 10 m²/g. In fact, the best reactivity with the AP-MO (M = Sr, Ca or Mg) is associated with the large surface area as well as the small size of the particles. Indeed, the size for the AP particles is less than 10 nm, versus 100 nm for the CP metal oxide

It is possible to enhance the reactivity of the nanoparticles by adding a small amount of transition metal oxides such as Fe₂O₃ as a surface coating (< 0.01 mole Fe₂O₃/mole CaO) (Klabunde et al., 1996). These overlayers provide a thermodynamic advantage that leads to enhanced interaction between the polluting molecule and the bulk nanoparticle reagent (eq. 2 and 3). For example, adsorbed carbon tetrachloride readily reacts with Fe₂O₃ to form FeCl₃. Calculated heats of formation suggests that FeCl₃ can in turn react with strontium oxide to regenerate the Fe₂O₃ species and form strontium chloride salt.



The aim of this work was to obtain more structural information about the effect of particle morphology on reactivity and about the CCl₄ and SO₂ decomposition mechanisms with coated and uncoated nanoparticles. Only XAFS can provide these results on the surface and bulk species. Indeed, others methods, like powder x-ray diffraction, have been carried out on these nanoparticles, but it was not possible to distinguish between the structures of AP and CP compounds. Indeed, Fe₂O₃ surface coatings were not detected.

In a previous paper (Decker et al., 1998), we have already reported some results concerning the nanoparticles before and after reaction with CCl₄. The new result presented in this paper is the structural behavior of the bulk and coated nanoparticles after reaction with SO₂.

2. Experiment

Using EXAFS spectroscopy, we have studied AP and CP SrO nanoparticles, with and without a Fe₂O₃ coating, and before and after reaction with CCl₄ and SO₂. We chose powdered commercial samples of SrO, SrCl₂, SrSO₄, FeCl₃, Fe₂(SO₄)₃ and FeS as model compounds. The EXAFS spectra were recorded at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique), Orsay, France on the EXAFS 3 and EXAFS 13 workstations in transmission mode for the Sr and Fe K-edges of the model compounds. The Fe K-edges of the coating were recorded in fluorescence. EXAFS data analysis was performed with the "EXAFS pour le mac" programs (Michalowicz, 1996). In this short publication, only qualitative results based on the discussion of the Fourier transform are presented.

3. Results and discussion

3.1 Sr K-edge

3.1.1 Before reaction

In a previous paper (Decker et al., 1998), we have shown that CP and AP SrO nanoparticles are much more disordered than commercial SrO. The first Sr-O peak is almost unchanged, but the second Sr-Sr peak is dramatically decreased. The AP compound, which is the most reactive, is also the most disordered. The decrease in amplitude of the Sr-Sr peak may be due partly to a decrease in number of neighbors for the surface

atoms. This surface effect is very well known in small particles. However, our nanoparticles are not small enough to explain totally the amplitude of this peak only by a decrease in number of neighbors. Moreover, the number of neighbors and Debye-Waller factors are highly correlated, and it is impossible to discriminate between surface and disorder effects just by fitting these two parameters. Figure 1 shows that a similar effect occurs for coated SrO AP and CP compounds. The corresponding EXAFS spectra are presented in Figure 2.

The EXAFS spectra of the uncoated SrO particles are affected by the so-called disorder effect and are similar to those of the Fe₂O₃ coated SrO samples.

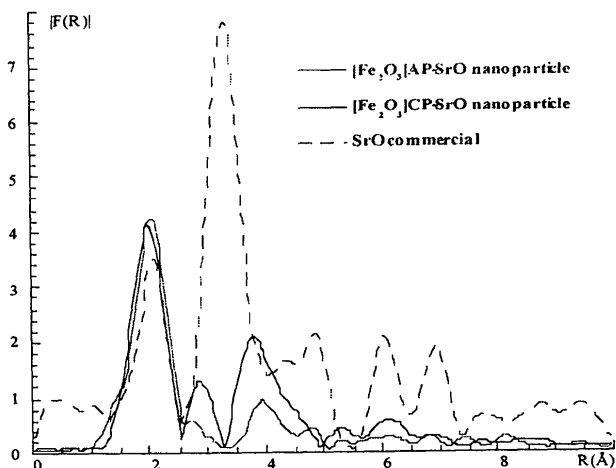


Figure 1
FT spectra of coated AP, CP-SrO and SrO commercial at the Sr K-edge before reaction

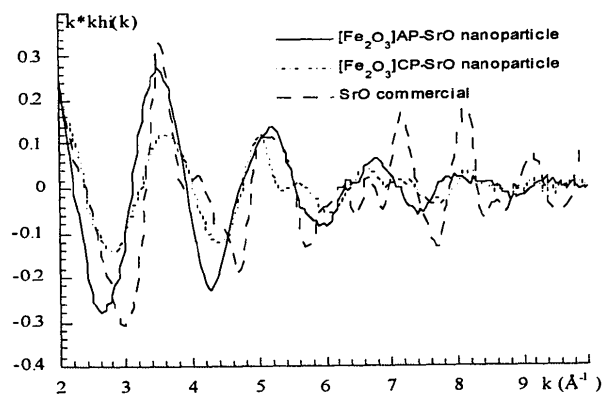


Figure 2
EXAFS spectra of coated AP-SrO, CP-SrO, and SrO commercial at the Sr K-edge before reaction

