

## XAS-Investigation of Local Disorder in Metallic Nickel and Raney-Nickel Catalyst

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**Abstract:** EXAFS measurements have been carried out at the Ni-K-edge both on a Raney-nickel sample and on a metallic nickel foil in the temperature range from 20 to 320 Kelvin using synchrotron radiation from the storage ring ELSA in Bonn. A cumulant data analysis shows that the first-shell distance distribution in nickel foil can be considered as nearly gaussian within the considered temperature range. In Raney-nickel catalyst, the non-negligible value of the third cumulant suggests an asymmetric distribution instead. The first-shell coordination number is much lower ( $N \simeq 6$ ) than for metallic nickel. The MSRD is similar to that of metallic nickel, suggesting a low degree of static disorder.

### 1 Introduction

Raney-nickel catalysts can be produced by removing the aluminium from a Ni-Al alloy with an alkaline solution. The residue is highly dispersed nickel with a large specific surface area, and pyrophoric in the dry state. Because of its high activity and selectivity, Raney-nickel is used as a hydration catalyst e.g. for anodes in liquid fuel cells [1].

A recent EXAFS study of a Raney-nickel catalyst made by a laboratory spectrometer at room temperature [1] revealed a quite low first-shell coordination number ( $N \simeq 6$ ). In this paper, we present the preliminary results of EXAFS measurements made with synchrotron radiation as a function of temperature on a Raney-nickel catalyst and on a reference metallic nickel foil. The data analysis was done by the cumulant method [2],[3], to monitor the asymmetry of the distance distribution. Temperature dependent data allowed the separation of thermal from static disorder.

### 2 Experimental

The Raney-nickel catalyst [4] was provided in aqueous suspension by Bayer AG, Leverkusen, Germany. It was dripped on filter paper for the measurements. The nickel foil with 99.99 % purity was from Exafs Materials, Danville, USA.

The EXAFS spectra were acquired in transmission mode at the beamline BN3 using synchrotron radiation from the Electron Stretcher Accelerator ELSA in Bonn, running in storage ring mode at 2.3 GeV with an average current of about 50 mA. The synchrotron radiation beam was monochromatized by a Lemonnier type double crystal X-ray monochromator [5] equipped with Ge<220> crystals. The photon flux was measured by ionization chambers filled with 90 mbar argon. The energy calibration was done with the nickel foil at the first inflection point of the nickel-K-edge ( $E_0 = 8333$  eV). The sample temperature was varied from 20 to 320 Kelvin.

The Fourier transform amplitudes of the EXAFS signals of both samples at 20 K are compared in Fig. 1A. The reduced height of the first-shell peak in the catalyst agrees with the coordination number reduction previously observed [1]; the signal from outer shells (second and third) is clearly separated in the present work.

The quantitative analysis of the Fourier-filtered first-shell EXAFS was independently done by two methods: (a) a harmonic analysis by the software package [6] containing a modification of FEFF V3.1 [7] for calculating backscattering amplitude, phaseshifts and inelastic terms; (b) the separate cumulant analysis of phases and amplitudes by the ratio method [3], utilizing the 20 K spectrum of nickel foil as reference for the backscattering amplitude, phaseshifts and inelastic terms.

### 3 Results and Discussion

A satisfactory agreement between the two methods (a) and (b) was found for the analysis of EXAFS amplitudes; actually, the 4th cumulant was negligible over the entire temperature range. The first-shell Ni-Ni coordination number in the catalyst was  $6 \pm 1$ , as previously observed [1].

In Fig. 1C the MSRDs are compared: method (a) (open symbols) directly gives absolute values for both nickel foil (circles) and catalyst (triangles). Method (b) gives values relative to the reference, say the 20 K nickel foil. Absolute

values for both nickel foil (full circles) and catalyst (full triangles) have been obtained by an Einstein model best fitting the slope of nickel foil experimental data. The MSRDS of the nickel foil from the two methods are in good agreement. The data for the catalyst are quite scattered; they suggest, however, a low degree of static disorder, amounting about  $0.005 \text{ \AA}^{-2}$ , and a thermal disorder similar to that of the nickel foil.

