ELSEVIER

Catalysis Today 27 (1996) 137–144

CATALYSIS TODAY

Catalytic properties of pure and Ni doped niobium sulfide catalysts for hydrodesulfurization

Nabil Allali [a], Annie Leblanc [a], Michel Danot [a], Christophe Geantet [b,*], Michel Vrinat [b], Michèle Breysse [b]

[a] *Laboratoire de Chimie des Solides, I.M.N.-C.N.R.S., U.M.R. 0110, Université de Nantes, 2, rue de la Houssinière, 44072 Nantes Cédex 03, France*

[b] *Institut de Recherches sur la Catalyse, CNRS, 2, avenue Albert-Einstein, 69626 Villeurbanne Cédex, France*

Abstract

New unsupported and carbon-supported niobium sulfide (pure or Ni doped) catalysts, characterized by EXAFS, demonstrate interesting properties for hydrodesulfurization.

Keywords: Niobium sulfide catalysts; Nickel; Hydrodesulfurization

1. Introduction

Lower legislative limits on sulfur contents in gas oil are placing higher demands on hydrotreating catalysts. Thus, new active phases different from the conventional NiMo or CoMo phases have attracted much interest in the last few years. In particular, niobium sulfides in the bulk state have been shown to present better activities than bulk MoS_2 in some hydrotreatment model-compound reactions [1,2]. Consequently, we considered of interest to prepare mixed unsupported as well as supported niobium-based sulfide catalysts and to evaluate their catalytic properties. Since no diffraction peaks could be observed from X-Ray diffraction, we used the EXAFS technique, with the aim to identify the active phase.

2. Experimental

2.1. Bulk niobium sulfides

The study of undoped massy samples was previously reported [1,2] and showed that the more active composition is NbS_3. Attempts to prepare nickel-doped NbS_3 were thus performed according to two different methods: starting from the elements or by intercalation of lithium and reaction of Li_xNbS_3 compound with nickel iodide solutions in acetonitrile. Before the characterization and catalytic measurements, the samples were sulfided by a N_2-H_2S (15%) flow, under atmospheric pressure, at 400°C, for 4 h. X-ray diffraction shows that the so-obtained compounds are two-phase systems containing NbS_3 and the NiS_2 pyrite type structure. Whatever the synthesis route, the formation of a Ni_xNbS_3 phase never could be evidenced. Due to the intercalation step, the second method gives compounds with larger

---

* Corresponding author.

SSDI 0920-5861(95)00181-6

surface area than the first one (25 and 3 m^2/g respectively).

2.2. The carbon-supported samples

The precursor used for the present study is niobium chloride, $NbCl_5$. The commercial product was first purified by sublimation under vacuum in order to eliminate traces of oxide impurity, which can result from accidental exposure to atmosphere. Niobium chloride was then dissolved under an inert atmosphere in 1M HCl and the impregnation was carried out according to the solution-excess method. The support used is the carbon 'Norit', with a surface area of 1200 m^2/g and porosity of 1 cm^3/g. The niobium amount introduced is 10 wt.-%. After impregnation and drying at room temperature, sulfurization was performed similarly to bulk samples. The nickel-doped catalysts were prepared using the co-impregnation method, adding nickel nitrate to the niobium chloride solution. The total amount of metal was kept equal to 10 wt.-%. Several samples were prepared with different r ($r = Ni/(Ni+Nb)$), atomic ratios.

2.3. EXAFS measurements

The EXAFS spectra were recorded at DCI, the French Synchrotron Radiation Laboratory LURE, on the EXAFS I spectrometer using a Si (311) channel cut monochromater. During the experiments, the storage ring used 1.85 GeV positrons with a 250 mA average intensity. The data were collected in the transmission mode (accumulation time was 1 s) at room temperature by the measurement of the beam intensities I_0 and I, respectively before and after passing through the sample, using ion chambers with argon fill gas. Measurements were performed at the Ni (from 8200 to 9200 eV with 2 eV steps) and the Nb (from 18850 to 19800 eV with 3 eV steps) K-edge respectively. 5 μm-thick samples were prepared with the aid of adhesive tape or by dilution in dehydrated boron nitride. The EXAFS results were analyzed according to a well-known procedure [3,4], using a program-chain written by Bonnin and Frétigny for PC microcomputers.

