

X-Ray Absorption Spectroscopy Investigation of the Activation Process of Raney Nickel Catalysts

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The formation of highly reactive Raney Nickel catalysts, which are commonly used in hydrogenation reactions, has been studied using X-ray absorption spectroscopy (XAS) with synchrotron radiation. Various samples representing different “frozen” states of the activation reaction have been prepared. The process has been quenched after different reaction times by neutralizing the alkaline solution leaching the aluminium from the two alloys used as educts. XANES spectra taken at the Ni K edge of the catalysts derived from an Ni/Al alloy and an Ni/Al/Fe alloy reveal that the transformation starts with a very rapid change of the electronic structure followed by a much slower change of the geometric structure of the alloys. Most noticeable is the sharp increase of the density of empty *d* band states, which partially redevelop when the reaction products slowly relax to an electronic as well as a lattice structure similar to that of *fcc*-Ni metal. Thus at least a well-defined local order is preserved in the final catalysts. The presence of Fe (6 wt%) in the starting alloy slows down the reaction, while the Fe K-XANES points to the oxidation of this component. © 2000 Academic Press

1. INTRODUCTION

Raney Nickel catalysts have found widespread application in the field of the hydrogenation of organic compounds, especially as anodes in liquid fuel cells (1). Traditionally they are produced by the removal of aluminium from an Ni/Al alloy with a strong alkaline solution (2). The residue after leaching of the Al component consists mainly of Ni in a highly dispersed state (surface areas of 50 to 120 m²/g). Nevertheless, the relatively high resistance of Raney Nickel to sintering has been attributed to alumina (Al₂O₃) and possibly alkali (3) retained in the activation process, which may stabilize the structure, thus acting as promoters. Another way to enhance the effectiveness of Raney Nickel catalysts for certain reactions is to start with a ternary alloy, e.g., Ni/Al/Fe. Much work has been done to investigate the surface composition and the effects of the aluminium content on the activity and selectivity of the catalyst (4–6). However,

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to our knowledge direct measurements of the influence of the leaching process on the electronic structure of the transition metal components have not yet been reported.

The purpose of the present work is to shed some light on the process of the formation of the otherwise well-characterized Raney Nickel catalyst. A better understanding of the activation process, especially in terms of the role of promoters like Fe present in a ternary starting alloy, may be of great benefit for the optimization of the catalyst design.

X-ray absorption spectroscopy (XAS or XANES for the investigation of the near-edge structure of the absorption coefficient up to 40 eV above the threshold, EXAFS for the analysis of the extended fine structure up to 1000 eV above the edge, respectively (7)) offers direct insight into the electronic as well as the geometric structure of an absorbing species of atoms. Especially due to the possibility of analyzing samples in the absence of a well-defined atomic long-range order, XAS has been established as a powerful tool for the investigation of catalytically active materials (8, 9). Recent XAS investigations of Raney Nickel were primarily focused on the deviations of the atomic structure of the highly porous catalyst from that of bulk-Ni (especially in terms of coordination numbers (4, 10)). This report primarily deals with the dramatic changes in the local density of empty electronic states (band structure) which we observed during the activation reaction prior to the final relaxation of the lattice structure.

2. EXPERIMENTAL

A. XANES-Measurements

Ni K-XANES measurements (Ni 1s binding energy: 8333 eV) and Fe K-XANES measurements (Fe 1s binding energy: 7112 eV (11)) have been performed at the beamline BN3 of the synchrotron radiation laboratory at the Electron Stretcher and Accelerator ELSA (12) (Bonn University, Institute of Physics) employing the standard transmission technique. For all measurements, ELSA was operated at an

