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Real time monitoring of the evolution of Ni^{2+} environment in faujasite upon rehydration by *in situ* dispersive-EXAFS

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The evolution of both oxygen and framework tetrahedral shells around Ni^{2+} cations in faujasite upon rehydration can be described in real time thanks to *in situ* dispersive-EXAFS. Such type of analysis permits precise experimental description of the coordination environment of cations in zeolite structures under different hydration conditions.

KEY WORDS: dispersive-EXAFS; nickel catalysts; zeolite science.

1. Introduction

The comprehension of the location of Ni^{2+} cations in zeolites has prompted a large number of works, particularly in the case of faujasite (X and Y zeolites) for which thorough XRD studies have determined sites occupancies as a function of thermal treatments. Rietveld refinement indicates that, after dehydration above 573 K, Ni^{2+} is preferentially located in sites SI (centre of the hexagonal prism) and the average Ni–O distance varies between 2.21 and 2.37 Å, with a coordination number of 6 [1–3]. It has been pointed out that this distance could be overestimated, since XRD gives long range average information, whereas, at the local level, all six O(3) oxygens around each Ni^{2+} cation shift 0.5 Å toward the centre of the double six-member ring [4,5]. Taking into account sites occupancies [3], a corrected Ni-O value of 2.16 Å was estimated [5]. This value is significantly higher than the Ni-O distances (from 1.87 to 2.05 Å) determined for dehydrated samples by EXAFS (Extended X-ray Absorption Fine Structure) [5–7], the number of nearest oxygen neighbours being furthermore lower (between 3 and 4). These discrepancies prompted us to analyse precisely the evolution upon rehydration of the coordination shell around Ni^{2+} in a NiNaX sample and this was made possible owing to the recent development of dispersive-EXAFS for the *in situ* study of catalytic materials, allowing the recording of complete absorption spectra in very short times [8,9].

2. Experimental

2.1. Materials

Pure NaX was obtained by ion exchange of the commercial 13X faujasite (Union Carbide) with 0.5 M sodium chloride solutions. In order to ensure a complete substitution with Na^+ cations, the ion exchange procedure was repeated three times.

$Ni_{2.6}NaX$ (unit cell formula $Ni_{7.3}Na_{67}Al_{82}Si_{110}O_{384}$), containing 2.6 wt% Ni, was prepared by refluxing 3 g of NaX with 300 cm^3 of a diluted $Ni(NO_3)_2$ solution (<0.1 M) for 24 h at 343 K (pH = 6.5). The sample was subsequently washed with distilled water and dried in air at 333 K. A portion of this material was dehydrated at 773 K in vacuum during 30 min and sealed in a glass ampoule to avoid rehydration.

2.2. X-ray absorption spectroscopy (XAS)

Ni K-edge (8333 eV) XAS spectra were collected at LURE (Orsay, France) on the Dispersive XAS beam line D11 on the DCI storage ring (1.85 GeV, 250 mA). A rectangular shaped crystal of Si (111) was bent to focus the polychromatic X-ray beam onto the sample. After absorption by the sample, the divergent beam was collected with a position sensitive CCD camera made of 1340 diodes (total 2500 mm high, 25 mm wide). The energy range available in one shot was 8200–9000 eV.

The sample was pressed in a wafer and mounted in controlled water-free N_2 atmosphere into a sealed cell with Kapton windows maintained at ambient temperature and pressure, and was aligned so that the focused

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X-ray beam, with an area of 0.2 cm^2, passed through it. The time to record one spectrum (with the whole energy range at the same time), which was already the average of 16 measurements, lasted less than 1 s. About 10 accumulated recordings were enough to achieve an acceptable signal-to-noise ratio out to $k = 12$ Å. In order to follow the rehydration of the Ni cation in the zeolite channels, the sealed cell was opened to ambient air at $t = 0$ and successive spectra were measured each 2 min.

In the transmission mode, the absorption is defined by $\ln(I_0/I)$, where I_0 and I are the incident and transmitted signals, respectively. With the dispersive geometry used, the I and I_0 signals must be recorded one after the other. In order to take into account the non completely negligible and energy-dependent absorption of the zeolite support, a blank zeolite wafer not containing nickel was used to record I_0.