2.4. Catalytic activities

Catalysts were tested in the thiophene hydrodesulfurization model reaction, under atmospheric pressure at 350°C, using a continuous flow micro-reactor working at low conversion rate. The hydrogen flow was saturated with thiophene vapor at 0°C ($P_{\text{thiophene}} = 2400$ Pa). The flow rate was 50 ml/min and varied from 20 to 100 ml/min. For this reaction, all the studied samples reached a quasi-stationary state after about 12 h and the activity values were measured after 16 h on stream.

3. Results and discussion

3.1. Catalytic activities

Unsupported catalysts

Table 1 gives the specific and intrinsic activities of niobium sulfide catalysts in the thiophene hydrodesulfurization reaction. The values for molybdenum based catalysts are given for comparison. For the studied composition, nickel-doping multiplies the intrinsic activity of NbS_3 by a factor of two. This synergetic effect is lower than in the case of bulk NiMoS ($r = 0.3$), whose activity is eight times that of undoped bulk MoS_2. The chemical nature of the Ni-doped niobium sulfide samples (mixtures of NbS_3 and NiS_2, no NiNbS mixed phase) can explain that Ni-doping does not enhance the activity of NbS_3 a lot.

Table 1
Textural and catalytic properties of unsupported catalysts

Catalyst	$A_s \times 10^{-8}$ (mol/gs)	$A_i \times 10^{-8}$ (mol/m^{2}s)	S_{BET} (m^2/g)
NbS_3	2.7	1.3	2
MoS_2	18	0.31	58
$0.5NiS_2$-NbS_3	25	2.3	11
NiMoS	15	2.3	7

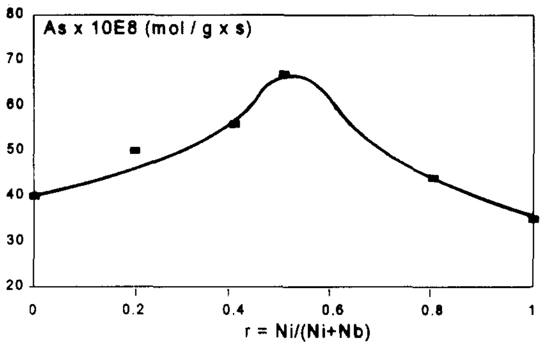

Fig. 1. Activity evolution of carbon supported catalysts with the doping ratio $r = \text{Ni}/(\text{Nb}+\text{Ni})$.

The carbon-supported catalysts

In order to be used as references, the activities of alumina-supported MoS_2 and carbon-supported MoS_2 were measured and found respectively equal to 30 and 80×10^{-8} mol/g s. The values obtained in the same conditions for the Nb catalysts are given on Fig. 1. Nickel-doping increases the activity which is doubled for $r = 0.5$, for which the maximum value is obtained. For supported molybdenum disulfide, nickel- or cobalt-doping multiplies the activity by 8 and 10 respectively. As in the case of the unsupported niobium sulfides, the doping effects appear to be weak.

3.2. Selectivity for hydrogenation

According to Massoth and Muralidhar [5], the thiophene hydrodesulfurization reaction mechanism can be represented by the reaction scheme of Fig. 2.

