Preparation of the mixed sulfide $Nb_2Mo_3S_{10}$ catalyst from the mixed oxide precursor

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Mixed sulfide $Nb_2Mo_3S_{10}$ was obtained by reaction of H_2S with the mixed oxide $Nb_2Mo_3O_{14}$ at 873 K. High-resolution electron microscopy and X-ray diffraction show the formation of homogeneous lamellar mixed sulfide. Due to the increased lability of oxygen, the sulfidation of the mixed oxide is easier compared to that of Nb_2O_5 oxide. As follows from the characterization of transient solid products, the transformation from the oxide to the sulfide includes the intermediate formation of a partially reduced "bronze" compound. For the thiophene hydrodesulfurization model reaction, the catalytic properties of $Nb_2Mo_3S_{10}$ mixed sulfide are intermediate between those of the individual MS_2 sulfides (M = Mo, Nb), but closer to those of the Nb compound.

Keywords: niobium, molybdenum, sulfide, preparation, hydrotreating catalysts, thiophene hydrodesulfurization

1. Introduction

Niobium sulfide NbS_2 is an interesting solid as concerns its catalytic properties in hydrotreating reactions. It possesses good activity in cracking and isomerisation as well as interesting hydrogenating properties [1,2]. The extensive application of niobium sulfide in catalysis is, however, limited by the difficulty of its preparation in a dispersed state. As compared to other oxides of transition metals applied in hydrotreating catalysis (Mo, W, Ni, Co), Nb oxospecies are difficult to transform into the sulfide phase using a treatment with H_2S. For that reason, severe sulfidation conditions are required with CS_2 in a steel bomb under high pressure. Sulfidation is also difficult if Nb oxospecies are dispersed on an oxide support, such as alumina [3]. Less resistant to sulfidation, but air-sensitive Nb alkoxides or chloride [2,4] lead to very sophisticated preparation techniques.

Sulfidation of Nb oxide under standard conditions is not thermodynamically favorable (ΔH for sulfidation of Nb_2O_5 is $+82$ kJ/mol whereas it is -119 kJ/mol for MoO_3 [5]). Our suggestion to overcome this difficulty was to use as the precursor a mixed oxide containing Nb and an easily sulfidable element, Mo for instance. Since for a mixed oxide the enthalpy of sulfidation should be decreased with respect to pure Nb_2O_5, sulfidation of Nb should probably be easier. If using this approach we obtain Nb into sulfide species, the solid product might be either a mixture of two different sulfides or a mixed sulfide containing Nb.

Molybdenum sulfide MoS_2 is widely used in hydrotreating catalysis. MoO_3 oxide easily reacts with H_2S leading to the hexagonal MoS_2 lamellar structure [6] closely related to that of NbS_2 [7]. A continuous row of mixed $Nb_xMo_{1-x}S_2$ sulfides can be prepared using high-temperature synthesis from the constituants [8]. Moreover, it has been shown that alumina-supported Nb–Mo mixed sulfides (obtained using sulfidation by CS_2) show interesting catalytic properties, at least as good as individual Nb sulfide, probably related to their acidity [9].

Thus, our purpose in this work was to verify whether the introduction of niobium into a mixed Nb–Mo oxide allows to facilitate formation of Nb sulfide species, in the form of mixed Nb–Mo sulfide, or a mixture of individual Nb and Mo sulfides.

2. Choice and synthesis of the oxide precursor

Among several Nb–Mo mixed oxides, we chose the composition $Nb_2Mo_3O_{14}$. This compound was reported to have a tunnel structure, isostructural to the partially reduced oxide Mo_5O_{14} [10,11]. This tetragonal structure contains MO_7 pentagonal bipyramides, surrounded by MO_6 octahedra.

$Nb_2Mo_3O_{14}$ was prepared by air heating at 1123 K of a well-ground mixture of commercial Nb and Mo oxides for 12 h, with subsequent cooling, then second grinding and recalcining. All the XRD lines of the resulting compound correspond to those of the expected mixed oxide (JCPDS 18-0840), but one (with weak intensity). EDX composition determination with the spot size of 15 nm showed good homogeneity of the solid ($0.6 < Nb/Mo < 0.8$) except in less than 5% of the measurements for which the Nb/Mo ratio was found to be 4 : 1. The impurity is probably also a mixed oxide $7Nb_2O_5$–$3MoO_3$ [12]. We believe that its presence as a separate phase cannot change significantly any of the conclusions which will be drawn.

