REPORT on Experiment ME-600:

EXAFS study of Cadmium adsorption on nickel particles in an aqueous medium

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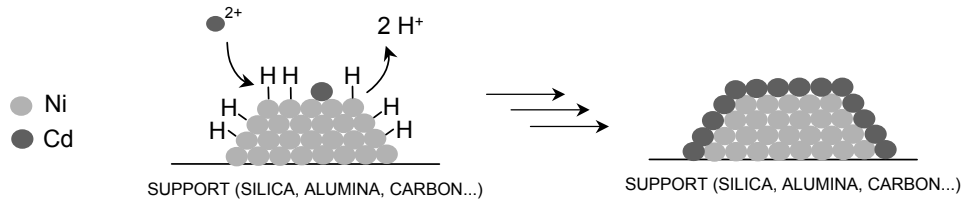
ID 26 / November 26th – December 2nd 2004

For this project we came a first time in June but the beam was not available because the monochromator crystals installed were broken. Thanks to Thomas Neisus we came back on ID 26 from November 26th to December 2nd 2004. Armida Sodo was our local contact.

The measurements were carried out in a glass cell equipped with a kapton window and on the top of which were connected a pH and a temperature probes, syringes, for the introduction of chemicals ($CdCl_2$ and NaOH solutions) via cannula and an inlet and an outlet for hydrogen. In the bottom part of the cell, a suspension of particles of alumina supported nickel catalysts were stirred in water with a magnetic stirrer under a slow bubbling of hydrogen (10 ml/mn)). This experimental set-up used to control the amount of cadmium adsorbed on the nickel particles worked fine. However when we tried to record data under stirring, the spectra obtained were too noisy due to the movement of the particles and to the magnetic field created by the stirrer (attraction of the Ni loaded powder on the magnetic stirrer). The samples were then studied *in-situ* but without stirring, once the powder had decanted and high quality data were obtained.

The samples were studied at the Cd K edge (26.711 KeV), using a Si(220) monochromator. A well characterized Ni/Al_2O_3 catalyst (59 wt % Ni; 50-100 Å particle size determined by magnetism; Ni dispersion = 8% from H_2 chemisorption measurments) was used as adsorbent for cadmium removal in water. We followed the evolution of the spectrum with the amount of cadmium adsorbed on the nickel catalyst:

$$2\ \text{Ni-H} + Cd^{2+} \rightarrow Ni_2Cd + 2\ H^+$$



The spectra of several samples were analysed either with the suite of programs developed by A. Michalowicz (using theoretical phase and amplitude files generated by FEFF7 based on model clusters in which atomic positions were taken from the crystal structure of the most similar complexes) or with PAXAS and EXCURVE programs. The

results obtained for the Cd-O or the Cd-Ni distances, the number of neighbours and the Debye-Waller factors were very similar whatever the type of program suite used for the data analysis. A representative spectrum corresponding to Cd/Ni_S = 0.1 (cadmium amount effectively adsorbed per surface nickel atom) I represented on figure 1.

