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Niobium sulfides as catalysts for hydrotreating reactions

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Abstract

Hydrotreating properties of unsupported and supported niobium sulfides are compared to those of molybdenum sulfide catalysts. Niobium catalysts demonstrate higher activities than molybdenum sulfide ones and remarkable selectivity in cracking and isomerisation reactions.

Keywords: Niobium sulfide catalysts; Hydrotreating

1. Introduction

The present environmental problems open up a challenge for the development of new hydrotreating catalysts which would be more efficient than the present ones for sulfur and nitrogen elimination from various petroleum cuts. Until now, research devoted to sulfide catalysts have been mainly focused on the molybdenum and tungsten systems and less attention has been paid to other transition metal sulfides. However, the comparison of the properties of the various transition metal sulfides either unsupported or supported on carbon for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) or hydrogenation reactions has shown that some other systems present high catalytic properties. The results obtained for the various reactions are not similar and the selectivities for the different functions, i.e., C–S, C–N, C–C bond cleavage or hydrogenation vary in a wide range. Particularly, the properties of niobium sulfides have attracted our attention. For biphenyl conversion, these catalysts were found more active than the conventional molybdenum or tungsten sulfides and, interestingly, they presented a particular ability for cracking. For these reasons, a comprehensive study devoted to niobium sulfides was undertaken in our laboratories (specialising in catalysis and solid state chemistry). The objective of the present paper is to give an overview of the studies carried out in the last few years concerning, (i) the properties of unsupported niobium sulfides, (ii) the transposition to the supported state and (iii) the doping effect of nickel.

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2. Experimental

2.1. Catalysts preparation

Unsupported niobium sulfides were obtained by direct combination of the elements in evacuated silica tubes [1]. In order to improve the surface area of NbS_3, an intercalation–deintercalation treatment was used [2]. This method resulted in a significant improvement of the surface areas up to 20 m^2/g. The niobium trisulfide obtained in this way is designated as NbS_3-D.

Carbon and alumina supported catalysts were prepared according to the method described in [3,4]. The supports used are a carbon "Norit", with a surface area of 1200 m^2/g and a pore volume of 1 cm^3/g and γ-alumina (Sp: 250 m^2/g and pore volume of 1 cm^3/g). The niobium amount introduced is 10 wt.-%. Excess technique was chosen for the impregnation of carbon and wetness impregnation method for the alumina.

The nickel-doped catalysts were prepared using the co-impregnation method, adding nickel nitrate to the niobium precursor salt [4]. The total amount of metal was kept equal to 10 wt.-%. Several samples were prepared with different r ($r = Ni/(Ni + Nb)$), atomic ratios.

2.2. Catalysts characterisations

Unsupported niobium sulfides were characterised by X-ray diffraction, using an INEL curved detector and Cu $K\alpha_1$ radiation. Their textural properties were determined by the BET method in a volumetric apparatus using N_2 as physisorbant. DTA–TGA experiments were performed under nitrogen with a Setaram TGA 92 16-18.

Attempts to obtain X-ray diffraction patterns of carbon-supported samples were unsuccessful, due to a poor crystalline organisation. Besides, electron microscopy gave images with very bad contrast. We could however characterise these catalysts with the aid of EXAFS (extended X-ray absorption fine structure) technique. EXAFS spectra were recorded on the EXAFS I spectrometer, at LURE, the French synchrotron radiation laboratory, using the DCI storage ring.

For some of the alumina-supported catalysts, X-ray diffraction patterns could be obtained. However, only one weak and broad line could be observed. For that reason, EXAFS and electron microscopy (Philips CM3O) were also used for the characterisation of the alumina supported samples.

2.3. Catalytic activity measurements

The reactions were carried out in the vapour phase using dynamic flow microreactors under atmospheric pressure or medium–high pressure as described in [2]. Specific activities, A_s, (10^{-8} mol/s g) were determined after 16 h on stream at the pseudostationary state. In order to compare the properties of catalysts, presenting various surface areas, we calculated the intrinsic rates A_i (per m^2 of catalyst after test, 10^{-8} mol/s m^2), using the surface area after test S_f (m^2/g). The catalytic properties of MoS_2 were measured as reference.