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3. Sulfidation experiments

Sulfidation of the Nb–Mo oxide was carried out under flow of pure or diluted H_2S (either H_2S/N_2 or H_2S/H_2 mixtures, both with 15 vol% of H_2S) for 4 h at 673, 773 and 873 K. The products were handled and kept in inert atmosphere (Ar). The products of sulfidation were studied by XRD and high-resolution electron microscopy with simultaneous EDX analysis, and several of them by temperature-programmed oxidation (TPO). The composition of gases produced during heating of the samples in air was continuously controlled with a mass spectrometer.

Treating $Nb_2Mo_3O_{14}$ with a H_2S/H_2 mixture did not lead to the formation of any sulfide in the temperature range 673–873 K. Instead, products of reduction are formed, containing NbO_2 and non-identified crystalline phases, which are black, strongly paramagnetic and probably contain partially reduced Nb–Mo mixed oxides. Therefore, further sulfidation experiments were done using pure H_2S or H_2S/N_2 mixture.

After sulfidation at 673 K, no sulfide phase could be detected by XRD, but the HREM images of as sulfided solid clearly showed that the surface of the particles is covered with lamellar sulfide (figure 2). The amount of sulfur determined by EDX analysis is very irregular ($0.05 < S/(Nb + Mo) < 1.75$), as expected for a sample containing bulk oxide and superficial islands of sulfide phase: depending on the domain analyzed either unchanged or completely sulfided matter is seen. The layers of sulfide are separated by a characteristic distance of ca. 0.61 nm. The bulk of the crystals remains in the oxide state, showing crystalline network similar to that of the initial oxide.

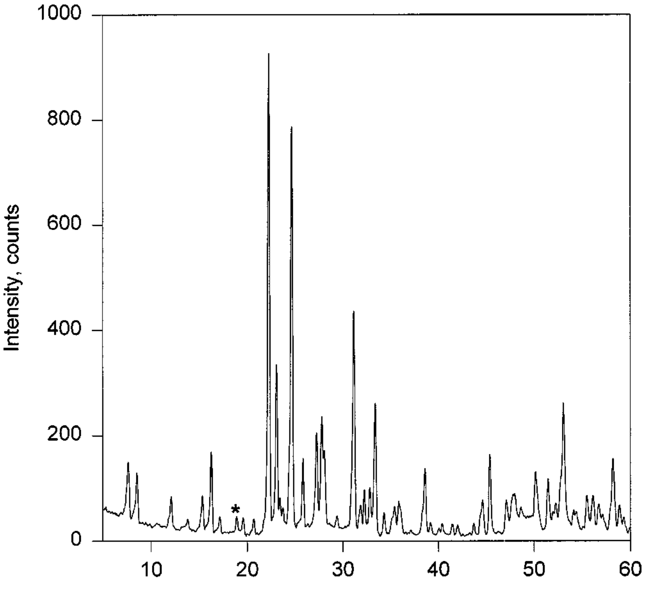

Figure 1. X-ray difftraction pattern of the initial Nb–Mo mixed oxide. Marked peak (*) – non-identified impurity, other peaks – $Nb_2Mo_3O_{14}$ (JCPDS 18-0840).

For sulfidation carried out at 873 K, transformation into sulfide was found deeper and almost complete after 8 h of treatment. Only the lamellar structure was seen by HREM in that case. The XRD pattern showed similar (but somewhat shifted) peaks as those in hexagonal MoS_2 (figure 3). Therefore, we suppose the presence of a unique mixed Nb–Mo sulfide phase belonging to the lamellar 2H type. From the positions of the 002 and 100 peaks we found an interlayer spacing (corresponding to half of the c lattice parameter) of 0.6023 nm, and a lattice parameter of ca. 0.321 nm (figure 4). It has been shown [8] that in the $Nb_xMo_{1-x}S_2$ compounds the interlayer spacing does not depend strongly on x whereas a increases significantly with the increase of the Nb content. The values of lattice parameters we obtained are in good agreement with the data of [8] ($a = 0.324$ nm, $c/2 = 0.601$ nm). The diffraction line of the impurity, detected in the initial sample, remained unchanged. Apparently this niobium-richer oxide is hardly sulfidable.

