

Standard Project

Experimental Report

Proposal title: Site-selective XES study of Al₂O₃-supported Ni catalysts		Proposal number: 30-02-1013
Beamline: BM30B	Date(s) of experiment: from: 02.06.11 to: 06.06.11	Date of report: 9.12.11
Shifts: 12	Local contact(s): Jean-Louis Hazemann	<i>Date of submission:</i> 13.12.11

Objective & expected results (less than 10 lines):

Nickel is a metal known for its catalytic activity in the hydrogenation of organic molecules. It is used as reduced Ni(0) nanoparticles dispersed over an oxidic support, such as γ -alumina, in order to maximize the number of surface atoms which are potential active sites. However, the metal is often present under two forms, i.e. metallic and oxidic, on the support. These two forms can be hardly characterized separately when supported phases are much dispersed, even by X-ray absorption spectroscopy, because EXAFS signals are superimposed. We have aimed here at implementing X-ray emission spectroscopy as a tool to discriminate between phases containing nickel in these oxidation states. The results we present below were obtained on reference compounds and commercial Ni catalysts. We show that recording signals in the fluorescence mode at two different emissions of nickel is feasible and that comparison between signals allows us to significantly decrease the observed contribution of metallic nickel both from the XANES and EXAFS standpoints.

Results and the conclusions of the study (main part):

Three series of samples were characterized during the run:

. reference compounds: NiO, supplied by Aldrich, NiAl₂O₄, prepared by coprecipitation of nickel and aluminium nitrate and calcination at 900°C; Ni/active carbon, prepared by deposition-precipitation and reduction, standing for the reference of reduced Ni nanoparticles (XRD)

. reference catalysts: a commercial Ni(60 wt%)/SiO₂-Al₂O₃ catalyst, supplied by Aldrich, and characterized both under its as-received form (mixture of NiO and Ni nanoparticles, XRD) and its fully oxidized form after thermal treatment in air; a Ni(10 wt%)/Al₂O₃ catalyst prepared by deposition-precipitation on alumina, and characterized under its fully reduced, partly reduced and fully oxidized forms.

. Ni/Al₂O₃ catalysts prepared with organic additives and currently tested at the IFP-EN in the framework of Faiza Bentaleb's PhD. Because of the time needed to record spectra on all reference samples, they could not be studied by X-ray emission spectroscopy; however, two spectra were recorded for each of them, in order to provide XAS data in the conventional transmission mode.

All samples were used as pellets after dilution in BN (2 to 9 mg of samples, pellets of 45 mg).

XES spectra were recorded at the K $\beta_{1,3}$ and K β' fluorescence lines (8.267 and 8.254 keV respectively), using the spectrometer developed recently on the FAME beamline (Hazemann et al JSR 2009) with the Si(444) reflexion. The K β line has been interpreted as a radiative transition by a spin-up electron, while the 6 times less intense K β' line originates from a transition involving a spin-down electron (H. Shoji et al., Jpn. J. Appl. Phys., 38, Suppl 38-1, 592, 1999). The K β' line is absent from the emission spectrum of metallic nickel; however, the Ni(0) K β line is strongly asymmetric and an attenuated signal, similar to that recorded at the K β energy, is still recorded at 8.254 keV.

Scan parameters were 1 eV between 8.2 and 8.32 keV (pre-edge); 0.3 eV between 8.32 and 8.375 eV (XANES); and in k-step of 0,05 Å⁻¹ between 8.375 and 9 keV. The peak of nickel inelastic scattering was recorded in all cases, in order to calibrate the signals in energy. Because the signal to noise ratio was low, a minimum of three scans were recorded at the K β line and six scans at the K β' line. Depending on the quality of individual data, the total time needed to complete measurements on one sample was between 10 and 12h, including about 1h30 to check energy calibration and set up the detector positions.