electron energy of 2.3 GeV in storage ring mode and at an average current of 40 mA. For the sequential recording of absorption spectra, a Lemonnier-type (13) double-crystal monochromator was equipped with a pair of plane Ge(422)-crystals ($2d = 2.306 \text{ \AA}$). At either edge, three different step widths (*Ni K*: 8200–8320 eV to 1.32 eV, 8320–8400 eV to 0.34 eV, 8400–8500 eV to 0.71 eV; *Fe K*: 7000–7090 eV to 0.82 eV, 7090–7170 eV to 0.21 eV, 7170–7250 eV to 0.44 eV) have been chosen to give adequate resolution in the different energy regions of the spectra. The intensity of the primary beam and the beam after sample transmission was monitored by means of *Ar*-filled ionization chambers (200 mbar at *Ni K*, 100 mbar at *Fe K*). Efforts to reduce harmonic intensity by detuning the parallel alignment of the crystals have been found to be without influence on the measurements. For the calibration of the energy scale of the monochromator, the *Ni 1s* and the *Fe 1s* binding energies were assigned to the first inflection points in the spectra of pure *Ni* and *Fe* foils, respectively (EXAFS Materials, Danville, CA, thickness of foils 6 and 5 μm , respectively). All XANES spectra reported here are calibrated relative to these assignments. For both edges, the calibration has been checked after each scan and was found to be stable within one monochromator step.

In order to compare the measured absorption curves quantitatively, a linear background was fitted to the pre-edge regions (*Ni K*: 8200–8300 eV, *Fe K*: 7000–7080 eV) and was subtracted before normalization of the spectra with respect to the edge-jump. At either edge, this quantity was determined as the average of the first EXAFS oscillations (i.e., the estimation of the atomic background) at 8400–8500 eV (*Ni K*) and 7170–7250 eV (*Fe K*), respectively.

The alloy samples (Ni50/Al50 from Bayer AG, Leverkusen, and Ni34/Al60/Fe6 from Goodfellow GmbH, Bad Nauheim—all numbers are in wt%), which also served as starting materials for the formation of the catalysts, were measured as finely ground powders produced by ball-milling of the granules in a tungsten-carbide mortar for 60 min. Transmission samples of high homogeneity were produced by fixing the fine powders on adhesive KAPTON tape. In the case of the catalysts, the samples were derived from suspensions of the reaction products (see below) spread on filter paper. A commercial Raney Nickel catalyst (iron-free, from Bayer AG, Leverkusen) has been measured as reference.

Inside the sample chamber the highly reactive catalysts were held in an *Ar* atmosphere in order to inhibit self-inflammation upon possible drying of the suspensions. All measurements have been performed at room temperature.

B. Preparation of Raney Nickel Samples

As described elsewhere (2), the active Raney Nickel catalysts are derived by leaching the aluminium from the bi-

or trimetallic composites using sodium hydroxide (*NaOH*) solution. In order to yield information about the electronic and geometric structure of the catalysts during various stages of the formation, in our experiments the leaching process was halted by neutralizing the solution after various reaction times. Details of the procedure are as follows: approximately 2 g of the ground alloys were covered with 50 ml of 1 M *NaOH* in a beaker. After various reaction times (10 s and 1, 3, 5, 10, 30, 60, and 120 min) the reaction product was rinsed several times with distilled water until no further evolution of hydrogen could be observed. Additionally, the neutrality of the suspensions was checked using pH indicator paper. After addition of *NaOH* a violent reaction and heating of the suspensions was observed. To keep the solutions boiling during the reaction time, the beakers were placed on a heating plate. The reaction products were kept immersed in water until performance of the X-ray absorption measurements.

