	Experiment title: Reactivity iron oxide nanoparticles: existence of a nano-effect?	**Experiment number**: 30-02-905
Beamline: BM 30b FAME	**Date of experiment**: from: 23/04/2008 to: 29/04/2008	**Date of report**: 24/08/08
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REPORT

Aims of the experiment and scientific background

The market of manufactured nanoparticles is developing all over the world. Their physical properties (magnetic, optic, electronic, surface reactivity ...) are studied in order to improve technologies useful for medicine, electronic, catalysis, glasses, cosmetic... as well as for environmental purpuses. For instance, a greater reactivity is often ascribed to nanoparticles due to an elevated surface/volume ratio: more than 40% of atoms are at the surface of particle for diameters lower than 10 nm (1). Such differences in reactivity might be exploited to improve surface-based reactions in engineered systems (water treatment or soil remediation processes).

For instance Yean et al (2) have recently observed that iron spinel oxide i.e magnetite exhibits enhanced adsorption of arsenic capacity when the size of the magnetite decreases from 300 to 20 and 11 nm. But when the quantity of adsorbed arsenic is normalised per surface unit of solid instead of mass unit, magnetite particles of 300 and 20 nm adsorb similar amounts of As (i.e. ~6 mmol/m^2 = 3.5 As/nm^2) suggesting similar adsorption mechanisms and reactivity. But, for particles smaller than 20nm, the adsorption capacity increases and magnetite of 11nm adsorbs 3 times more As per nm^2 (~18 mmol/m^2= 10.9 As/nm^2) than does 20 nm-diameter magnetite (2). This increase adsorption quantity per surface unit suggests different adsorption mechanisms and reveals a particular "nano-effect" but its origin remains unclear. Such nano-scale effect has also been observed for the adsorption of Co ions on magnetite. But to go further in term of adsorption mechanisms, it is necessary to rigorously characterize the mechanisms of adsorption at the surface of nanoparticles below 10nm. Therefore the aim of our project was to study the mechanisms of cobalt adsorption at the surface of nano-maghemite at various surface coverages and for particles with different sizes ranging from 20 to 6 nm.

First Results

Previous experiments performed on the FAME beamline concerning the adsorption of AsIII on 6 nm maghemite (γ-Fe2O3) revealed an enhanced adsorption capacity compared to 20 nm

maghemite (3) as it was previously reported in the literature of magnetite (Fe_3O_4). So it seems that this nano-effect exists for iron oxides with various redox states.

In a recent paper, we have determined that two parameters contribute to this 'nano' effect. The first one is related to a modification of the atomic structure of the surface of particles when the size decreases (4). In the particular case of nano-maghemite, the size-dependant decrease of the occupancy of the tetrahedral site leaves vacant high reactive sites, which are available to adsorb arsenic such as a site localized in a sixmembered iron octahedral ring. The second parameter is related to the thermodynamic of nano-system and the decrease of the surface free energy for nanoparticles smaller than 10 nm. Therefore, the saturation of the nano-maghemite surface by AsIII can be considered thermodynamically as a crystal growth (3).

To extrapolate our results it is crucial to study the adsorption of various metalllic cations with various charges and coordination environment. In the case of cobalt our first results indicate that the quantity of cobalt adsorbed on 8nm nanomaghemite ranges from 0.02 to 5 mmol/g depending on the surface surface coverage of maghemite and the size of the maghemite (1 to 25 Cobalt atoms per nm^2). At saturation the quantity of cobalt adsorbed is at least twice the amount of arsenic per spinel surface nm^2. Such high quantity of cobalt can not be explained by only one monolayer of cobalt atoms (10-12 at maximum on Fe spinel). Therefore the hypothesis of surface precipitation of a Cobalt phase (Co hydroxide, Co oxide, Co ferrite) or cobalt diffusion into the spinel matrix via Co-Fe replacement become realistics.

Experiments

The initial goal was to perform EXAFS experiments at the Co K edge on the Fame beamline. For each nano-maghemite (6, 12 and 20 nm) we wanted to examine the cobalt surface structure at various surface coverages.

