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Niobium sulfide as a dopant for hydrotreating NiMo catalysts

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Abstract

Niobium sulfide has been recently found to be an interesting new active phase for hydrodesulfurization. In this work, niobium was used as a dopant for a conventional hydrotreating catalyst. A NiMo hydrotreating catalyst in the oxide form was doped with various contents of Nb precursor salt ($0<\text{Nb wt.\%}<7$). After drying, the activation of the catalyst was performed with CS_2 sulfiding agent in a high pressure vessel. The use of this new dopant increased the catalytic activity in both HDS and HYD model reactions. Highest activities were obtained with an optimum Nb content of 5 wt.%. The selectivity of the products was also modified since more isomerized compounds where produced. Various techniques were used to determine structural and morphological characteristics of the materials. TEM pictures only showed the presence of lamellar particles similar to MoS_2. EDX analysis demonstrated the homogeneous distribution of the transition metal elements (Ni, Mo, Nb) even with small electron probes at high magnification. EXAFS was used to determine the local environment of Nb atoms and showed that Nb was present in the form of "NbS_2" entities similar to the bulk phase. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to the evolution of the legislation concerning the sulfur content of fuels, the development of new hydrotreating catalysts continues to attract intensive research both in academic and industrial laboratories [1,2]. In the last decade, new formulations of CoMo and NiMo industrial catalysts appeared combining a higher Mo content and an additional element such as phosphorus [1], resulting in an improved activity and stability of the catalyst. Other additives such as fluoride or boron were also studied [3,4]. The introduction of the additive may have several effects, mainly as support modifiers [5,6] and also probably the active phase [7]. Some attempts to modify the acidity of the support were also made by using mixed oxides systems such as ZrO_2–Al_2O_3 [8,9], TiO_2–Al_2O_3 [10] or La_2O_3–Al_2O_3 [11]. Niobia–alumina mixtures have revealed enhanced acidities which provide interesting hydroprocessing properties [12]. Besides, some attempts have been made to increase the activity of a conventional catalyst by adding a small quantity of another active phase, ruthenium for instance. Several studies of the hydrotreating activity of unsupported transition metal sulfides yielded volcano plots with ruthenium sulfide at the top [13,14]. Thus, small

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amounts of ruthenium have been added to CoMo or NiMo catalysts [15,16]. Noble metal catalysts were found highly efficient for the activation of hydrogen and are expected to increase the quality and nature of the hydrogenation sites of the HDT catalyst. The main handicap in the use of such metals is the high costs. Other transition metals such as W were also used as secondary promoters of a CoMo catalyst [17].

Recently, the properties of niobium sulfides have particularly attracted our attention. In the unsupported state, these sulfides exhibit unique acidic properties [18]. Supported on carbon or alumina, they reach catalytic activities higher than those of a MoS_2 supported catalyst with equivalent metal loading [19,20].

The purpose of the present study was to use Nb as a new dopant for a NiMo catalyst, considering that the acidic properties of Nb–S entities could favourably modify activities or selectivities. Catalytic properties of the samples have been studied and various techniques have been used for their characterisation.

2. Experimental

2.1. Catalysts preparation

Oxidic form of an alumina-supported NiMo industrial catalyst (2 wt.% of Ni and 9 wt.% of Mo) the so-called “IC” was doped with various amounts of Nb (up to 7 wt.%), using impregnation with a niobium oxalate solution buffered with ammonium oxalate. Then, catalysts were dried at room temperature. An excess of liquid CS_2 was introduced into a high pressure vessel filled with nitrogen with respect to the amount required to transform the Ni, Mo and Nb oxides into sulfides. Temperature was raised up to 723 K for 10 h; under these conditions, the pressure inside the vessel was 40 bars [20].

2.2. High resolution electron microscopy (HREM)

High resolution electron microscopy was performed with a STEM VG HB501 instrument equipped with an EDX LINK-ISIS detector and a Phillips CM30. Freshly sulfided samples were grinded under inert atmosphere and were ultrasonically dispersed in ethanol. The suspension was collected on carbon-coated grids.