3. RESULTS OF THE XAS MEASUREMENTS

We want to start the presentation of the X-ray spectroscopic investigation of the formation of Raney Nickel with a comparison of the alloys—measured prior to the leaching of the *Al*—and the pure transition metals. Figure 1a shows the *Ni K*-XANES spectra of the *Ni* foil, the Ni50/Al50 alloy, and the Ni34/Al40/Fe6 alloy; the first derivatives of the spectra are plotted as an insert. The agreement of the energy position of the first inflection point in all three spectra (8333 eV) clearly indicates the zerovalent state of the *Ni* component in the alloys; i.e., no net charge transfer takes place between the transition metals (*Ni*, *Fe*) or between the transition metals and the *Al* component, respectively. Nevertheless, the spectra reveal that the structures of the empty electronic states (conduction bands) accessible by the *Ni 1s* electron, as well as the geometric or lattice structures within the local surroundings of the absorbing atoms, differ considerably from those of the pure metal. There is still some dispute in the literature as to the assignment of shoulder A in the *K* edge spectra of 3*d* transition metals, leading to the first absorption maximum (B, B'). The common interpretation as electronic transitions to empty 3*d* band states at the Fermi level, which must be overlapping with 4*p* states to obey to the dipole selection rules (14), would indicate a different *s-p-d* hybridization scheme in the alloys, resulting in a reduced occupation of *d* levels. On the other hand, the strong peak above 8360 eV, as well as the phase shift observed for the first EXAFS oscillations (minimum at about 8380 eV in the alloy spectra matches maximum in the spectrum of the pure metal), point to a completely different local order around *Ni* atoms in the alloys as compared to *fcc-Ni* metal. In both respects, the presence of *Fe* causes slight but significant differences between the two alloys themselves.