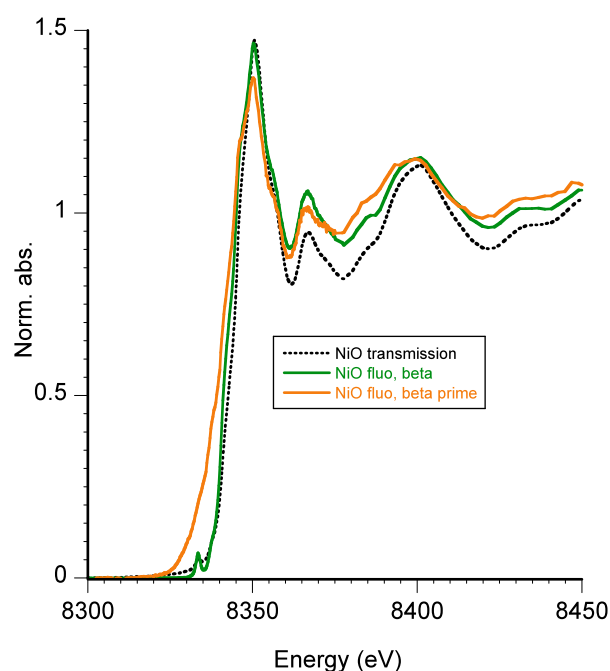


Fig. 1: XANES spectra of NiO recorded in the transmission mode and in the fluorescence mode at the $K\beta$ and $K\beta'$ lines

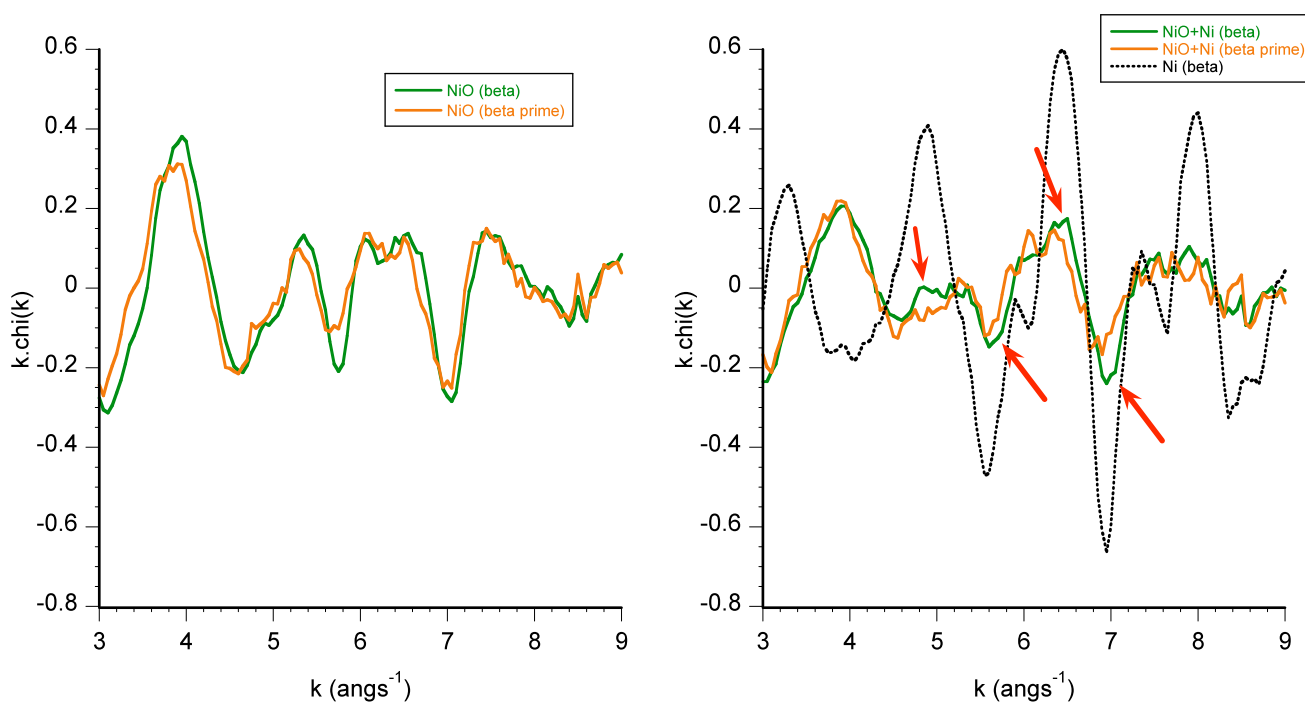


Fig. 2: Comparison of the EXAFS oscillations recorded at the $K\beta$ and $K\beta'$ lines for fully oxidized (left) and partly reduced (right) Ni/SiO₂-Al₂O₃ catalysts