2.3. EXAFS analysis

EXAFS spectra were recorded at LURE (Centre Universitaire Paris-Sud) on the XAS 2 spectrometer, using a Si(311) channel cut monochromator. The storage ring (DCI) used 1.85 GeV positrons with an average intensity of 250 mA. Samples were prepared in a glove-box and sandwiched between two X-ray transparent adhesive tapes (Kapton). Data were recorded in transmission mode and measurements performed at liquid nitrogen temperature at the Mo K-edge (from 19 900 to 21 100 eV) and Nb K-edge (from 18 850 to 19 800 eV). The data processing was performed with the package developed by A. Michalowicz [21], which allows disorder to be described according to an asymmetric distance distribution function which already proved to be relevant for calculations on disordered systems [22]. Calculated phase and amplitude files have been used [23].

2.4. Catalytic tests

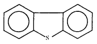
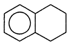
Hydrodesulfurization (HDS) of dibenzothiophene and hydrogenation (HYD) of tetraline model reaction test have been used to determine the catalytic properties of the catalysts. The tests were performed under dynamic conditions at medium hydrogen pressure, under conditions given in Table 1. Specific activity in the case of tetraline hydrogenation and rate constant for DBT HDS were determined, according to first-order kinetics, after 16 h on stream in the pseudo-stationary state. Activities are accurate to within 10%.

3. Results and discussion

3.1. Catalytic activities

Fig. 1 shows that in both reactions a maximum of activity was reached for a Nb loading of 5 wt.%. For this particular loading the activity gain was close to 25%. We found that addition of an equivalent amount of Mo (5 wt.%) to the industrial catalyst slightly decreased the catalytic activity.

Table 1
Conditions of high pressure model hydrodesulfurization and hydrogenation tests

Reaction	Reactant	Molecule	Total flow rate (ml/min)	T_{reaction} (K)	P_{total} (Pa)	$P_{\mathrm{H_2S}}$ (Pa)	P_{reactant} (Pa)
HDS	DBT[a]		80	573	33×10^5	28×10^3	577
HYD	Tetraline		300	573	45×10^5	77×10^3	8900

[a] DBT=dibenzothiophene, H_2S added as gas with H_2/H_2S mixture.

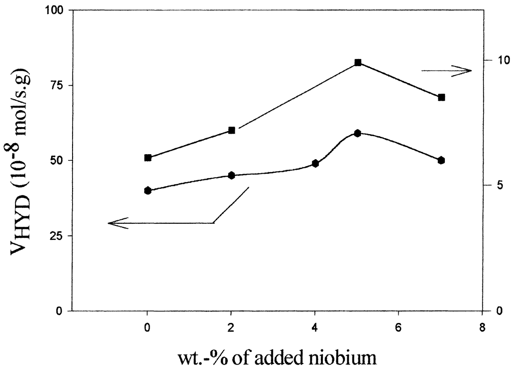


Fig. 1. Tetraline hydrogenation and DBT desulfurization of Nb doped NiMo catalysts.

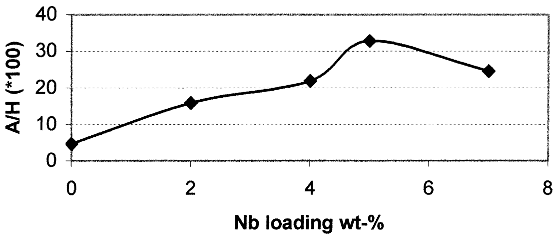
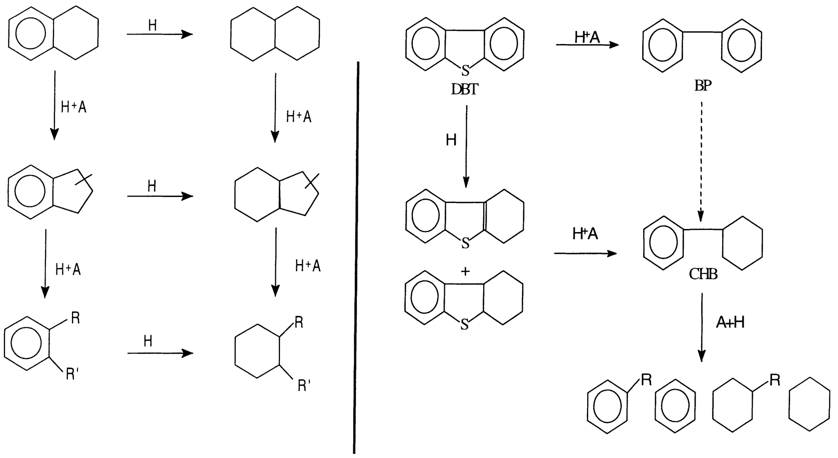


Fig. 2. Selectivity (A/H) in tetraline hydrogenation versus niobium content.