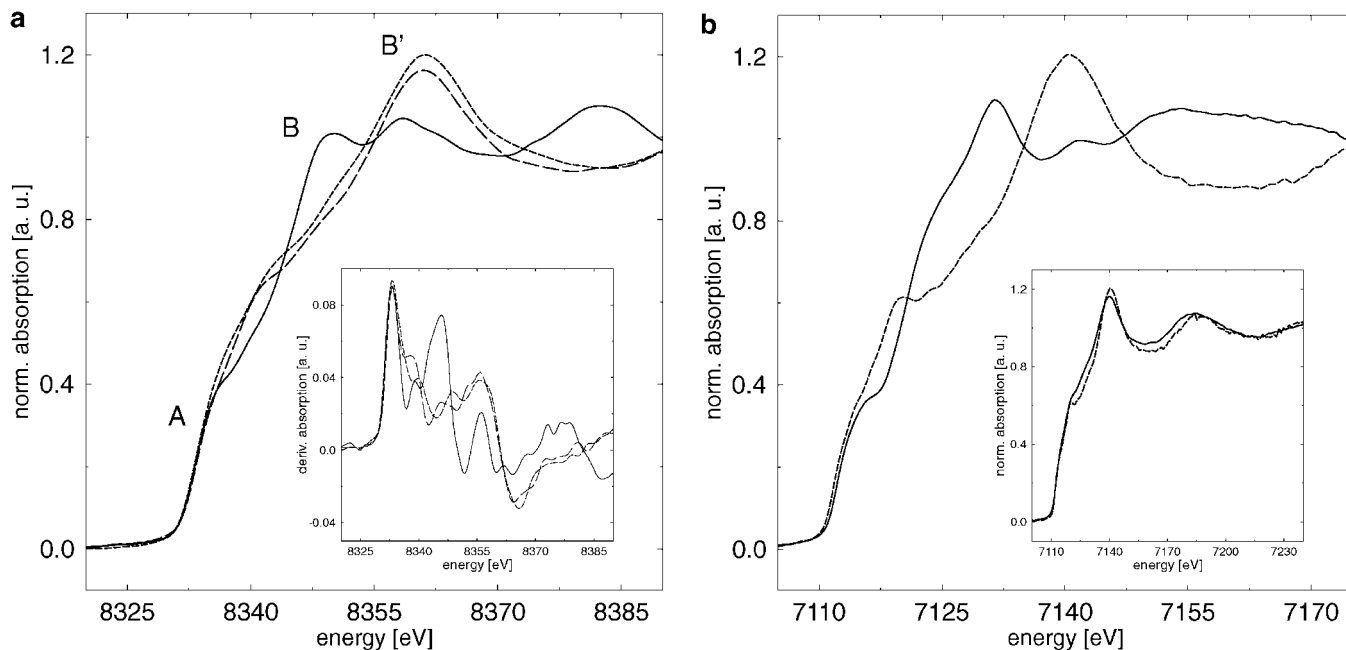


FIG. 1. (a) *Ni K*-XANES: (solid line) *fcc-Ni* foil; (short dashes) *Ni/Al* alloy; (long dashes) *Ni/Al/Fe* alloy. The respective derivatives are plotted as an insert. (b) *Fe K*-XANES: (solid line) *bcc-Fe* foil; (short dashes) *Ni/Al/Fe* alloy. A comparison between *Ni* (solid line) and *Fe* (dashed line) *K*XANES of the *Ni/Al/Fe* alloy is plotted as an insert (the *Ni* spectrum has been shifted by 1221 eV to lower energies).

Similar conclusions can be drawn from an investigation of the *Fe K* edge at the *Ni/Al/Fe* compound when comparing the XANES of the pure metal and the alloy, depicted in Fig. 1b. Again the zerovalent state of the transition metal is preserved, whereas the electronic and geometric structure of the alloy differ significantly. Interestingly, overplotting the XANES spectra taken at both transition metal edges (insert in Fig. 1b, the *Ni K* spectrum has been shifted by the difference of the *Ni 1s* and the *Fe 1s* binding energies, 1221 eV, to lower energies) reveals the striking similarity between both absorption curves. This can be seen as a strong hint as to the formation of a homogeneous alloy; i.e., the electrons excited at both edges probe a very similar electronic and geometric structure.

After 120 min reaction time no further evolution of H_2 was observed for either the binary or the ternary educt, meaning that the accessible amount of *Al* had been completely transformed to an oxide or hydroxide state, most likely tetrahydroxylaluminate ($[Al(OH)_4]^-$) (6) (visible as a white precipitate at the walls of the beakers), by that time. In the case of the product derived from *Ni/Al* the basic features of the electronic as well as the geometric structure of *fcc-Ni* have developed. This can be concluded from the comparison in Fig. 2a, especially