EDX analysis confirms that sulfidation does not lead to the separation of Nb and Mo in different phases. The atomic ratios Nb/Mo were found in the same range as in the precursor oxide ($0.6 < Nb/Mo < 0.8$) and the $S/(Nb + Mo)$ ones in a rather narrow range between 1.8 and 2.1, the average value being 1.94, which means that homogeneous sulfide has been obtained.

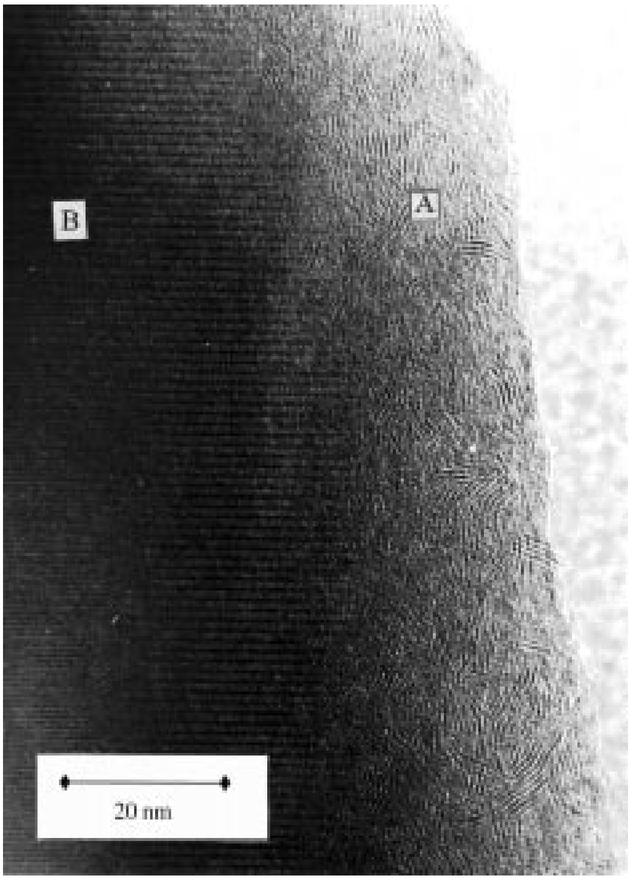

Figure 2. HREM image of the sample treated with H_2S at 673 K for 4 h. (A) Sulfide layers on the surface and (B) bulk oxide.

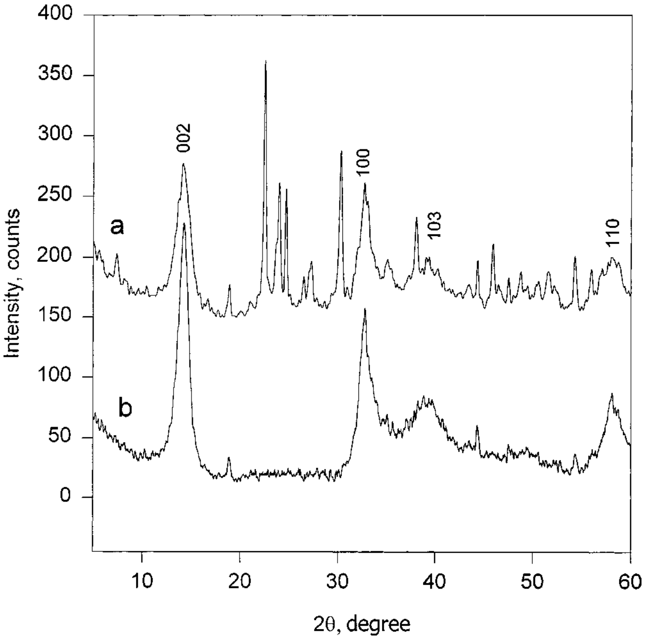

Figure 3. X-ray diffraction patterns of $Nb_2Mo_3O_{14}$ treated with H_2S at 873 K for 2 (a) and 8 h (b). Number over the peaks – (*hkl*) indexes of the hexagonal MoS_2 phase (JCPDS 6-0097), narrow unmarked peaks – impurity of Nb-rich phase (b) and residual oxide phase (a).