Let us now consider the phase analysis. Methods (a) and (b) give consistent results for the interatomic distance in nickel foil (Fig. 1B), indicating that the hypothesis of a gaussian distribution of distances is correct. On the other hand a significant difference is found for the catalyst. Method (a), based on harmonic approximation, gives a Ni-Ni distance  $0.01 \text{ \AA}$  shorter than in the nickel foil, in agreement with previous measurements [1]. Method (b) is based on the cumulant analysis. The third cumulant of the first-shell in the catalyst is not negligible (Fig. 1D), clearly indicating an asymmetry of the distance distribution. Correspondingly, the first cumulant, giving the variations of the interatomic distance, is about  $0.01 \text{ \AA}$  larger than in the nickel foil.

The asymmetric distribution of distances found by the cumulant method (b) seems more consistent with the reduction of the coordination number observed in the catalyst.

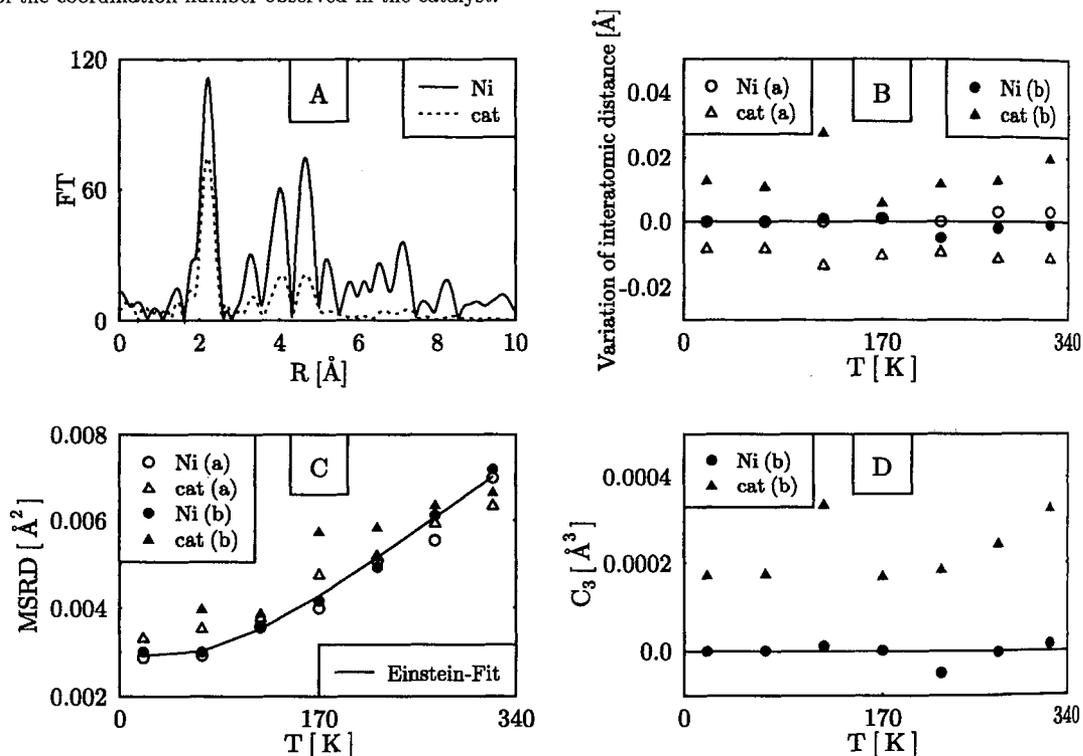


Figure 1: (A): Magnitude of Fourier transforms of EXAFS of the nickel foil (solid line) and the catalyst (dotted) at 20 K. (B)-(D): Temperature dependence of the first three cumulants of the nickel foil (circles) and the catalyst (triangles). Open symbols refer to harmonic analysis, full symbols to cumulant analysis.

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