While XANES spectra recorded on oxidized systems at the $K\beta$ line are very similar to those recorded in transmission (Fig.1: note the pre-edge peak clearly visible on the green curve), XANES spectra recorded at the $K\beta'$ line lack of any pre-edge feature. This trend appears to be characteristic of the $K\beta'$ emission of Ni²⁺, because XANES spectra recorded at the two energies on reduced metallic systems (which do not emit $K\beta'$ fluorescence) are similar. The white line is also less intense at the $K\beta'$ line. EXAFS oscillations of quite similar intensities are extracted for the two emission spectra. The positions of the peaks on the Fourier transform are consistent with FEFF modelling, and they are also consistent between samples of identical chemical nature (for

instance, NiO-containing samples). Due to a lesser intensity before normalization, oscillations are somewhat noisier at the $K\beta'$ emission, leading to less defined features on some Fourier transforms above $R=3 \text{ \AA}$, compared with $K\beta$. Some minor shifts of the oscillations (and consequently of the peaks on the FT) are sometimes detected (see Fig 2. left, between $k = 3$ and 4 \AA). The first peak on the FT usually exhibits the same intensity, regardless of the emission line. The peak of next-nearest neighbours significantly decreases on the $K\beta'$ emission spectrum, compared to $K\beta$.

The most striking result was obtained on the catalyst supported on silica-alumina. Oscillations recorded at the $K\beta$ and $K\beta'$ lines on the fully oxidized sample are very similar (Fig. 2, left). In contrast, EXAFS signals recorded on the partly reduced sample exhibit significant differences (Fig. 2, right). While contributions arising from metallic nickel are seen at the $K\beta$ line, as is the case for the transmission spectrum (red arrows), they are greatly reduced on the signal recorded at the $K\beta'$ line, in agreement with the lower response of metallic nickel at that energy. The strong decrease of the Ni contribution on the FT is obvious (Fig. 3, red arrow). Differences are not as marked on the $\text{Ni}/\text{Al}_2\text{O}_3$ sample, probably because of a lower content in metallic Ni in the partly reduced sample; nevertheless, differences in the imaginary part of the FT are visible between $R = 1$ and 2.5 \AA .

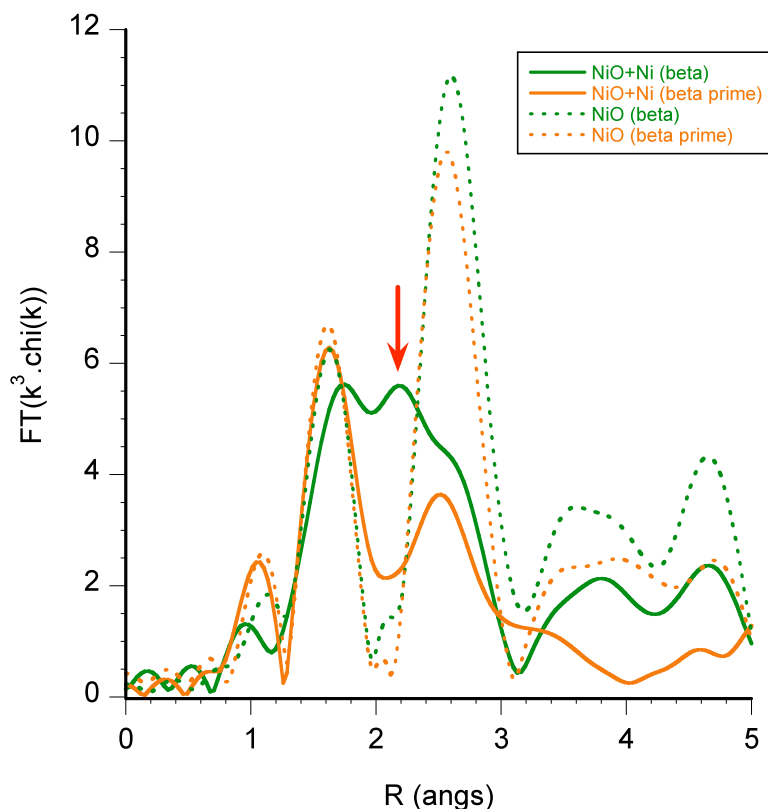


Fig. 3: Comparison of the Fourier transforms from signals recorded at the $K\beta$ and $K\beta'$ lines for fully oxidized and partly reduced $\text{Ni}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts

Interesting results have also been obtained on the samples prepared with organic additives and studied in the transmission mode. Catalysts were supplied as passivated in air after calcination at varied temperatures and reduction at 410°C . It was first confirmed that NiAl_2O_4 has a mixed spinel structure, with distances attributed to edge-sharing octahedra containing Ni or Al (Fig. 4, left). Nickel speciation on catalysts calcined at 750°C is very similar to nickel aluminate, with a stronger contribution of Ni-centered octahedra, possible due to the existence of small NiO domains (rock-salt structure). Catalysts calcined at 500°C prior to reduction and passivation exhibit different FT depending on whether they have been prepared with an organic additive or not (Fig. 4, right). Without organic additive, a peak characteristic of metallic nickel is seen on the FT. This shows that after reduction, larger metallic particles which have not been fully reoxidized during passivation are present on this sample, in contrast to the sample prepared with an organic additive. The organic additive thus helps to disperse nickel during the catalyst preparation.