First experiments using a multi-element fluorescence detector revealed that the fluorescence of iron (the so called "matrix effect") was extremely high, even higher that expected. This lead to a real dilema : the high fluorescence from iron imposed to put off the detector from the sample. But by doing so the signal from adsorbed cobalt was low. The use of filters just slightly improved the Cobalt fluorescence contrast. Therefore the signal was more noisy than expected leading to very high counting time. Therefore we only scanned high maghemite and magnetite surface coverage (100 %). The XANES and EXAFS spectra at the Co K edge are presented in the next figure and compared to reference spectra.
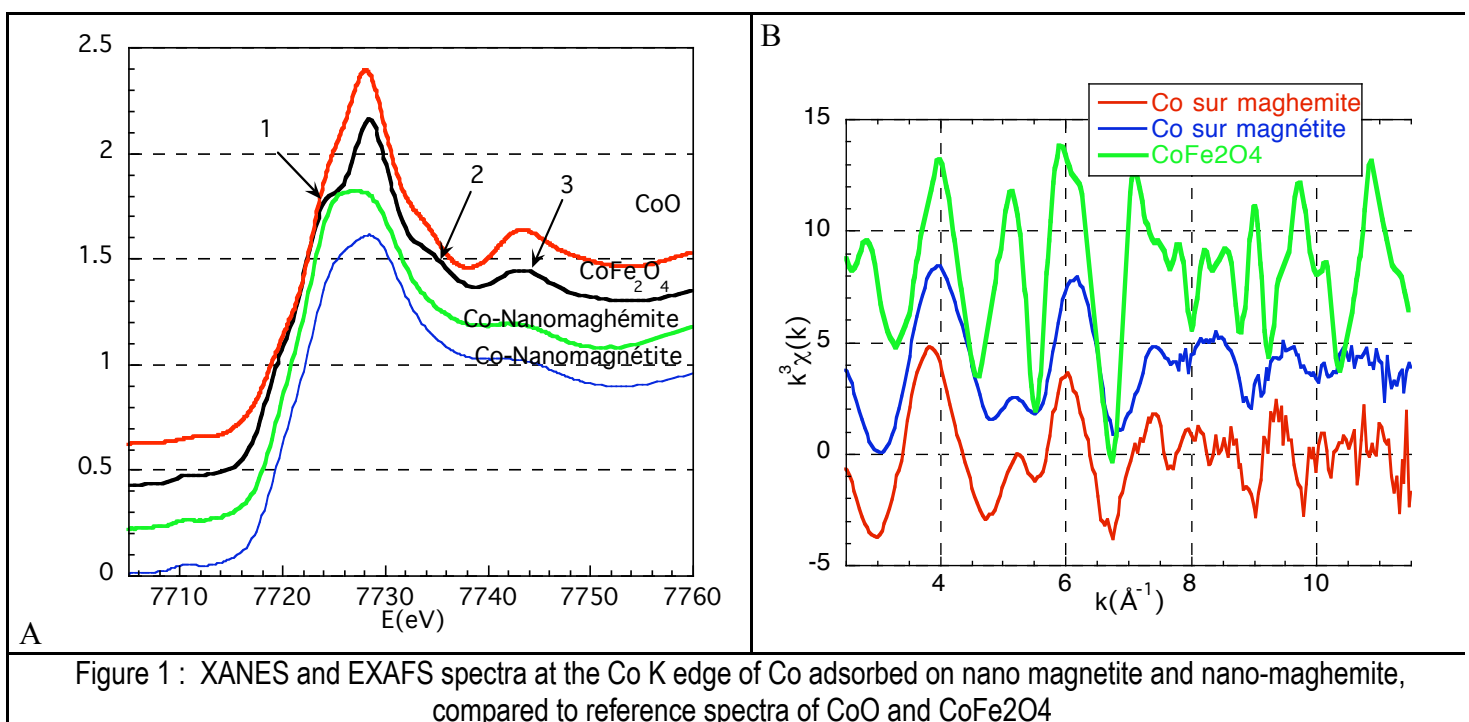

Figure 1 : XANES and EXAFS spectra at the Co K edge of Co adsorbed on nano magnetite and nano-maghemite, compared to reference spectra of CoO and CoFe2O4

First it is while noting that both the EXAFS and XANES spectra of both samples (Co adsorbed on nano-maghemite and Co adsorbed on nano-magnetite) are very similar but quite different from refence samples. The spectra of Co adsorbed on iron spinel are different from pure cobalt oxide and cobalt ferrite (Cobalt in the spinel structure). The first EXAFS modellings tend to indicate that cobalt is in tetrahedral and octahedral sites surrounded by iron and/or cobalt at 2.95 and 3.45 Å respectively. Such atomic environment may support an epitaxial adsorption of cobalt on iron spinel. The low number of second neighbours (Co and/or Fe) is more in agreement with adsorption than cobalt diffusion (atomic structure of pure $CoFe_2O_4$). But due to the noisy character of the curves it is difficult to accurately recalculate both EXAFS spectra. More over since only high surface cobalt surface coverage were investigated we are far from a complete vision of the sorption mechanisms.