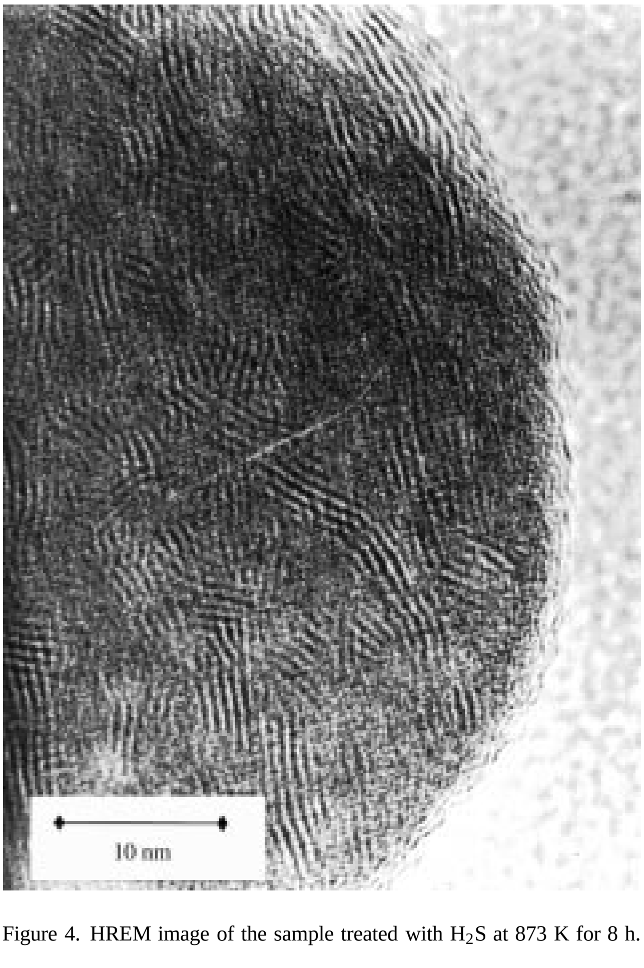

Figure 4. HREM image of the sample treated with H_2S at 873 K for 8 h.

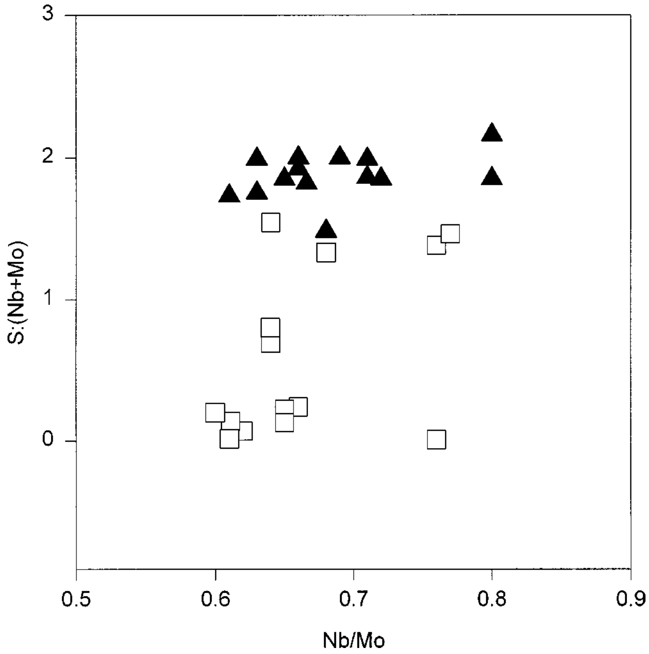

Figure 5. Results of EDX analysis of various crystallites of $Nb_2Mo_3O_{14}$ treated with H_2S at 673 K for 4 h (☐) and at 873 K for 8 h (▲).

The surface area determined by BET measurement was 4 m^2/g. In the impurity particles the S/(Nb + Mo) ratio was found to be 0.8, consistently with XRD data showing their bad sulfidability.

Summarizing the results of XRD, HREM and EDX measurements, we can state that the homogeneous lamellar $Nb_2Mo_3S_{10}$ (or $Nb_{0.4}Mo_{0.6}S_2$) sulfide phase is formed upon treatment of the $Nb_2Mo_3O_{14}$ oxide with H_2S. It is formed on the surface already at 673 K, then quantitatively at 873 K. Comparison with a reference Nb_2O_5 demonstrates that the sulfidation of the mixed Nb–Mo oxide is much easier. Commercial Nb_2O_5, if treated with H_2S at 673 K, does not undergo any changes, whereas at 873 K only weak diffraction lines of NbS_2 appear, the most part of the solid remaining unchanged Nb_2O_5. In the same conditions, $Nb_2Mo_3O_{14}$ is almost completely sulfided. Therefore, easier sulfidation of Nb–Mo oxide compared to Nb_2O_5 is proven.