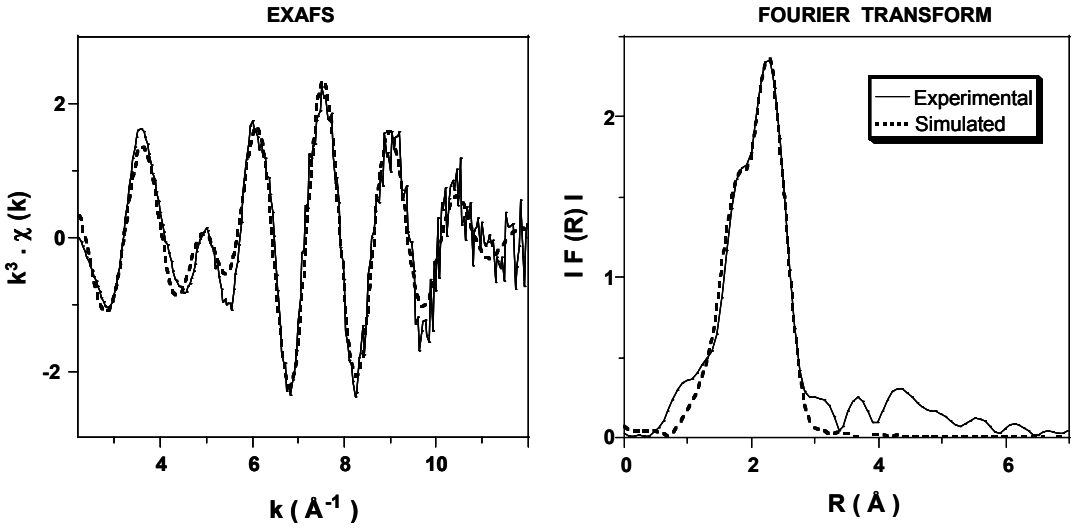


Figure 1: Cd K-edge k^3-weighted EXAFS signal (left) and its Fourier transform (right) for a Ni/Al_2O_3 sample on which 0.1 monolayer eq. of Cd has been deposited (Cd/Ni_S = 0.1). Points: experimental, solid lines: spherical wave theory. Fit residue, ρ = 4 %.

$Cd_{grafted}$ / Ni_s	Neighbour	Number of Neighbors	Distance to Cd (Å)
0.05 - 0.6	Ni	3.0 – 4.0	2.61 – 2.64
	O	2.0 – 2.5	2.24 – 2.26

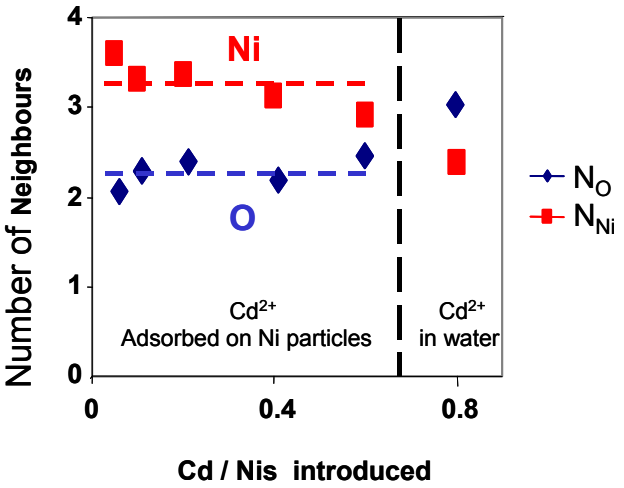


Table 1 and Figure 2 : Evolution of the coordination sphere of cadmium with the amount of cadmium grafted on the nickel particles.

On Table 1 and Figure 2 are shown the results concerning the coordination sphere of cadmium and its very weak evolution with the amount of cadmium grafted on the nickel particles. The results were very similar when a large excess of $MgCl_2$ was introduced at the beginning of the experiment in order to saturate the alumina surface. The oxygen contribution then don't seem to come from a Cd^{2+} adsorption site on alumina. The XANES is currently under study but a precise analysis is uneasy due to the fact that the stability in energy of the beam was not very good, even during one scan.

In conclusion, we could thus validate the mechanism proposed for the reduction and chemisorption of cadmium to form a maximum of one monolayer on the nickel particles (in particular, formation of Cd-Ni bonds were demonstrated) and propose a first model to describe the cadmium adsorption on nickel particles (Figure 3).

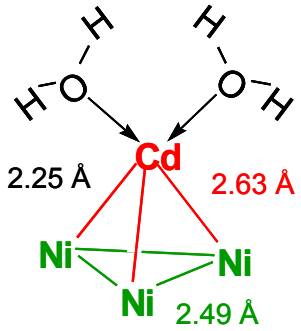


Figure 3: Local model proposed for cadmium adsorption on nickel particles