3. Results and discussion

3.1. Structural features

In the Mo–S system, several phases exists but MoS_2 is the only phase observed in catalysis. The Nb–S system is complex and different phases may be observed. The structural features of these phases are described below:

Hexagonal niobium disulfide NbS_2 exhibits the same overall features as MoS_2, i.e., a lamellar arrangement of trigonal prisms $[NbS_6]$ (Nb–Nb = 0.332 nm). A rhombohedral modification can be stabilised by the presence of extra niobium atoms located in the van der Waals space. This structure may also accommodate a large excess of metal atoms ($Nb_{1+x}S_2$ with x nearly equal to 1 also known as $Nb_{1-y}S$). In this

Table 1
Conditions of the laboratory tests

Reactant	H_2 pressure (10^5 Pa)	H_2S pressure (10^2Pa)	Hydrocarbon pressure (10^2 Pa)	Temperature (K)
Biphenyl	23.5	4.5	8	530
Thiophene	1	–	24	623
Pyridine	30	665	266	573
n-Pentylamine	1	4	1.33	548
Isooctane	1	4 or 40	1.33	548
Toluene	27	73 or 733	40	573

structure, the niobium cations are associated in triangular clusters with Nb–Nb in short distances (2.92 Å). The structure of NbS_3 is completely different, even if built from the same $[NbS_6]$ prismatic units. In NbS_3, these prisms share their triangular faces to constitute infinite fibres which are associated, due to inter fibre Nb–S bonds, and form corrugated slabs. The formula can be written as $Nb^{IV+}S^{II-}(S_2)^{II-}$, with sulfur pairs $(S_2)^{II-}$ similar to those present in pyrite structures. In NbS_3, d^1–d^1 Nb–Nb bonds are established.

The stability of NbS_3 under hydrogen at atmospheric pressure was studied at 723 K. The sample lost weight until a final state corresponding to $Nb_{1.12}S_2$ [1] was reached. This result means that the structure of the niobium sulfide catalyst could be modified under test conditions depending on the experimental parameters, temperature, and partial pressures of hydrogen and hydrogen sulfide.

3.2. Unsupported niobium sulfides

In order to evaluate the catalytic properties of niobium sulfides we used model molecules such as biphenyl and toluene for hydrogenation, pyridine and n-pentylamine for HDN and isooctane as a specific reaction for measuring acidity.

Under the conditions described in Table 1, the conversion of biphenyl leads to cyclohexylbenzene (CHB), dicyclohexyl (DCH) and cracked products: cyclohexane (C) and benzene (B). The selectivity in cracked products was defined by the following relation:

$$S_{ck} = \frac{\frac{1}{2}(B+C)}{\mathrm{CHB} + \mathrm{DCH} + \frac{1}{2}(B+C)}$$

The results, given in Table 2, show that the niobium sulfides present higher intrinsic activity than MoS_2. The selectivity for cracking products is very high for all the niobium sulfides and much lower for molybdenum sulfide.

The low surface area NbS_3 sample is stable under the conditions used whereas the higher surface area sample NbS_3-D is partially converted into $Nb_{1.12}S_2$. Experiments started with the NbS_3 phase provide better catalytic activities.

Table 3 presents the results obtained in the hydrogenation of toluene. Toluene is hydrogenated in methylcyclohexane but a cracking

Table 2
Catalytic activities in biphenyl conversion, structures, surface areas and stability under hydrogen pressure

Structure before test	Structure after test	S_f (m^2/g)	A_s	A_i	S_{ck}
NbS_3	$NbS_2 + \epsilon\text{-}Nb_{1.12}S_2$	2.5	2.3	0.92	88
NbS_3-D	$NbS_3 + Nb_{1.12}S_2$	7	4.8	0.69	88
$Nb_{1.12}S_2$	$Nb_{1.12}S_2$	9	2.7	0.30	80
MoS_2	MoS_2	38	65	0.16	19

Table 3
Catalytic activities in toluene conversion, under different partial pressures of H_2S

Catalyst	73×10^2 Pa H_2S				733×10^2 Pa H_2S			
	S_f	A_s	A_i	A_{ic} [a]	S_f	A_s	A_i	A_{ic}
NbS_3-D	15	19	12.7	1.3	14	12.2	8.7	2.4
MoS_2	40	40	10	–	43	27.6	6.4	0.1

[a] A_{ic}: intrinsic activity for benzene production.

