Following the reduction under H₂ of supported cobalt catalysts through the *L* absorption edges

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Soft X-ray absorption experiments have been performed on industrial cobalt containing catalysts, known to be effective in the Fischer-Tropsch synthesis. Firstly, we have studied a set of reference compounds CoO, SiCo₂O₄ and Co₃O₄ and numerical simulations based on the multiplets theory have been done in order to simulate their Co $L_{III,II}$ absorption spectra. Then, Co $L_{III,II}$ absorption spectra obtained on two Co based catalysts are discussed.

Keywords : electronic state; Co; Catalysts.

1. Introduction

In heterogeneous catalysis, synchrotron radiation related studies have allowed correlation of catalytic activity to structural characteristics for monometallic and multimetallic systems supported on different high specific surface light oxides (Bazin et al., 1989; Guyot-Sionnest et al. 1991).

Most of these experimental results have been obtained using photons with an energy around 10 - 20 KeV corresponding to the K edge of 3d and 4d transition metals and to L edges of 5d transition metals (Bazin et al., 1995, Bazin et al., 1997).

In this work, we report soft X-ray absorption experiments performed on cobalt containing catalysts, known to be effective in the Fischer-Tropsch synthesis (Khodakov et al., 1997).

2. Preparation of the catalysts

Two Co supported catalysts (cobalt loading 13%wt) were studied. High surface area silica was impregnated with cobalt nitrate solution to incipient wetness. The samples were then dried for 24-48 h at 373 K and calcined for 3 h at 873 K. After calcination part of the solid was reduced under H₂, passivated and saturated with water before being recalcined.

The samples were then characterised by XRD (Cu(Kα)). From the analysis of the EXAFS oscillations beyond the cobalt K edge, these two samples have been designed as "Co₃O₄"/SiO₂ and a-"SiCo₂O₄"/SiO₂.

The first one, the "Co₃O₄"/SiO₂ is associated with the presence at the surface of the carrier of large clusters of Co₃O₄.

For the second sample, an amorphous phase close to SiCo₂O₄ has been identified on the support.

3. Experimental conditions

EXAFS spectra were collected at the LURE synchrotron facility in Orsay using the synchrotron radiation from the SuperACO storage ring running at 800 MeV with an average current of 300 mA and a lifetime of 5 hours.

The SA 22 beamline placed after a bending magnet is equipped with a high-resolution plane grating monochromator (P.G.M. 12m) coupled with a spherical focusing mirror. The monochromator resolution was about 0.15 eV (fwhm) for the cobalt L_{III} edge.

The spectra were recorded in partial electron yield mode and were corrected for beam intensity variations during measurements using the secondary electron emission from a golden grid. Finally, data were normalised according previous works (De Groot, 1994).

4. Results obtained on the reference compounds : CoO, SiCo₂O₄ and Co₃O₄.
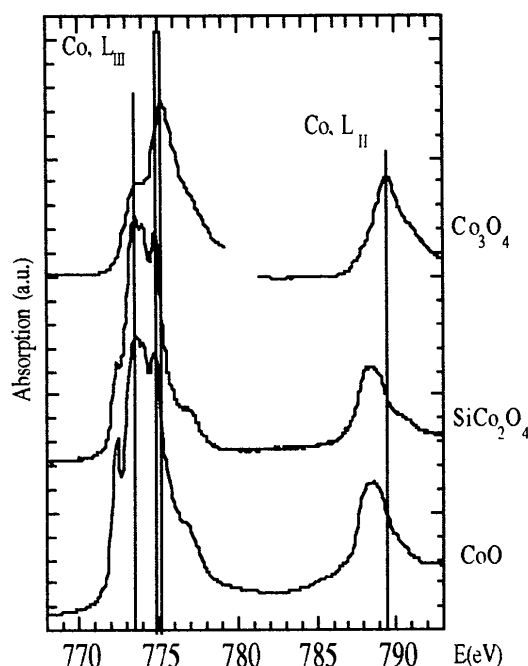
Figure 1
Co $L_{III,II}$ edge normalised spectra of several reference compounds (CoO, SiCo₂O₄ and Co₃O₄).