2.3. XAS Data Analysis

Since collected absorption data are function of the position of the diodes on the detector, they must be converted into the corresponding incident photon energy (E). This pixel-energy conversion requires the acquisition of a reference spectrum, whose $\mu = f(E)$ relation is known. To this end, we used the Ni K-edge of a Ni- metal foil.

The EXAFS signals ($k\cdot\chi(k)$) were extracted by standard procedures [10] using the Michalowicz's software package. [11,12] The Fourier Transforms (FT) of the $w(k) \cdot \chi(k) \cdot k^3$ data were then carried out in the range 2.0–11.3 $Å^{-1}$ ($w(k)$ is a Kaiser–Bessel window with a smoothness parameter of 3).

Simulations of spectra were performed by FT filtering and by multiple-shell quantitative fitting using Ni–O and Ni–Si back-scattering pairs. Attempts made by including also Ni–Ni back-scattering pairs were, on the contrary, not successful. For all simulations, filtering was performed in the 1.1–3.5 Å range. Phase and amplitude functions were calculated using FEFF 7.02 starting from the crystal structures of $Ni(NO_3)_2 \cdot 6H_2O$ and Ni_2SiO_4. The values of coordination number (N), Debye–Waller factor (σ) and radial distances (R) resulting from the fitting procedure are detailed in Table 1 for dehydrated and rehydrated $Ni_{2.6}NaX$.

Table 1
Coordination number of Ni^{2+} ions (N), interatomic distance (R), Debye–Waller factor (σ) and agreement factors (ρ) obtained from spectra simulations for dehydrated and rehydrated $Ni_{2.6}NaX$

$Ni_{2.6}NaX$	Ni–O			Ni–T			ρ
	R* (Å)	N**	σ(Å)	R*(Å)	N**	σ(Å)	
Dehydrated	2.11	5.5	0.11	2.73 3.33	0.5 4.0	0.07 0.07	1.58E-2
Rehydrated	2.06	6.0	0.08		n.d.***		1.01E-2

* ±0.02, ** ±0.5, ***not determined (see text).

3. Results and discussion

3.1. Ni^{2+} neighbouring in dehydrated and rehydrated $Ni_{2.6}NaX$

The EXAFS signals of the $Ni_{2.6}NaX$ sample before ($t = 0$) and after full rehydration ($t = 150$ min) are shown in figure 1, together with their relative Fourier transformed data. The two EXAFS signals are fairly different, the one of the dry sample showing the contribution of at least two ligand shells, whereas a simple contribution is visible in the spectra of the re-hydrated sample.

For both samples, the shell at the lower distance in the FT window is attributable without doubt to oxygen nearest neighbours. For the fully hydrated $Ni_{2.6}NaX$, a Ni–O bond distance of 2.06 Å and a coordination number of 6 (Table 1) are obtained. At the same time the low value of the Debye–Waller factor suggests a strong symmetry and homogeneous Ni–O distances. These values resemble closely those of isolated $Ni(H_2O)_6{}^{2+}$ ions, as measured in the $Ni(NO_3)_2 \cdot 6H_2O$ reference compound, and are in line with the presence of a full hydration sphere around exchanged Ni^{2+} ions.

For the de-hydrated $Ni_{2.6}NaX$, the first of the two shells present in the spectrum (figure 1a′) is also clearly attributable to oxygen neighbours. However, a slightly longer Ni–O bond distance than in the hydrated sample is observed (Table 1), together with a higher value of the Debye–Waller factor, indicative of a larger disorder. Such values are in line with previous EXAFS reports, and are typical of the interaction of the Ni^{2+} cation with the framework oxygen [1]. Interestingly, the Ni–O distance of 2.11 Å in dehydrated $Ni_{2.6}NaX$ is close to a value previously proposed considering that faujasite is able to accommodate effectively Ni^{2+} at SI sites with six framework O atoms at a distance of 2.10 Å.[5] Moreover, this value is not very different from the above-mentioned XRD estimation of 2.16 Å.