when considering the agreement in the fine structure of the first derivatives (plotted as an insert) and the characteristic double peak at the crest of the *Ni K* absorption edge. Nevertheless, our product differs significantly from the commercial Raney Nickel catalyst, which shows more intense “*d* band transitions.” For now there is only speculation about this deviation. One

may think of a reduced particle size or a higher amount of *Al* retained in the commercial catalyst (see discussion below).

Figures 2b and 2c show the XANES obtained for the bimetallic catalyst at the *Ni K* and the *Fe K* edges, respectively. Although at the *Ni K* edge the agreement between the pure metal and the catalyst turned out to be diminished in this case, the development of the main features of the metal spectrum were again evident. On the other hand, the *Fe K* edge revealed a completely different shape of the catalyst spectrum compared to *bcc-Fe* metal, possibly due to the partial oxidation of this component (see the spectrum of *FeO* also shown in Fig. 2c). As we will see next, *Fe* as the minor constituent of the ternary alloy seems to have a considerable influence on the reaction leading to the active catalyst, as well as on the structure of the final product.

The XANES spectra derived from samples where the strongly exothermal leaching reaction had been stopped after various periods of time are shown in Figs. 3a (*Ni/Al* alloy, *Ni K* edge), 3b (*Ni/Al/Fe* alloy, *Ni K* edge), and 3d (*Ni/Al/Fe* alloy, *Fe K* edge), respectively. Additionally, for the case of the *Ni/Al* system the difference spectra (i.e., the spectrum of the educt material minus the alloy spectrum at time *t*) are plotted as an insert to Fig. 3a. Considering the course of the reaction as depicted in Fig. 3a, two general observations can be made:

1. An almost instantaneous change in the electronic structure occurs, even visible after reaction times as short as 10 s

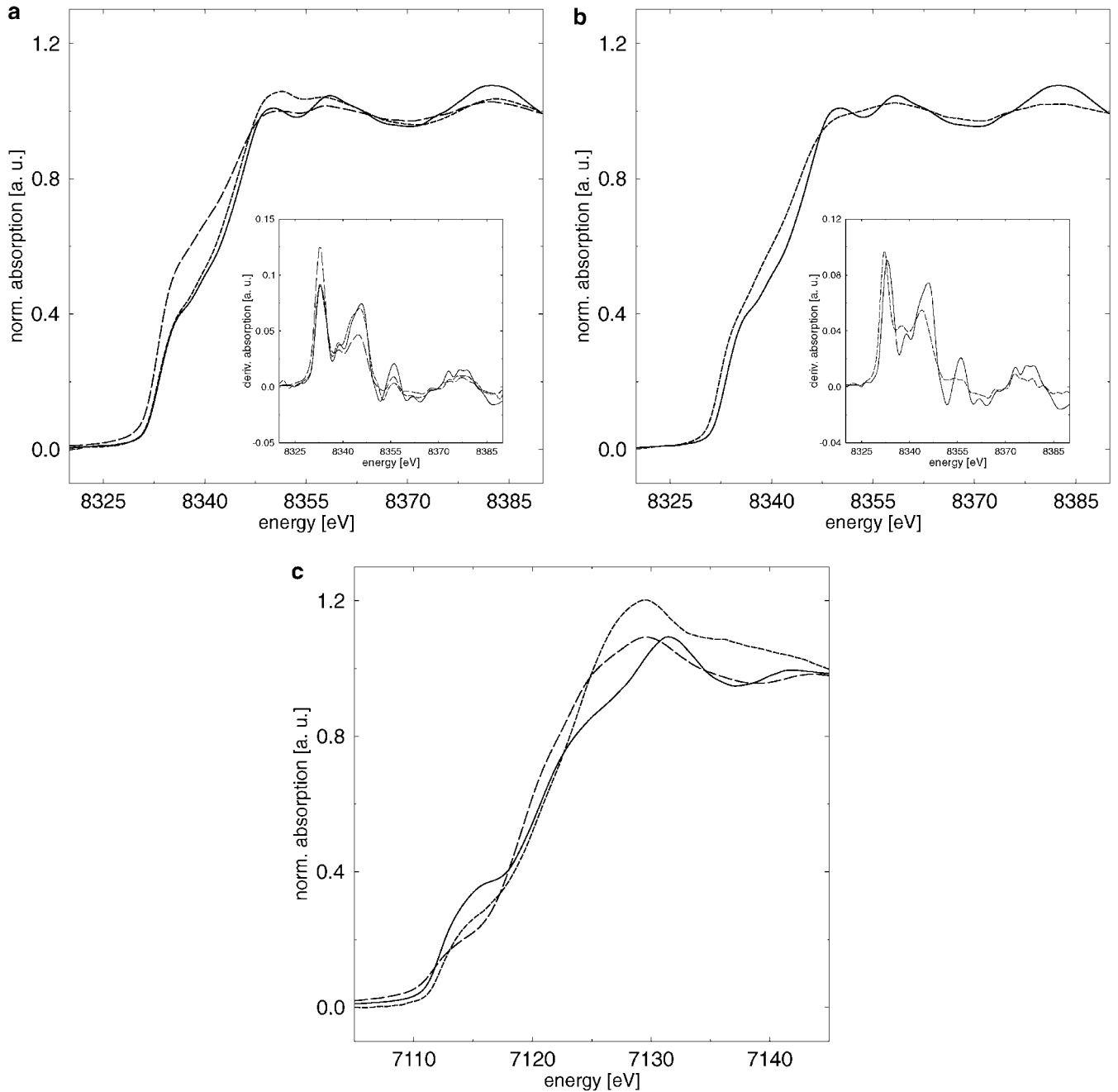


FIG. 2. (a) *Ni K-XANES*: (solid line) *fcc-Ni* foil; (short dashes) catalyst derived from *Ni/Al* (reaction time 120 min); (long dashes) commercial catalyst. The respective derivatives are plotted as an insert. (b) *Ni K-XANES*: (solid line) *fcc-Ni* foil; (dashed line) catalyst derived from *Ni/Al/Fe* (reaction time 120 min). The respective derivatives are plotted as an insert. (c) *Fe K-XANES*: (solid line) *bcc-Fe* foil; (short dashes) catalyst derived from *Ni/Al/Fe* (reaction time 120 min); (long dashes) *FeO*.

as the drastic inflation of the spectrum in the range of the *d* band transitions, whereas

2. the amplitudes at the onset of the EXAFS regime as well as the intensity of the dominant peak above 8360 eV, most likely due to a multiple scattering resonance, are strongly dampened, thus indicating the transition from the alloy to a highly distorted atomic neighborhood around the *Ni* absorber atoms.

The increase of the absorption in the area of the rising edge reaches its maximum after about 5 min (see insert), before the redevelopment to an edge shape very similar to that of *fcc-Ni* takes place. To quantify the drastic changes of the density of empty electronic states accessible by the *Ni 1s* electrons, in Fig. 3c the differences between the integrated spectra in the range of the near edge structure (8325–8375 eV) of the catalysts (after various stages of