Table 4
Catalytic activities in pyridine conversion

Catalyst	Structure after test	S_f	A_s	A_i
NbS_3	$NbS_3 + Nb_{1.12}S_2$	2	24	9.2
NbS_3-D	$Nb_{1.12}S_2$	15	113	7.5
MoS_2	MoS_2	20	130	6.5

Table 5
Catalytic activities in n-pentylamine conversion [a], structures and surface areas

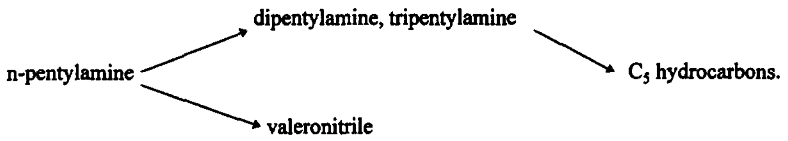
Catalyst	Surface after test (m^2/g)	A_s	A_i	A_sC_5 [b]	A_iC_5 [c]
NbS_3-D	5.3	12.4	2.3	7	1.3
MoS_2	28	45	1.6	6	0.21

[a] Measured at a global conversion of 15%.
[b] A_sC_5: specific activity for C_5 production.
[c] A_iC_5: intrinsic activity for C_5 production.

route also exists and forms benzene and methane. Similarly to the previous reaction, the rate of benzene appearance indicates a high selectivity for cracked products.

Another important aspect is the role of H_2S in the selectivity of the products. A ten times increase of the hydrogen sulfide partial pressure reduces the global conversion (H_2S is an inhibitor) but increases the selectivity in cracking. This effect was already mentioned in the literature [5] and attributed to the formation of S–H Brønsted sites.

Pyridine is very often utilised as a test molecule for the HDN process. Its conversion includes several consecutive steps corresponding to hydrogenation (piperidine) and C–N bond cleavage. Niobium trisulfide is slightly more active than MoS_2 (Table 4). In order to get more information, we studied the final step of this reaction, i.e., n-pentylamine conversion (Table 5). The reaction scheme of the conversion of n-pentylamine can be written as follows:



The C_5 hydrocarbon rate formation is much higher on niobium sulfide than on molybdenum sulfide, or other sulfides [6] and does not vary when the H_2S partial pressure is 10 times higher.

In order to understand the acid basic properties of niobium sulfides, we used the model isooctane conversion, which is indicative of the presence of medium strength acid sites [7]. Isooctane is cracked in isobutene and isobutane. Small quantities of propane, propene, and neopentene and neopentane are also observed.

According to these data, it can be emphasised that the acidity of niobium sulfide is two or three times higher than that of molybdenum sulfide.

Fig. 1 summarises the comparison between intrinsic activities of MoS_2 and NbS_3 in several model reactions. Niobium sulfide catalysts is always more active than molybdenum sulfide.

The most striking feature of these results must be related to the acidic properties of niobium catalysts evidenced in Fig. 2. In hydrogenation reactions, the high selectivities in cracking clearly indicates the acidic nature of the surface of the catalyst. Results obtained with n-pentylamine conversion also reinforce this result since the mechanisms of the C–N bond cleavage involves Brønsted sites [8,9].

3.3. Supported niobium sulfides

Our first attempts to prepare niobium supported catalysts were performed on oxide supports: alumina and silica. On these supports, and

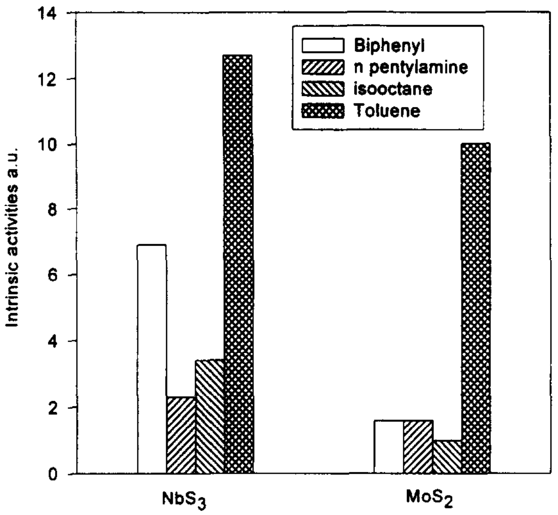


Fig. 1. Comparison between intrinsic activities of MoS_2 and NbS_3 in several model reactions.