Preliminary experiments showed that in presence of supported undoped niobium sulfides, the thiophene hydrodesulfurization leads to a higher proportion of butane than on molybdenum catalysts. In order to obtain quantitative information concerning this property, we studied the $r = 0$ (undoped) Nb/C sample at various total conversion. The total conversion (TTG) can be varied using different amounts of the catalyst and different contact time between the catalyst and the reactive atmosphere. For each TTG, we measured the partial conversion (TTI) for butenes and butane production. For comparison, carbon-supported MoS_2 (Mo/C) was studied in a similar way. For the two samples, TTI are plotted vs. TTG in Fig. 3. It can be observed that, at a given total conversion, for Nb/C the relative amount of butene is systematically lower than for Mo/C, whatever the TTG chosen for comparison. Considering that the amount of tetrahydrothiophene and butadiene are always found very small, the reaction mechanism was simplified according to a two-step model:

$$\text{Thiophene} \xrightarrow{k_1} \text{Butenes} \xrightarrow{k_2} \text{Butane}$$

The first reaction is the hydrogenolysis of the C–S bond (rate constant k_1), the second one the hydrogenation of butenes (rate constant k_2). Since butenes are the intermediate products of the global reaction, their relative amount is controlled by two competing phenomena: their formation from thiophene (k_1) and their transformation into butane (k_2).

The TTG value for which the maximum of the butene production is reached (TTG_{max}) reflects this competition: the larger the k_2/k_1 ratio the smaller TTG_{max}. Fig. 3 shows that TTG_{max} is smaller for Nb/C (ca. 40%) than for Mo/C (ca. 50%), which quantitatively confirms the greater selectivity of Nb/C for hydrogenation.

Quantitative information can be derived from these data on the basis of the kinetic treatment established by Germain [6], who demonstrated that $K = k_2/k_1$ can be deduced from TTG_{maxBe} using the relation:

$$TTG_{maxBe} = 1 - K^{(1/(1-K))}$$

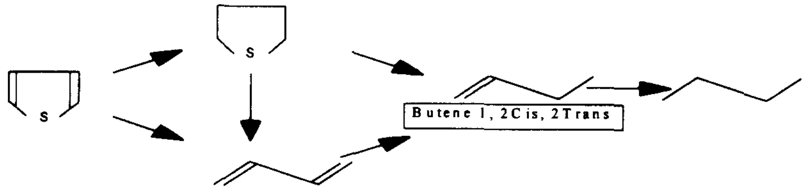

Fig. 2. Mechanism of thiophene hydrodesulfurization.

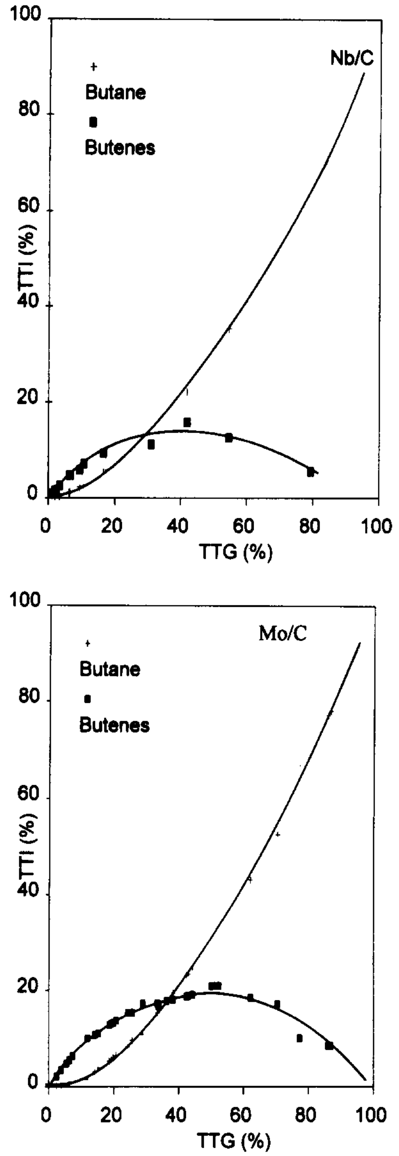

Fig. 3. TTI vs. TTG curves for Nb/C and Mo/C sulfided catalysts.

K is found equal to 3.0 for Nb/C niobium catalyst, to be compared to 1.8 for the Mo/C sample.