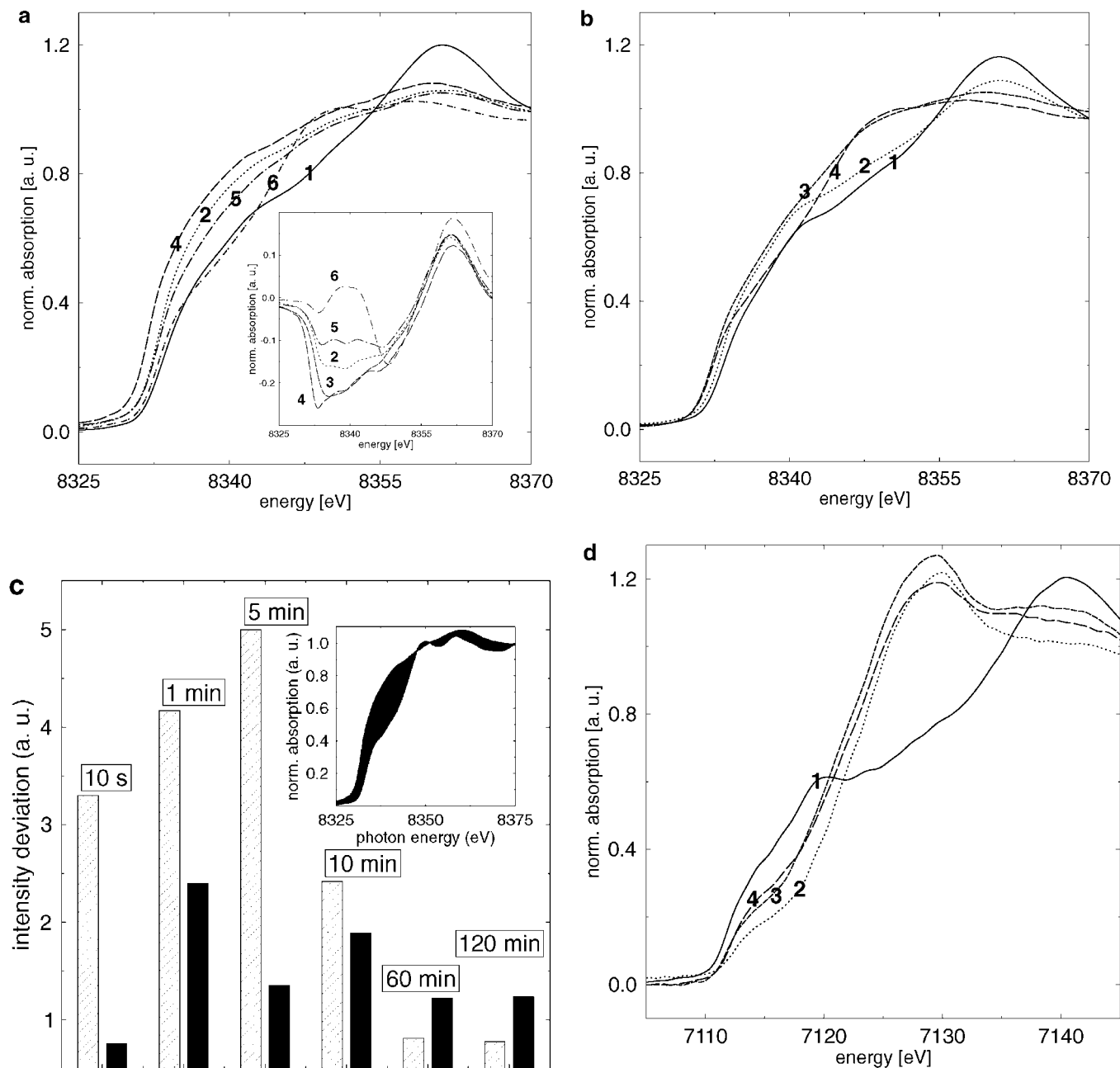


FIG. 3. (a) *Ni* K-XANES, spectra taken after various reaction times: (1) Ni/Al alloy; (2) 10 s; (3) 3 min; (4) 5 min; (5) 10 min; (6) 60 min. The corresponding difference spectra are plotted as an insert. Note that for quenching after 3 min only the difference spectrum has been plotted. (b) *Ni* K-XANES, spectra taken after various reaction times: (1) Ni/Al/Fe alloy; (2) 10 s; (3) 1 min; (4) 60 min. (c) Deviation of the integrated spectral intensity of the catalyst samples after various reaction times from *fcc*-Ni (insert: Ni/Al alloy after 5 min vs *fcc*-Ni): (shaded bars) Ni/Al alloy; (black bars) Ni/Al/Fe alloy. (d) *Fe* K-XANES, spectra taken after various reaction times: (1) Ni/Al/Fe alloy; (2) 10 s; (3) 1 min; (4) 60 min.

development) and of *fcc*-Ni metal have been plotted (shaded bars). As mentioned above, the electronic redevelopment goes along with the phase change at the beginning of the EXAFS region, pointing to the relaxation of the atomic structure to an *fcc*-Ni-like geometry after the leaching of the Al component. The adjustment of the final geometric structure is a much slower process and cannot be seen as being completed before 60–120 min.

In principle, the fate of the Ni component in the Ni/Al/Fe system (Fig. 3b) is very similar. However, the reaction of NaOH with the ternary alloy leads to less drastic changes in the Ni K XANES (Fig. 3c, black bars). In this case, the redevelopment of the electronic structure starts after 1 min, but it takes place over an extended period of time. This may correspond to the fact that the reaction observed was also less violent than with the binary alloy. The final state of the

Fe component reflected by the corresponding *K*-edge absorption spectra is similar to neither the educt alloy nor the *bcc-Fe* metal. Although the XANES undergoes a development as well at the *Ni* edge, the basic features of the final spectrum are already visible after 10 s (Figs. 2c and 3d), basically distinct from the final state by intensity variations.

4. DISCUSSION

In the course of the reactions occurring during the transformation of the Ni/Al and the Ni/Al/Fe alloy into the corresponding Raney Nickel catalysts, we observed drastic changes in the X-ray absorption spectra. From these observations, several conclusions can be drawn which elucidate the underlying activation processes taking place during alkaline treatment of the alloys.