3.1.2 After reaction with CCl₄

We have proved in our previous paper that for AP-SrO the oxygen atoms are replaced by chlorine and the first coordination sphere is comparable to that of the standard SrCl₂. Because the reaction of CCl₄ with CP-SrO is incomplete, the signature of a small amount of oxygen is always present in the EXAFS spectrum. This peak disappeared for the coated CP-SrO compound (data not shown), confirming that the iron oxide coating enhances the reaction of the inner structural layer with CCl₄.

3.1.3 After reaction with SO₂

Figure 3 shows the results obtained on AP-SrO and CP-SrO after reaction with SO₂. Figure 3a shows the Fourier transform of AP-SrO after reaction with SO₂ and the Fourier transform of SrSO₄. The spectra of these two compounds are similar. From this result, it seems that the AP-SrO compound after reaction with SO₂ is essentially composed of strontium sulfate. Figure 3b exhibits the modulus of the Fourier transform of CP-SrO after reaction compared with the FT modulus of commercial SrO. We compare these two spectra because of the similarity in amplitude and position of the first-shell peaks. Unlike the AP-SrO compound, the CP nanoparticles do not react completely to form SrSO₄. The second Sr-Sr peak reappears, proving that a non-negligible part of the sample is recrystallized as Sr oxide. Results obtained for the coated samples are not presented since they show the same behavior.

3.2 Fe K-edge (coated species)

3.2.1 Before reaction

Figure 4 presents the Fourier transform spectra of coated AP-SrO and CP-SrO and the pure iron oxide (Fe₂O₃) before reaction. The corresponding EXAFS spectra are presented in Figure 5. These fluorescence spectra are quite noisy, reflecting the very small amount of Fe. However, it is possible to get qualitative information from these data.

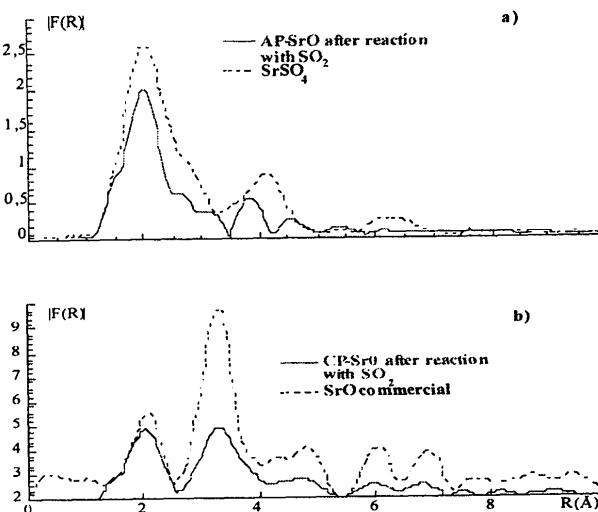


Figure 3
Fourier transforms of Sr K-edge spectra of uncoated AP-SrO and CP-SrO after reaction with SO₂ compared with SrO commercial and SrSO₄