The L edge spectra can be divided in two parts, denoted as L_{III} and L_{II} because they are dominated by respectively $2p_{3/2}$ and $2p_{1/2}$ character of the core hole.

Figure 1 displays the Co 2p X-ray absorption spectra of the different reference compounds namely CoO, SiCo₂O₄ and Co₃O₄. A salient point is the large amount of fine structure.

The spectra of the compound CoO (obtained from Co₃O₄ after an heating process at 500°C during 10 hours under high vacuum) is in line with previous measurements (Van Elp et al., 1991, De Groot, 1994). At this point, we just recall that for this compound (Co²⁺, Oₕ), the ground state is described as a state with a single configuration of $3d^7$ character with high spin $^4T_1$ symmetry. The influence of $3d^8L$ character is neglected. The Co L_{III} spectra as well as

the Co L_{II} spectra of the two reference compounds CoO and $SiCo_2O_4$ are very similar. This experimental fact indicates that the valency of the cobalt atoms as well as the symmetry of the site are the same, a result in line with the crystallography.

The recent advances in theoretical background related to soft X-ray experiments has motivated a set of numerical simulations shown on figure 2 corresponding to the following configurations : Co^{2+} T_d, Co^{3+} O_h and Co^{2+} O_h. These calculations show the great sensitivity of 2p spectroscopy with the valence state of the cobalt atoms as well as the symmetry of the site. Note that the major features of the Co $L_{III,II}$ spectra of $SiCo_2O_4$ (and thus CoO) have been significantly reproduced (Co^{2+}, O_h).

Nevertheless, the absolute energies of the Co^{2+} and Co^{3+} spectra are calculated in case of isolated ions and thus due to electronic screening effects in solids, these numbers are shifted by some electronvolts.

Finally, regarding the spectrum of Co_3O_4, as previously noted, its structural crystallography indicates that the spectra is the result of a mixing of Co^{2+} (T_d) and Co^{3+} (O_h).
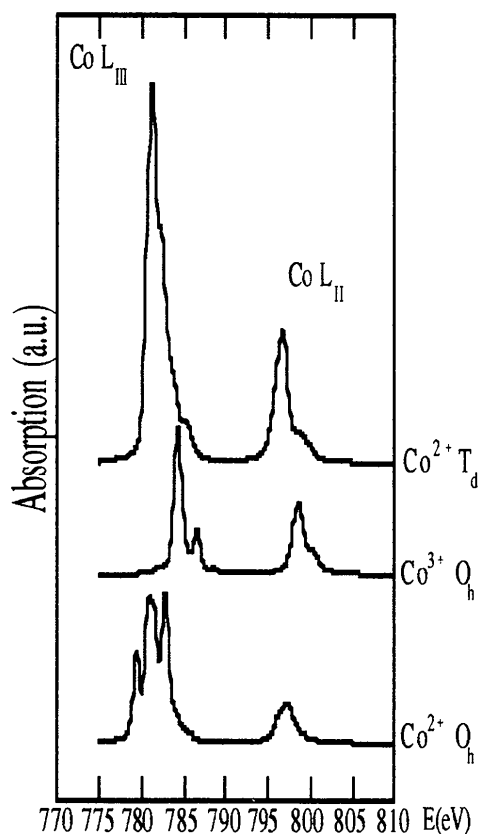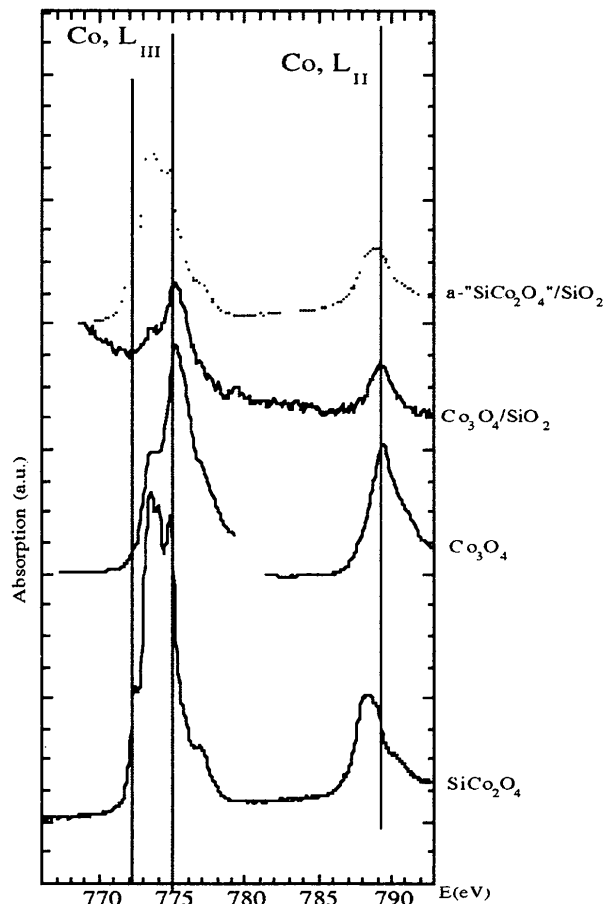