First of all, the rapid onset of the reaction upon addition of NaOH solution, accompanied by the loss of the ordered structure of the Ni-containing alloys, points to an almost instantaneous transformation of the available Al into a soluble state. However, the transport of the aluminium out of the starting materials appears to be strongly inhibited, its diffusion rate through the arising porous network of the remaining Ni or Ni-Fe compound during the activation procedure possibly being a limiting factor. The inflation of the spectra in the main edge region reflects a decreasing density of electronic states at the Fermi level. This transient decrease might be due to the loss of nearest neighbors during the leaching process. However, our observations are not reflected by XANES data obtained for nm-sized transition metal clusters isolated in solid argon, e.g., (15, 16). It seems to be more likely that the observation is related to the interaction of the Ni matrix with the just-formed Al cations. The effect of these cations could arise from their taking some electronic density from Ni^d , thus increasing the density of empty states. In the case of the binary alloy, the final product relaxes almost completely into the Ni *fcc*-structure. On the other hand, the presence of Fe as the minor constituent in the ternary alloy obviously inhibits this geometric readjustment of the nickel atoms, a more disordered local structure around the Ni absorbers being the result. This special structure is reflected as well by a significant 1-eV shift of the Ni *K* absorption edge to lower energies as compared to the spectra of Ni metal and the catalyst derived from the binary alloy, respectively (Fig. 2b). The presence of iron noticeably slows down the reaction. The inhibition of the geometric readjustment of the Ni atoms might be just a thermal effect: if the alkaline attack of Al is less violent, the local temperature increase will be smaller, leading to slower atomic diffusion. Moreover, it can be expected that the Fe cations produce an electronic effect similar to that of the Al cations when interacting with Ni upon the formation of the catalyst. In contrast with the Al cations, the Fe cations cannot be washed away easily with the solution. Thus, their

electronic effect on the Ni component is partially retained at the end of the reaction.

Although we have not performed an EXAFS analysis of our reaction products in the present study, some remarks concerning the measurement of the extended fine structure of the Ni *K* absorption of Raney Nickel are worthwhile at this point. Recent studies of plate-type Raney Nickel electrodes by Nakabayashi *et al.* (4) and of commercial Raney Nickel powder by Frenzel *et al.* (10) revealed the drop of the first-shell coordination number from 12 in *fcc-Ni* metal to about 6 in the catalyst, while the nearest-neighbor distance (2.48 Å) remained unchanged. In the former paper, this finding has been generally ascribed to the high amorphicity of the activated catalyst, i.e., to a great number of point defects and dislocations in the lattice structure. The latter publication, however, emphasizes the asymmetric distance distribution derived from a detailed cumulant analysis (17) (using a 20 K measurement of the Ni foil as standard) as more likely to be responsible for the observed reduction. In accordance with these recent studies the spectrum of our own reaction product exhibits strongly damped amplitudes at the onset of the EXAFS region compared to the pure metal. This observation indicates a much higher degree of local disorder (i.e., a more anharmonic Ni-Ni pair distribution) in the catalyst sample. Nevertheless, after the leaching of the aluminium the lattice structure seems to relax to a geometry closely matching that of the pure metal, therefore giving rise to a very similar absorption fine structure.

5. CONCLUSIONS

Additional spectroscopic experiments are required to further clarify the role of Fe in the processes during the activation procedure of Raney Nickel catalysts. In particular, the questions to be addressed are whether the Fe component merely precipitates as an oxide layer on top of the catalyst particles, or whether iron is retained in a strongly distorted *fcc*-structure as part of the network generated during alkaline treatment of the Ni/Al-based alloys. As the transport of aluminium appears to be rate determining for the activation process, it will be helpful to elucidate the chemical state and further quantify the amount of Al remaining for each sample quenched after different reaction times.

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