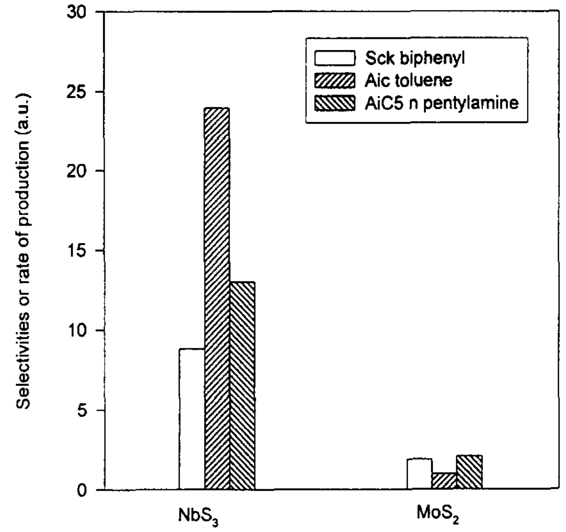


Fig. 2. Comparison between selectivities or production rates of cracked products of MoS_2 and NbS_3 in several model reactions.

using conventional sulfurising treatments (H_2S-based flows under atmospheric pressure), significant sulfurisation can be obtained only at high temperature (800°C) [10]. In these conditions, sintering of the formed niobium sulfide occurs which results in very low catalytic activities. Such difficulties for niobium to be sulfurised on oxide supports can be attributed to strong support–cation interactions. Fig. 3. shows the radial distribution function of neighbours around niobium (obtained from EXAFS data) for an alumina supported sample calcined under air atmosphere or treated at 673 K with a H_2/H_2S mixture. The similarity of the two radial distribution functions clearly demonstrates that this sulfurisation procedure is inefficient. In fact, thermodynamical data show that free energy of sulfurisation of niobium oxide is positive and clearly indicate that this reaction should not be easily compared to that of Mo oxide. Besides, support effect has a crucial role in the preparation of Nb catalysts. This will be demonstrated with the following example: Niobium oxalate was used as a precursor and impregnated on carbon and alumina. TGA–DTA experiments, presented in Fig. 4, show that on carbon, water is first eliminated at 373 K, then the precursor salt decomposes at 513–523 K; on alumina, a higher temperature (643 K) is needed (see Fig. 5). This indicates that weak interactions with active cations on carbon and strong ones on alumina are established. Considering these results, we used two different routes for supported niobium sulfide to be obtained. First, instead of oxides, we chose carbon as a support, because of the weakness of the interactions it establishes with metallic cations. Second, using oxide supports, we carried out the sulfurisation

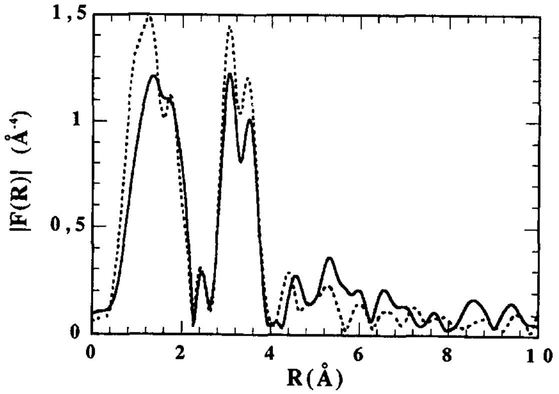


Fig. 3. Radial distribution function (Nb K-edge) of Nb/Al_2O_3 sample calcined at 673 K (full line) or treated by N_2/H_2S (dotted line).

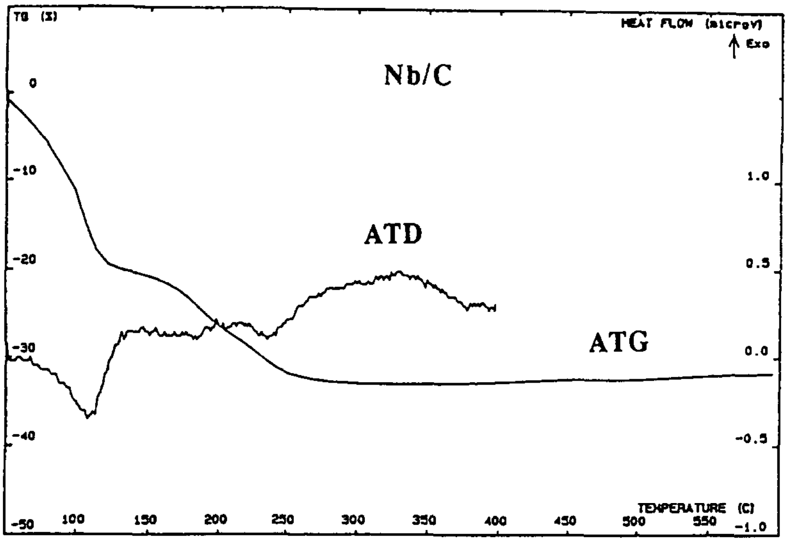


Fig. 4. DTA–TGA curves of Nb/C sample.

treatment in conditions more severe than the conventional ones.