Figure 2
Numerical simulations done using the multiplet theory for the cobalt.

5. Results on the different catalysts : "Co₃O₄"/SiO₂ and a-"SiCo₂O₄"/SiO₂.

The Co $L_{III,II}$ edges of the first catalyst namely "Co₃O₄"/SiO₂ are shown in figure 3. We have found that consistent with our previous results obtained at the Co K edge, this cobalt based catalyst contains a large number of Co₃O₄ clusters. The Co L_{III} edge contains two structures, a measurement very similar with the spectra obtained for the Co₃O₄ reference compound. It is clear thus that for this catalyst, Co

atoms are both in the Co^{2+} (T_d) and Co^{3+} (O_h) electronic state. Note that a small shift is observed for the Co L_{II} edge if a comparison is made between this catalyst and the reference compound Co₃O₄.

Regarding the second catalyst, namely a-"SiCo₂O₄"/SiO₂, the Co L_{III} edge looks very close to SiCo₂O₄ (or CoO). Cobalt atoms seems to be thus in the Co^{2+} electronic state, the symmetry of the first oxygen coordination sphere being octahedral.

Figure 3
Co $L_{III,II}$ edge normalised spectra of reference compounds and catalysts.

6. Discussion

We can consider also the absorption length of the photoelectron. Its high value at low kinetic energy allows multiple scattering processes and for the K edge of 3d transition metal for example, the calculation is done on the scattering of the emitted electron.

It has been already shown that the size of the cluster change the morphology of the absorption K edge (Bazin et al. 1996, Wu et al. 1997).

In multiplet calculations, one completely forgets how the electron will scatter, and one 'only' calculates the dipole transitions themselves (that the neighbours are oxygen is not taken into account explicitly). The fact that the oxygen atoms break the symmetry from atomic to cubic (octahedral) is used and thus the L edge calculation is quasi-atomic. The crucial extra ingredient with respect to multiple scattering is the large overlap of the core and valence wave functions.

We can also compare this soft X-ray approach to more conventional one such as ELNES (Energy Loss Near Edge Structure). In a previous study. the ELNES of a set of reference oxide have been used as a fingerprint (Szymansky & Payen, 1990). The spectra of the compound Co_3O_4 illustrates one major limitation of this electron related technique. Increasing the number of energy scans to improve the noise level has modified the Co $L_{3,2}$ profile through a reduction of a part of Co^{3+} species.

7. Conclusion

If K level edge and EXAFS can be considered as a tool in material science, soft X-ray absorption spectroscopy can give some specific information (Koningsberger & Prins, 1988). More precisely, we have shown that major electronic information are available through the measurement of $L_{III,II}$ Co edge even on true industrial catalysts.

This new opportunity is surface sensitive (due to the low value of the photon absorption length), give the electronic state as well as the symmetry of the metal atoms (through multiplet calculations) and is non destructive (versus ELNES).

Moreover, due to the sharpness of the different features present at the Co $L_{III,II}$, we have shown that it can be used also as a phase sensitive method. All these particular advantages indicate that soft X-ray experiment will be probably consider as an invaluable technic with the confluence of better source, monochromators detectors and theoretical procedure.

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