This comparison of the two values indicates a noticeable selectivity of the niobium catalyst for hydrogenation. The selectivities towards butene and butane production were determined for the nickel-doped samples at a TTG equal to 10%. Fig. 4 allows these results to be compared to those obtained for the undoped sample ($r=0$). It clearly appears that the butane proportion is decreased when the nickel amount is increased. Consequently, selectivity for hydrogenation can be considered as a property of niobium sulfide.

3.3. EXAFS study

For the carbon supported samples, dispersion of the active phase on the amorphous support did not allow to observe any line by X-Ray diffraction. An EXAFS study was thus undertaken on the $r=0.5$ sample (NiNb/C). Two samples have been studied, one after preparation and the other after the thiophene hydrodesulfurization test.

Results obtained at the nickel K-edge

The radial distribution functions (RDF) obtained (before and after the catalytic test) by Fourier transforms of the experimental signals exhibit only one peak (Fig. 5a and Fig. 5b). The intensity of this peak is not significantly enhanced after the test which means that this treatment (16 h at 350°C) does not improve the crystalline organization of the nickel-containing entities a lot.

After back Fourier transform of this peak, the fits were performed using as the reference $NiPS_3$ for which the Ni–S distance is $R_{Ni-S}=2.46$ Å and the number of sulfur neighbours $N_S=6$. The Debye–Waller factor (σ) was taken equal to 0.02 for the reference compound. The refinements give the results indicated in Table 2.

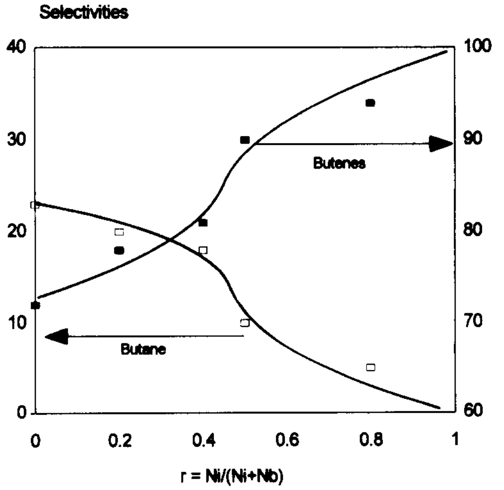

Fig. 4. Selectivities for butene and butane production for nickel-doped niobium sulfide catalysts.

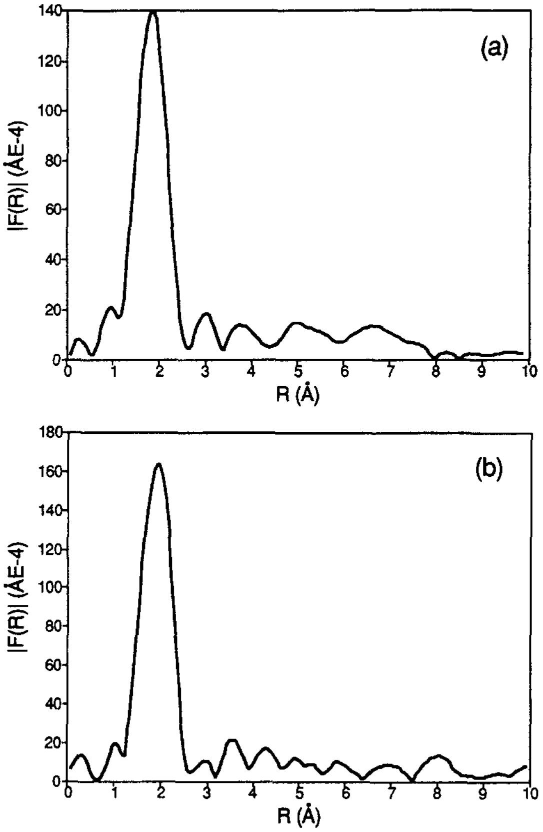

Fig. 5. Radial distribution function for nickel in NiNb/C before (a) and after (b) the catalytic test.