Schematic representation of tetraline [24] hydrogenation and dibenzothiophene hydrodesulfurization [25].

In both tetraline HYD and DBT HDS reactions, hydrogenating sites (H) and/or acidic sites (A) are involved. In tetraline HYD for instance, the main reaction products are decalins, methyl indans and alkyl benzene and methyl cyclohexane. Naphtalene formed on dehydrogenating sites was also formed. For this HYD reaction (Fig. 2), the selectivities associated to the acidic route were increased in the presence of the Nb dopant. In these experiments, the conversion rates varied from 15% for the IC to 22% for the best Nb-doped catalysts. In this narrow range of conversion, the presence of Nb rapidly increased the A/H ratio, where A expressed the conversion in methyl indans, alkyl benzene, and methyl cyclohexane and H the conversion in decalines and naphtalene. In the case of DBT HDS, the selectivity for cracked products

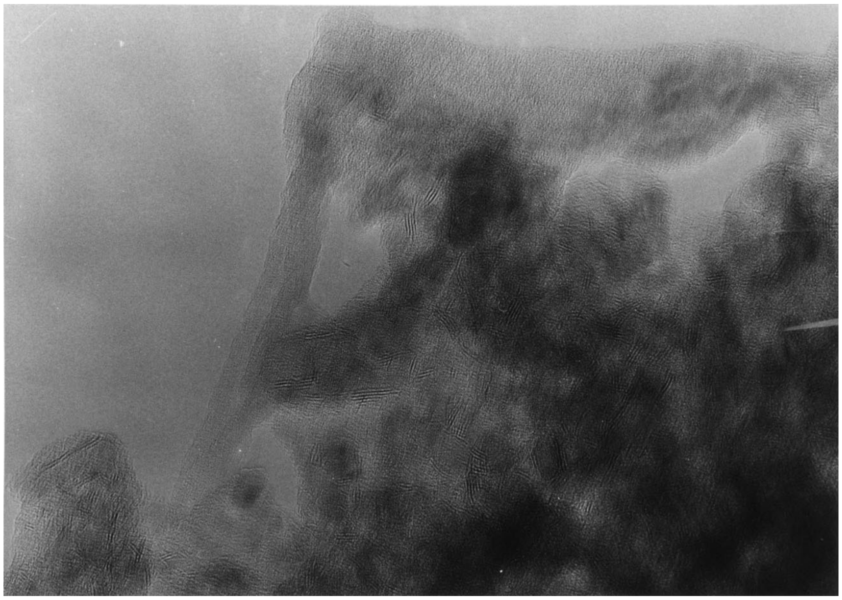


Fig. 3. TEM picture of a 5% Nb doped NiMo catalyst.

increased and isoalkylbenzenes appeared when Nb was added. These effects demonstrated that niobium sulfide enhanced the acidic properties of the catalysts.

3.2. Electron microscopy

As in the case of usual CoMo or NiMo catalysts, only lamellar structures were observed, with interplanar spacing of about 0.6 nm. These crystallites could correspond either to MoS_2 (0.615 nm) or to NbS_2 (0.633 nm) species, the two sulfides having similar crystallographic structure. TEM picture (Fig. 3) of Nb 5 wt.% doped sample and statistics performed on several pictures showed that the presence of Nb enhanced the average length (4.7 nm) and stacking (3.2 layers per crystallite) of the crystallites as compared to the undoped catalyst (3.1 nm and 2 layers).

EDX analysis has been performed on the same sample, using various magnifications and probe sizes and the presence of the four active elements (Ni, Mo, Nb, S) was always observed. At 1 million magnification, probes of 2.5 nm ϕ were used and focused on lamellar crystallites. Fig. 4 demonstrates the rather good homogeneity of the Nb–Mo distribution: even at high magnification, no individual Nb or Mo sulfides could be detected, and the atomic ratio Nb/Mo remained in the small range 0.5–1.6, indicating close proximity of Nb and Mo atoms in the analysed areas.