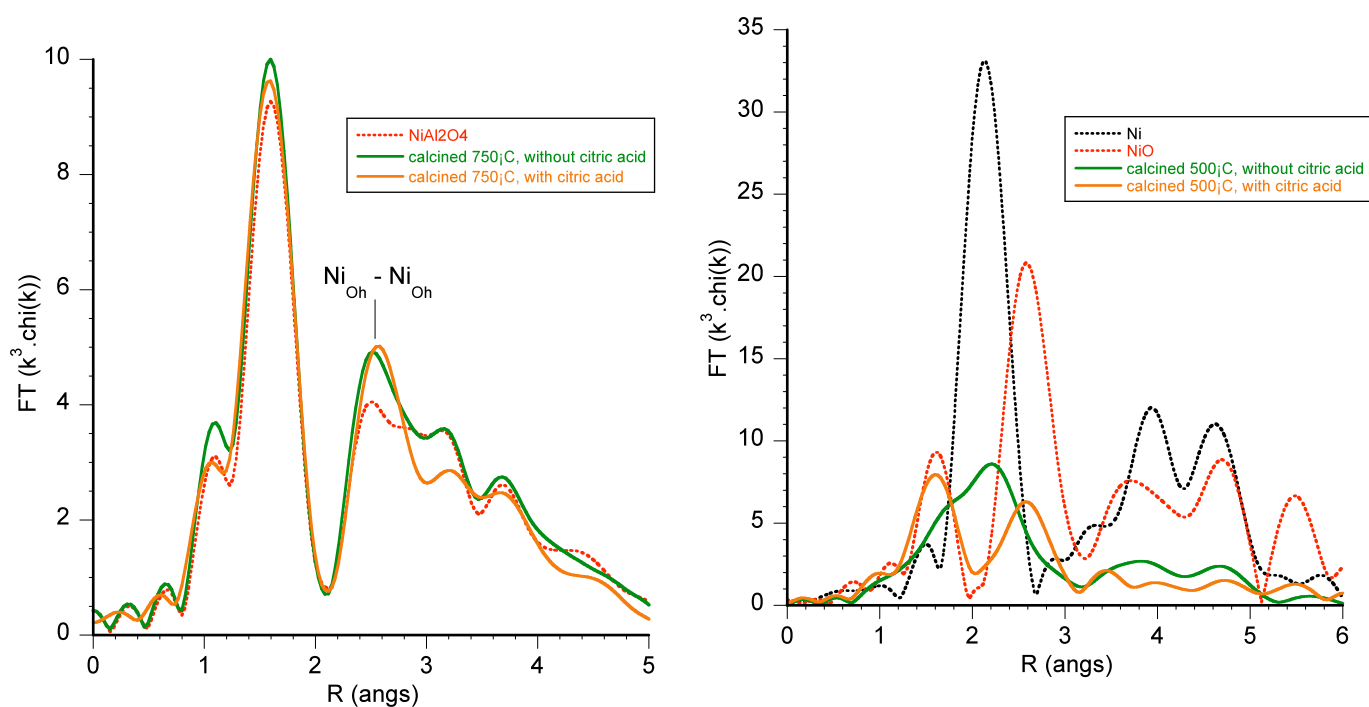


Fig. 4: Comparison of FT recorded on catalysts prepared with organic additives, calcined at 750 °C (left) or 500 °C (right), reduced at 410 °C and passivated in air

Justification and comments about the use of beam time (5 lines max.):

To our knowledge, this is the first time that differences in EXAFS signals and FT as a function of the nanoparticles chemical composition are evidenced using XES at two different energies. Comparison with mixtures involving metal and another oxide, such as nickel aluminate, should allow us to check if XES measurements at the $K\beta'$ line always lead to the selective detection and identification of the oxidic species. It should be noted that at the present time, recording cannot be performed under controlled atmosphere, which limits the study of systems containing dispersed metal nanoparticles prone to reoxidation in ambient air.

Publication(s):

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