Table 2
Structural parameters refined for nickel in the NiNb/C catalyst

	$R_{(\mathrm{Ni-S})}$ (Å)	N	$\Delta\sigma$ (Å)
Before the test	2.31	4	0.06
After the test	2.27	3.8	0.03

For the two samples, after preparation and after the test, the number of sulfur neighbours is equal to 4 within the usual ± 10% calculation accuracy. The Ni–S distances refined for the two samples do not differ a lot and are in good agreement with a tetrahedral sulfur surrounding similar to that of Ni_3S_2 ($d_{\mathrm{Ni-S}} = 2.28$ Å). These results show that concerning nickel no chemical evolution occurs during the catalytic test since the nickel surrounding is the same, before and after the test. Besides, the similarity with Ni_3S_2 makes unlikely the eventuality of a NiNbS mixed phase similar to the NiWS or NiMoS systems which were studied by Ermakov [7] or Louwers and Prins [8]. For silica-supported Ni-W-S catalysts, Ermakov determined from EXAFS data a short Ni–S distance: 2.22 Å. A similar distance was observed for NiMo supported on carbon or alumina in [8]. Compared to this bond length, the longer distance obtained indicates that no NiNbS mixed phase was formed and that nickel and niobium have formed separated sulfides.

Results obtained at the niobium K-edge

First of all the EXAFS results obtained on massy NbS_2 and NbS_3 will be given, which will then be used as terms of comparison.

NbS_2 and NbS_3 in the bulk state.

The radial distribution functions obtained for massy NbS_2 and NbS_3 exhibit two peaks (Fig. 6a and Fig. 6b). The first one, Nb–S, does not allow

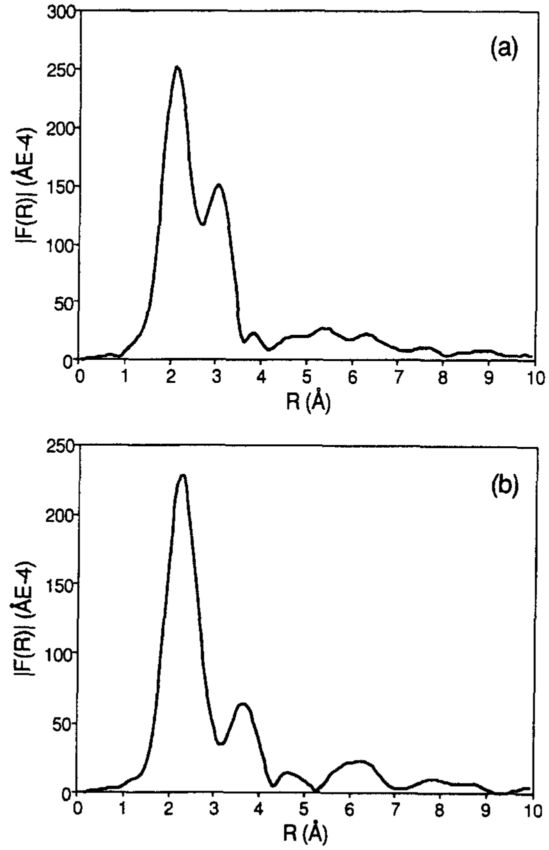

Fig. 6. Radial distribution function for niobium in NbS_2 (a) and NbS_3 (b).

the two compounds to be unambiguously distinguished since the distances are too close (0.248 nm for NbS_2 and 0.257 nm NbS_3). On the contrary, the second one (Nb–Nb) corresponds to different distances for the di- and trisulfide. It is located at 3.0 Å for NbS_2 and at 3.7 Å for NbS_3, as it can be seen on Fig. 6 (R values uncorrected from phase and amplitude shifts). This Nb–Nb peak will be a good indication concerning the nature of the niobium sulfide entities in the supported samples.