3.3. EXAFS results

The radial distribution function around niobium (Nb K-edge, Fig. 5) showed a first peak which corresponded to sulfur neighbours, with a Nb–S distance of 0.249 nm (Table 2) close to the value observed in NbS_2 (0.248 nm). However, the number of sulfur neighbours ($N<4$, Table 2) was lower than expected ($N=6$), which can be due to disorder effects. Effectively, such a N decrease is often observed for disordered samples processed with usual programs,

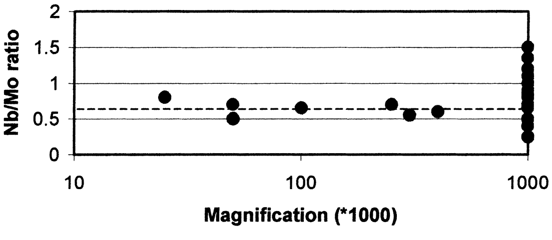


Fig. 4. EDX analysis ratios Nb/Mo at various magnification (theoretical value: dashed line).

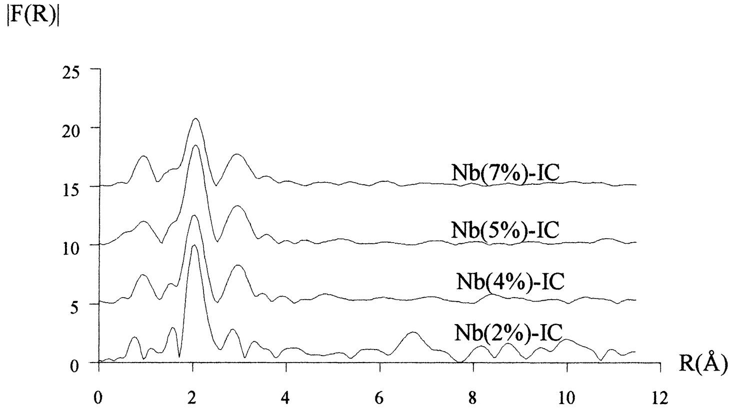


Fig. 5. Radial distribution function at Nb K-edge for Nb-doped NiMo catalysts.

i.e., using symmetrical distribution function of the distances. For this reason, further refinements were performed using an asymmetric distance distribution function [22], which was already successfully used for dispersed niobium sulfides [23]. These refinements led to more satisfactory coordination numbers (Table 3), even if disorder did not appear to be very important (the asymmetric parameter remaining small: s=0.08). These results showed that in our catalysts, whatever their composition, niobium was involved in Nb–S entities similar to those involved in bulk NbS_2 (R=0.248 nm, N=6). The second coordination shell (second peak, Fig. 5) consists of in-plane nearest cationic neighbours of niobium. They were found at a distance of 0.331 nm (Table 2), in good agreement with the Nb–Nb distance in NbS_2 (0.333 nm). The number of cationic neighbours reached a value (N=1.5) lower than expected (N=6), which could be attributed to disorder effects already evidenced for the first shell; however, the distance asymmetric distribution function cannot in principle be used in this case of a second coordination sphere. Nb K-edge EXAFS results thus showed that niobium composed of disordered [NbS_2] entities similar to bulk NbS_2.

Table 3
Results of the fits at the Nb K-edge using an asymmetric distance distribution

Catalyst	R(S) nm	N(S)	σ(S) 10^{-2}	ΔE_1 (eV)	s[a]
+2 wt.% Nb	0.245	5.16	1	6	–
+4 wt.% Nb	0.245	5.7	5	4	0.08
+5 wt.% Nb	0.245	6	4	3	0.08
+7 wt.% Nb	0.245	3.9	4	3	0.08

[a] Asymmetric disorder parameter [21,22].