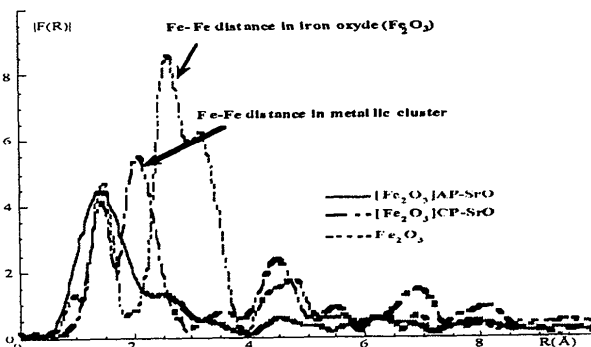


Figure 4
FT spectra of coated AP-SrO, CP-SrO, and Fe₂O₃ at the Fe K-edge

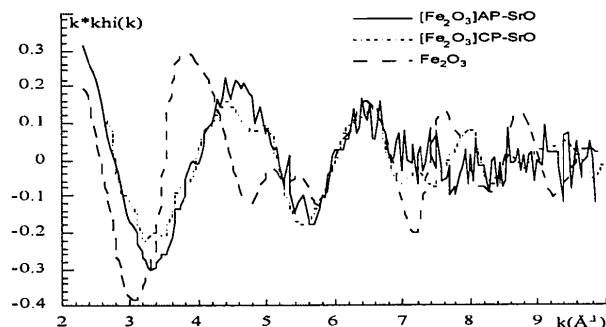


Figure 5
EXAFS spectra of coated AP-SrO, CP-SrO, and Fe₂O₃ at the Fe K-edge

The coated AP-SrO spectrum has been previously discussed (Decker et al., 1998), and has essentially one Fe-O peak with only very low amplitude features at high distances compared to commercial Fe₂O₃ (Fig. 4). This compound is typical of a very disordered iron(III) oxide. In contrast, the Fe K-edge spectrum of the CP-SrO coated sample before reaction has an extra peak at 2.5 Å (phase corrected). This peak is definitely not due to the standard Fe₂O₃ second shell (Fe-Fe). We interpret this new peak as the signature of a mixing of disordered iron(III) oxide with a non-negligible amount of metallic iron clusters. The partial reduction of Fe(III) into metallic iron during the coating process is due to the presence of graphite, a by-product of the decomposition of the acetylacetonate Fe(III) complex. We have also observed the presence of Fe metallic clusters in coated calcium oxide nanoparticles (unpublished results). It is notable that only this EXAFS work was able to detect the presence of Fe clusters on the nanoparticle surfaces. The amount of iron is too small to detect anything by powder diffraction. A possible catalytic role of these clusters is under discussion, but is not clear at present.

3.2.2 After reaction with CCl₄

We have already shown the comparison between [Fe₂O₃]AP-SrO and FeCl₃ (Decker et al., 1998, Figure 4), and we have proved that there is no Fe-Cl signal in the nanoparticle confirming that in the decomposition of the CCl₄, all the chlorine atoms migrate through the surface and replace bulk oxygen atoms by exchange. The main result of this previous study is that after reaction with CCl₄, the Fe₂O₃ coating forms well structured nanocrystals, invisible by XRD, but very well observed by the second characteristic Fe-Fe second peak.

3.2.3 After reaction with SO₂

Figure 6 shows FT spectra after reaction of AP-SrO and CP-SrO with SO₂. Figure 6a shows the Fourier transforms for coated AP-SrO, CP-SrO and Fe₂(SO₄)₃. Figure 6b shows the FT spectra of coated AP-SrO and FeS. In all of these samples, the Fourier transform consists essentially of a single Fe-O peak. From this result we conclude that: i) there is no Fe-S signal characteristic of iron sulfide, ii) by contrast with the reaction with CCl₄, there is no Fe-Fe correlation at 3 Å, characteristic of the recrystallization of Fe₂O₃, and iii) all metallic clusters have been oxidized, as indicated by the disappearance of the characteristic Fe-Fe peak at 2.5 Å. Unfortunately, it is impossible to discriminate between two possible structures for the iron coating after SO₂ reaction: either highly disordered Fe₂O₃ or Fe₂(SO₄)₃. Both have a similar first Fe-O peak, and a mixing of these two species is not impossible.

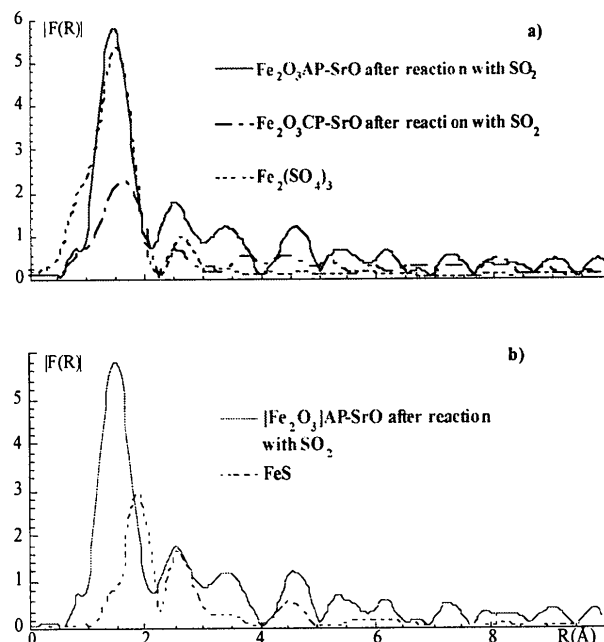


Figure 6
Fourier transforms the Fe K-edge EXAFS spectra of Fe₂O₃-coated AP-SrO and CP-SrO after reaction with SO₂ compared to Fe₂(SO₄)₃ and FeS

4. Conclusion

In this work and related work by Decker et al. (1998), we have confirmed that the local structure of the Sr ions in the SrO nanoparticles depends on the synthesis process, the most reactive compound being also the most disordered. As for the reaction with CCl₄ presented in previous work, the reaction of SrO with SO₂, has been shown to be total for the AP compound, independent of the presence of a Fe₂O₃ coating. For the CP compound, a partial recrystallization of SrO appears during the reaction with SO₂ (but not for CCl₄). It is impossible to characterize the local environment of Fe following the reaction of Fe₂O₃-coated nanoparticles with SO₂ as precisely as with CCl₄; in the later case, it was possible to confirm that the all of the Cl is stored in the bulk of the nanoparticle, without observable interaction with the iron surface coating. The crystallization of the surface iron(III) oxide was also detected. In the case of the reaction with SO₂, our EXAFS results cannot eliminate the possibility of some amount of iron sulfate remaining on the surface, and we have not seen any evidence of crystallization of Fe₂O₃.

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(Received 10 August 1998; accepted 28 January 1999)