3.4. Carbon supported catalysts

Different precursor salts were used with a 10 wt.-% loading: niobium chloride, niobium oxalate and ammonium niobate, respectively, referred to as NbCl, NbOX and NbN. Sulfurisation of the carbon supported catalyst was optimised [3]. Best conditions were found to be 4 h at 400°C, using N_2/H_2S (15%) gas mixture. Fig. 6 presents the HDS activities of Nb/C catalysts prepared with the different precursor salts. The optimised preparation provides an activity higher than that of Mo/C catalyst. Furthermore, Nb catalysts present an original selectivity toward hydrogenation [4].

In the conversion of n-pentylamine, Nb/C catalysts present a selectivity in C5 production

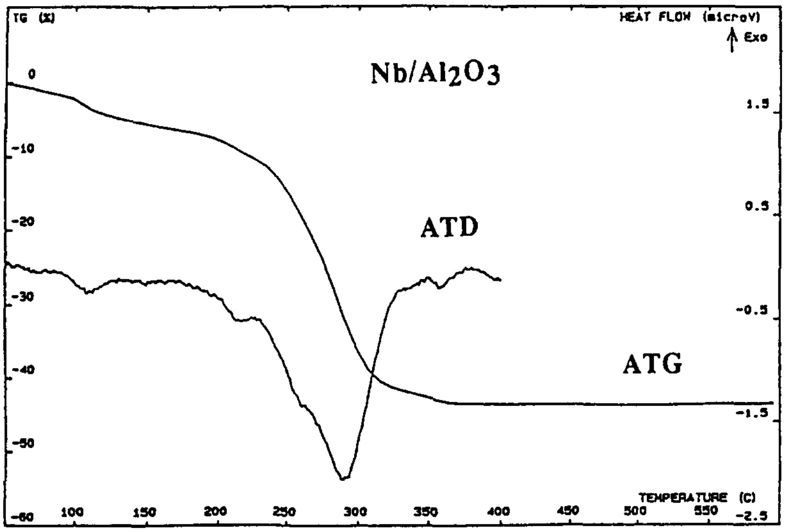


Fig. 5. DTA–TGA curves of Nb/Al_2O_3 sample.

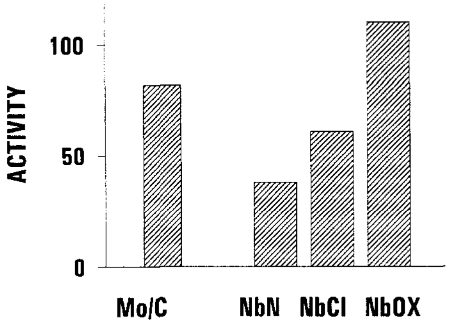


Fig. 6. Comparison of HDS catalytic activities between Mo and Nb sulfide catalysts.

twice higher than that of a Mo supported catalyst [11]. This results indicates that the properties of supported niobium sulfides resemble those observed on bulk niobium sulfide phases.

Evidence of sulfidation of niobium is given in Fig. 7. It can be seen that the Nb–O distance, observed after impregnation, is replaced by a Nb–S distance after sulfidation. By using unsupported NbS_3 and NbS_2 as references, it is possible to characterise the supported species with EXAFS and TPR techniques. The specific Nb–Nb distances of each phase (in the case of EXAFS) and characteristic reduction peaks in the case of TPR allow to discriminate these two phases in the supported state [3]. Depending on the sulfidation procedure, NbS_3 or NbS_2 species may be obtained in the supported state. The highest catalytic activities are related to the presence of NbS_3-like entities.

Attempts to prepare mixed NiNb/C catalysts were performed [4]. The 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 the EXAFS results, Ni does not form a 'mixed phase' with niobium as it was observed in the case of Ni–W–S [12] or Ni–Mo–S [13] catalysts.