In agreement with the coordinator and other investigators we therefore decided to somehow modify our initial plan and strategy. Indeed we realised that the use of the 30 elements fluorescence detector was limited by the fluorescence of the matrix. With such experimental setup it was almost impossible to study low nanoparticule surface coverage. We decided to take advantage of the new X-ray emission spectrometer developed on the FAME beamline to study the evolution of the iron matrix with size and determine the sensitivity of the emission spectrometer. Indeed the iron spinel magnetite and maghemite are very sensitive to adsorbed species. For example our first results tend to indicate that Cobalt while initialy octaherally coordinated, may be adsorbed in the tetrahedral coordination. Such mechanism may result from exchange with iron tetrahedra from the spinel surface. More over Cobalt may exchange electron with the iron spinel as stated in the litterature (reduction of iron and oxidation of cobalt).

First the sensitivity of the X-ray emission spectrometer enabled to distinguish Fe2+ and Fe3+ (figure 2). Then we have shown that the scan of the XANES spectra using the Kbeta fluorecence line lead to a more structured XANES (figure 3).
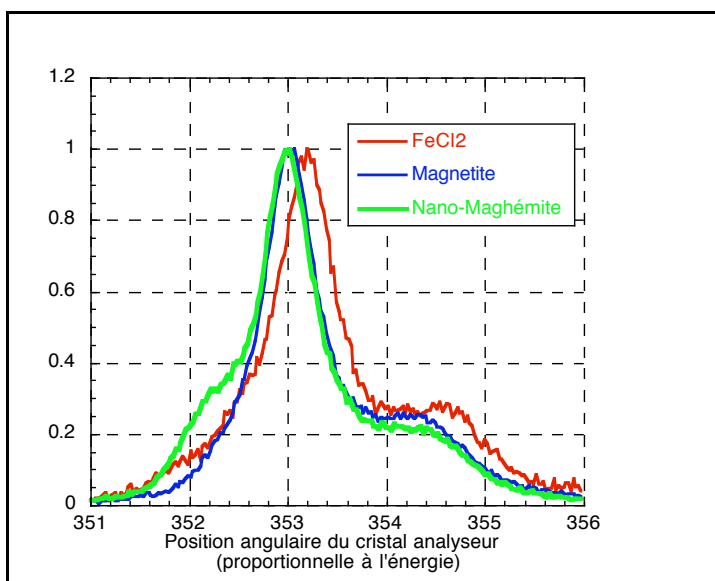

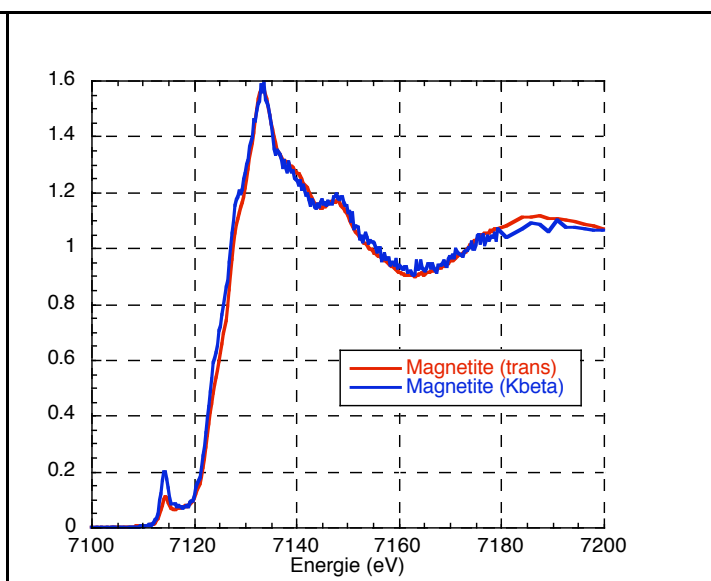| Figure 2 : emission spectra of Various iron redox states	Figure 3 : XANES spectra scanned in transmission mode and using the Kbeta emission line.

The enhancement of the different features of the XANES is extremely important to better determine both the redox state and the symetry of Fe sites.

Then we have shown that the use of the X-ray emission spectrometer is more adapted to study the structure and reactivity of spinel nanoparticles. The next step will be to record the Co K edge XAS spectra using the X-ray emission spectrometer. This will eliminate the matrix effect and enhance the XANES features.

References.

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