The supported catalyst after preparation and before test

The experimental spectrum presents only two weak oscillations, which is characteristic of a poorly organized compound. The consequence is that the intensity of the peaks in the RDF (Fig. 7a) is weak too, as shown by comparing the vertical scales we used for this compound and for massy NbS_2 and NbS_3 (cf. Fig. 6). The nickel-containing compound gives before the test a rather intense Ni–S peak (Fig. 5a), which denotes a rather good crystalline organization, contrary to what is indicated above for the niobium-containing compound.

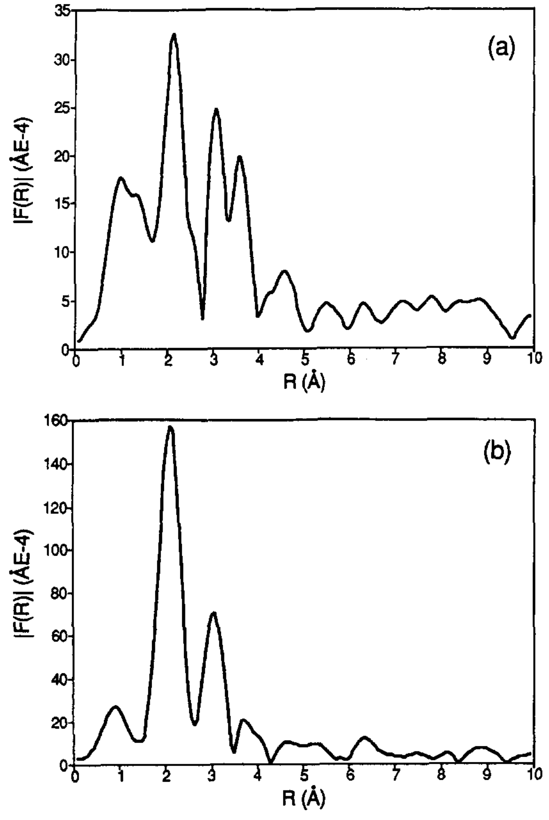

Fig. 7. Radial distribution function for niobium in NiNb/C before (a) and after (b) the catalytic test.

Four peaks can be observed on the RDF (Fig. 7a). The first one, which cannot represent a neighbouring shell due to the too small distance value, has to be considered as a mathematical effect of disorder. The second one is due to the Nb–S contribution (see Fig. 6). The third and fourth ones correspond to the Nb–Nb peaks respectively observed in NbS_2 and NbS_3. This suggests that our sample contains NbS_2- and NbS_3-like entities.

The refinements of the structural parameters were not performed for these data because, due to the highly-disordered character of this compound, the fits cannot give precise results, especially concerning the number of neighbours and the Debye–Waller factor, and even the distance. Indeed, the usual calculation programs take into account a gaussian distribution of the static component (related to disorder) of the Debye–Waller factor, which is not the case for such important disorders.

The supported catalyst after test

If compared to that of the previous sample, the experimental signal obtained after the test exhibits more numerous and more intense oscillations, which explains the greater intensity of the peaks in the RDF (Fig. 7b). Besides, no disorder-induced contribution appears in the RDF, contrary to what observed before the test (first peak in Fig. 7a). It can be concluded that the catalytic use results in annealing effects which improve the crystalline organization. On the contrary, at the Ni edge, no significant improvement of the crystalline organization could be observed after test. Here can be found another evidence for the existence of separate Ni- and Nb-containing sulfides.

Only two peaks are present in the RDF. The first one is due to the Nb–S contribution and the second one closely resembles the Nb–Nb peak of NbS_2. The Nb–Nb signal of NbS_3 cannot be

Table 3
Structural parameters refined for niobium in the NiNb/C catalyst after the test

	R(Å)	N	$\Delta\sigma$(Å)
Nb–S	2.48	5	0.05
Nb–Nb	3.31	2.8	0.03

observed here. Due to the similarity of the studied spectrum with that of NbS_2, the fits were performed on the basis of amplitude and phase functions, extracted from NbS_2 experimental data, and using for this reference the following parameters: $R_{Nb-S} = 2.48$ Å, $N_S = 6$, $\sigma = 0.02$, $R_{Nb-Nb} = 3.33$ Å, $N_{Nb} = 6$, $\sigma = 0.02$. The refined parameters are reported in Table 3 (corrected R values).