3.5. Alumina supported catalysts

Ellingham's diagram [14] shows that carbon disulfide CS_2 is, thermodynamically speaking, a better sulfurising agent than H_2S, up to 1573 K. Besides, since CS_2 is liquid at room temperature, it can be easily introduced in a high-pressure vessel in order to perform the treatment under pressure. Such a method was used for the sulfurisation of Nb/Al_2O_3 catalysts and, again, the conditions (temperature, duration) were optimised [3]. The highest activity was obtained after treatment at 673 K for 10 h.

Radial distribution functions (Fig. 8) of the neighbours of niobium (derived from EXAFS

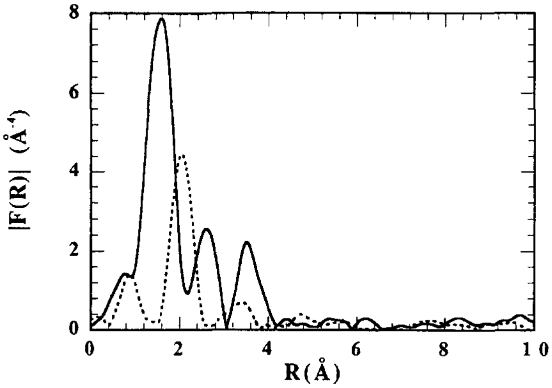


Fig. 7. Radial distribution function (Nb K-edge) of Nb/C sample after impregnation (full line) and after sulfidation with N_2/H_2S gas mixture (dotted line).

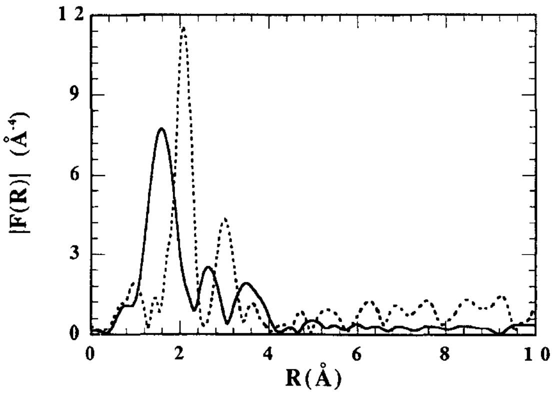


Fig. 8. Radial distribution function (Nb K-edge) of Nb/Al_2O_3 after impregnation (full line) and after sulfidation under CS_2 pressure (dotted line).

data) demonstrate that under CS_2 atmosphere Nb on alumina has been sulfurised, since Nb–S bonds appear. Depending on the sulfiding conditions, different phases are identified by EXAFS: NbS_2 and $Nb_{1-y}S$.

In the first case, electron microscopy provides pictures of the lamellar NbS_2 phase. Stacking and length of the slabs are, respectively, 5 and 2 times higher than those observed on alumina catalysts. Even with a worse dispersion, catalytic activity in HDS of thiophene is 1.5 times better for Nb than Mo alumina supported catalysts (with an equivalent loading).

4. Conclusion

The acidic properties of niobia-containing materials have received much attention in the past decade [15]. The present work evidenced that not only niobium oxide but also niobium sulfide present unique acidic properties related to hydrotreating reactions. As compared to the classical molybdenum sulfide catalysts, niobium sulfides present higher activities and, moreover, different and interesting selectivities. NbS_3 presents the highest activities as compared to the other phases of Nb–S system, its stability toward reduction under the conditions of catalytic test depends on the H_2S partial pressure. It is difficult to define the origin of these properties. Either concentration of SH groups, resulting from adsorption of H_2S on a Lewis site, or the proton acidic properties of SH groups, play a key role. For NbS_3, the presence of sulfur pairs and their reactivity towards hydrogen may also be invoked. Based on our work, Topsö et al. [16] recently proposed the use of a bond energy model to account for the hydrotreating properties of transition metal sulfides. However, the different structures existing in this system were not considered and further theoretical support is needed in order to describe the surface properties of niobium sulfides. The transition to the supported state was performed but depends largely on the nature of the support. However, optimised preparations give activities higher than those of supported MoS_2 and specific properties of niobium catalysts remain in the dispersed state. We failed in our intent to obtain a mixed phase by nickel-doping, but numerous perspectives exist in this field.

Acknowledgements

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