The best fit for the simulation of the O shell of the dehydrated sample is obtained for a coordination number N of about 5.5. This result is in line with the shape of XANES spectra (figure 2a), which is between spectra reported for octahedral and five-coordinated Ni [13], suggesting that both coordinations or a slightly distorted intermediate one might exist. This attribution is comforted by the absence of a strong pre-edge peak in the XANES spectrum of the dehydrated sample (see inserts a and b, figure 2). In fact, its broadness and weakness allows one to exclude tetrahedral or square planar geometries that give typical 1s → 3d pre-edge intense peaks for transition metal ions such as Ni^{2+} in such coordinations [14].

As mentioned before, a second ligand shell contributing to the EXAFS signal of dehydrated $Ni_{2.6}NaX$ is present. The best fit of this shell is obtained assuming two subshells of tetrahedral framework atoms (T = Si, Al) located at Ni–T distances of 2.73 and 3.33 Å,

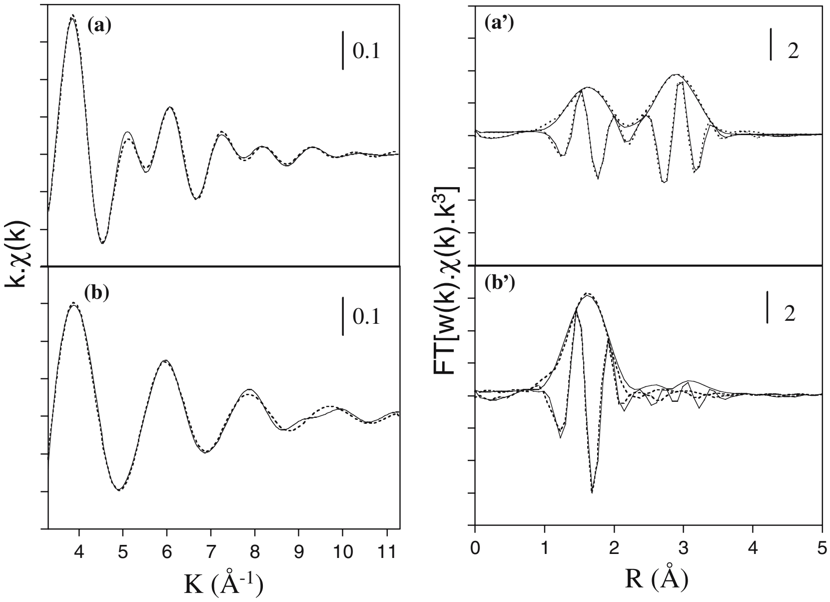

Figure 1. Experimental (solid line) and calculated (dotted line) XAS spectra (Ni–K-edge) of (a,a′) dehydrated and (b,b′) rehydrated $Ni_{2.6}NaX$: (a,b) $k \cdot \chi(k)$ and (a′,b′) FT of $w(k) \cdot \chi(k) \cdot k^3$ (modulus and imaginary parts).

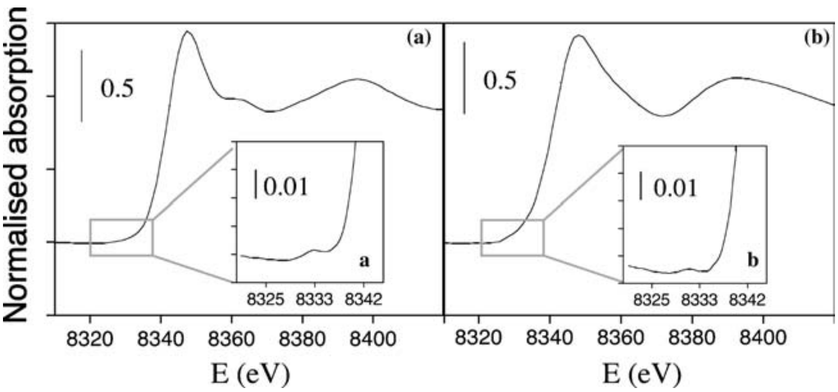

Figure 2. XANES spectra (Ni–K-edge) of (A) dehydrated and (B) rehydrated $Ni_{2.6}NaX$ and (a, b) their respective preedges.

respectively. To our knowledge, such an accurate identification of T neighbours was never reported before. It permits a precise description of the Ni^{2+}-framework interaction. This information will be used in the future, with the aid of DFT molecular modelling calculations, to definitively locate the cation in a precise location at the interior of the structure of the zeolite.