The distances are found equal to that of the NbS_2 reference. Considering the calculation uncertainty (up to ±20%), the number of sulfur neighbours does not differ a lot from the ideal value ($N_S = 6$). As for the number of niobium neighbours, it is only half the expected value. This indicates that contrary to the first neighbouring shell, the second one is not perfectly organized after the test. The refined distance values clearly show that, after the catalytic test, niobium sulfide is present only as NbS_2-like entities or small crystallites, in agreement with the RDF where no Nb–Nb contribution corresponding to NbS_3 can be detected. Consequently, in the conditions of our test, the NbS_3-like species are not stable, due to the reducing character of the reactive atmosphere. Along with the crystallization improvement, the disappearance of the NbS_3-like species can explain the observed deactivation, insofar as these supported entities are more active than NbS_2-like ones as it was evidenced in the massy state [1,2].

4. Conclusion

Unsupported niobium trisulfide was found to be a better catalyst in thiophene conversion than molybdenum disulfide. Furthermore, intrinsic activities of mixed Ni-Nb unsupported sulfides are similar to those observed on NiMoS unsupported catalysts. These results suggested that high HDS activities may be obtained on mixed Ni-Nb supported sulfides. In fact, we found the activity of undoped niobium sulfide carbon-supported catalysts lower than to Mo/C catalyst. Besides, these compounds present an interesting selectivity for hydrogenation. Ni dopant gives a two fold increase of the catalytic activity similarly to unsupported systems but does not allow to reach the activity of a NiMo/C catalyst. Moreover, the presence of Ni decreases the selectivity for hydrogenation. As evidenced from EXAFS results, Ni does not form a mixed phase with niobium. This absence of a mixed phase could be due to the structural particularity of the niobium sulfide phases. The EXAFS measurements show that they contain NbS_2- and NbS_3-like entities. The presence of NbS_3-like species can at the first sight be considered as interesting since in the massy state NbS_3 is more active than NbS_2. However, the structure of NbS_2 closely resembles that of MoS_2, which is not the case for NbS_3 [2]. It can so be thought that NbS_2 could form a NiNbS mixed phase, and not NbS_3.

These results shows that supported niobium catalysts present original properties but the knowledge on these systems, compared to Mo based catalysts, is scarce and further works are needed.

Acknowledgements

This work was carried out in the framework of the contract 'Hydrogenation of Aromatics'. It received support from Elf, IFP, TOTAL and from the CNRS (ECOTECH). The authors thank Eric Prouzet for his participation to the EXAFS study.

References

[1] M. Vrinat, C. Guillard, M. Lacroix, M. Breysse, M. Kurdi and M. Danot, Bull. Soc. Chim. Belg., 96 (1987) 1017.
[2] M. Danot, J. Afonso, J.L. Portefaix, M. Breysse and T. des Courières, Catal. Today, 10 (1991) 629.
[3] F.W. Lyttle, D.E. Sayers and E.A. Stern, Phys. Rev. B, 11 (1975) 4825.

[4] E.A. Stern, D.E. Sayers and F.W. Lyttle, Phys. Rev. B, 11 (1975) 4836.

[5] F.E. Massoth and G. Muralidhar, in H.F. Barry (Editor), Fourth Int. Conf. on the Chem. and ses of Molybdenum, Golden, Colorado, Climax Molybdenum Co., 1982.

[6] J.E. Germain, Catalyse de contact, Techniques de l'Ingénieur, Paris, 1979.

[7] Yu.I. Ermakov, Russ. Chem. Rev., 55(3) (1986) 247.

[8] S.P.A. Louwers and R. Prins, J. Catal., 133 (1992) 94.