The measurements performed at the Mo K-edge (Fig. 6) (Table 4) showed that niobium addition did not induce any modification of molybdenum surrounding with respect to the industrial NiMo catalyst or to bulk MoS_2 (d_{Mo-S}=0.242 nm, in-plane

Table 2
Nb K-edge EXAFS results: structural parameters of niobium in Nb-doped $NiMo/Al_2O_3$ sulfide catalysts[a]

Catalyst	R(S) nm	N(S)	σ^b(S) 10^{-2}	$\Delta E^c{}_1$ (eV)	R(Nb) nm	N(Nb)	σ(Nb) 10^{-2}	ΔE_2 (eV)
+2 wt.% Nb	0.249	2.6	3	4	–	–	–	–
+4 wt.% Nb	0.249	3.3	6	3	0.331	1.5	5	0
+5 wt.% Nb	0.249	3.7	6	2	0.331	1.5	6	−1
+7 wt.% Nb	0.249	2.5	6	3	0.331	1.3	6	−2

[a] Reliability of the fits: $2.5\times10^{-2}<\rho<4.7\times10^{-2}$, where ρ is the fit residue.
[b] σ: Debye–Waller factor.
[c] ΔE_1: Energy origin shift.

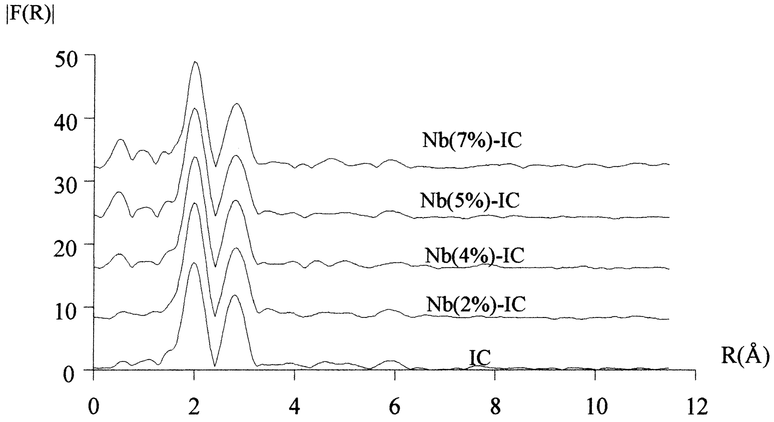


Fig. 6. Radial distribution function at Mo K-edge for Nb-doped and undoped NiMo catalysts.

Table 4
Mo K-edge EXAFS results: structural parameters of molybdenum in Nb-doped $NiMo/Al_2O_3$ sulfide catalysts[a]

Catalyst	R(S) nm	N(S)	σ(S) 10^{-2}	ΔE_1 (eV)	R(Mo) nm	N(Mo)	σ(Nb) 10^{-2}	ΔE_2 (eV)
$NiMo/Al_2O_3$	0.242	6.2	6	2	0.317	2.7	5	0
+2 wt.% Nb	0.242	6	5	4	0.317	2.4	3	2
+4 wt.% Nb	0.242	6	5	4	0.317	2.6	4	2
+5 wt.% Nb	0.242	5.9	5	4	0.317	2.6	4	0
+7 wt.% Nb	0.242	5.8	5	3	0.317	2.4	4	0

[a] Reliability of the fits: $2\times10^{-2}<\rho<3.1\times10^{-2}$.

$d_{Mo\text{–}Mo}$=0.316 nm). On the basis of usual symmetrical distribution function of the distances, the number of sulfur neighbours refined to $N\approx6$; the number of cationic neighbours ($N\approx2.5$) was found to be decreased by disorder effects, but the reduction is less important than in the case of niobium: these two facts show that organisation of the MoS_2 layers is better than that of NbS_2 ones.

No modification of Mo–M or Nb–M distances (M=Mo or Nb) were observed indicating that no solid solution $Nb_{1-x}Mo_xS_2$ was formed. The proximity of the Nb and Mo evidenced by EDX and the disorder observed by EXAFS suggest that small crystallites of NbS_2 are located at the periphery of larger MoS_2 slabs.

4. Conclusion

In both tetraline hydrogenation and dibenzothiophene HDS reactions, catalytic activities of an industrial NiMo were enhanced by the presence of Nb dopant. The optimum niobium amount was found to be around 5 wt.% and a 25% gain in activity was obtained. Niobium was present in the form of NbS_2 layers, well dispersed on the support and in close contact with the other active components. Even at low loading, the specific acidic properties of niobium sulfide were reflected by the selectivity of the HYD and HDS products. Usually acidity are induced on sulfide catalysts by mixed supports such as silica–alumina or zeolites–alumina mixture, this work gives an example of acidic properties supplied with another active sulfide.

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