3.2. *Evolution of radial distribution and tetrahedral neighbouring with rehydration time*

Dispersive-EXAFS allows one to measure spectra with a good signal-to-noise ratio in relatively short times, of the order of a fraction of a second. In our case, a glimpse of the quality of the spectra in spite of the low Ni loading (2.6 wt%) can be already seen by looking at the data shown in figure 1. Therefore, this technique allowed us to measure, in addition to the spectra of the fully hydrated and the fully dehydrated sample, spectra with a very good signal-to-noise ratio of the sample along the process of hydration of the zeolite. Since such a process is relatively slow, the measurement of spectra with the frequency of 2 min allowed us to follow satisfactorily the real time monitoring of changes in this interaction upon rehydration.

The radial distribution functions are plotted in figure 3 as a function of rehydration time. At $t = 0$ (dehydrated sample), two distinct peaks are observed, indicative of the presence of two coordination shells. With rehydration time, the shell at higher distance progressively vanishes whereas the one at lower distance increases in intensity.

In figure 4, the progressive disappearance of T neighbours is evidenced. After full rehydration, weak FT signals are still visible around 2.5 Å (figure 1b′) possibly indicating that a low amount of T neighbours

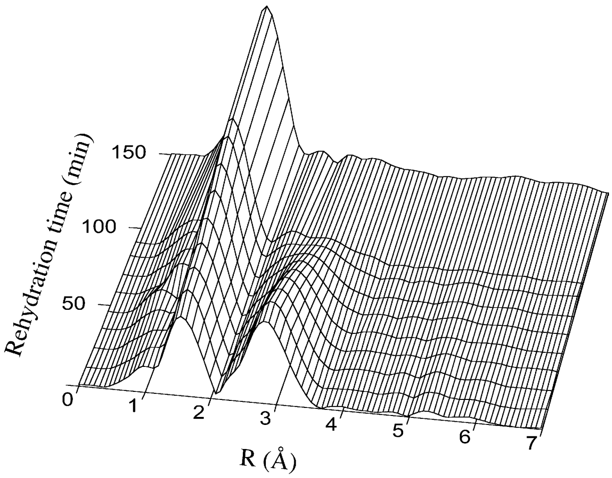

Figure 3. Evolution with rehydration time of the radial distribution functions (FT of $w(k) \cdot \chi(k) \cdot k^3$ data, Ni K-edge, without phase shift correction).

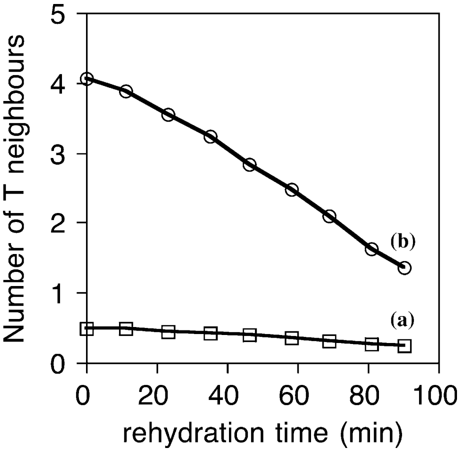

Figure 4. Evolution with rehydration time of the number of tetrahedral framework neighbours located at Ni–T distances of (a) 2.73 and (b) 3.33 Å.

still interact with Ni^{2+} ions. However, a fit of this shell with the same Si or Al neighbours gives coordination numbers always lower than 0.3, with unsatisfying Debye–Waller values. Since such weak peaks might also be due to the possible occurrence of FT filtering artefacts, the results of these fits are not considered in Table 1.

These results show how, upon increasing hydration, the Ni^{2+} cations gradually move from precise locations in the framework and, surrounded by a coordination sphere of water molecules, are liberated in the zeolite channels. Under current ambient conditions and for a sample in the form of a wafer, this process is relatively slow and occurs within about a few hours.

4. Conclusion

Summarising, a breakthrough of this work is the precise identification of Ni^{2+} neighbours in zeolites, involving not only oxygen atoms but also tetrahedral (Si, Al) framework atoms. In addition, this work thoroughly illustrates the potential of Dispersive-EXAFS to supply a real time accurate quantitative description of chemical and/or environmental changes in zeolitic systems, even for low loadings of the X-ray absorbing species, thus providing a powerful tool in the fields of catalysis and zeolite science.

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