4. The sulfidation mechanism

Even if it does not contain any line of sulfide phases, the XRD pattern of initial $Nb_2Mo_3O_{14}$ oxide is strongly affected upon treatment with H_2S already at 673 K. The number and relative intensity of lines does not change, but significant shift of all the lines of the initial oxide occurs, the shift direction depending on the (*hkl*) indexes (figure 6). Using the TREOR and DICVOL programs [13,14], the shifted XRD pattern was indexed as a tetragonal cell with good figures of merit ($M_{20} = 36$, $F_{20} = 49$ for TREOR). Refinement of the cell parameters using a least square full profile fitting program gave the values of $a = 2.344$ nm and $c = 0.397$ nm (mean square deviation R parameter is

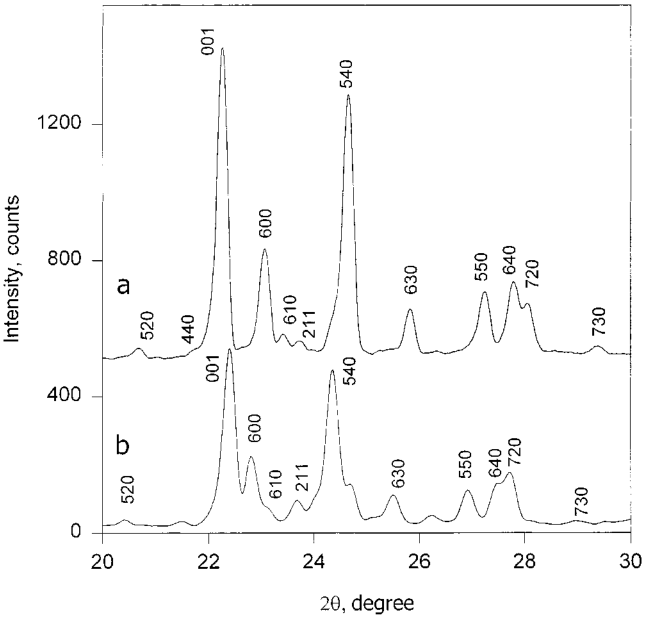

Figure 6. Fragments of XRD patterns of the initial $Nb_2Mo_3O_{14}$ (a) and the product of its reaction with H_2S at 673 K (b). Numbers over the peaks – (hkl) indexes.

0.011). The values of new lattice parameters are not very far but significantly different from those of the initial oxide ($a = 2.312$ nm, $c = 0.400$ nm). Therefore, the first step of sulfidation leads to the distortion of the initial phase cell. Such a changed oxide phase may correspond to a partially reduced oxide or a "bronze".

5. TPO results

As shown by the mass spectra, a considerable amount of water is evolved upon air heating of the sample treated with H_2S at 673 K. Water is produced in the temperature range 400–650 K (figure 7(a)), obviously too high for the desorption of physisorbed water. Moreover, no such water peak was noticed for the non-sulfided or completely sulfided at 873 K (figure 7(b)) sample. We suggest that this water production is due to the hydrogen included into the structure of the oxide phase during the treatment with H_2S, resulting probably in formation of a compound similar to the molybdenum and tungsten bronzes [15], which keeps the structure close to that of the initial oxide. Sulfidation by H_2S thus includes preliminary reduction of the oxide,

$$Nb_2Mo_3O_{14} + xH_2S \rightarrow Nb_2Mo_3O_{14}H_{2x} + xS$$

The mechanism of sulfidation of the mixed oxide seems to be different from that of Nb_2O_5, in which the intermediate products of sulfidation contained only NbS_2 and unchanged Nb_2O_5. By contrast, when MoO_3 is treated with H_2S, bulk MoO_2 is formed on the initial stages, and covered with a thin layer of sulfide. In the case of the mixed Nb–Mo oxide we observe an intermediate case where the initial oxide is affected but not so strongly reduced.

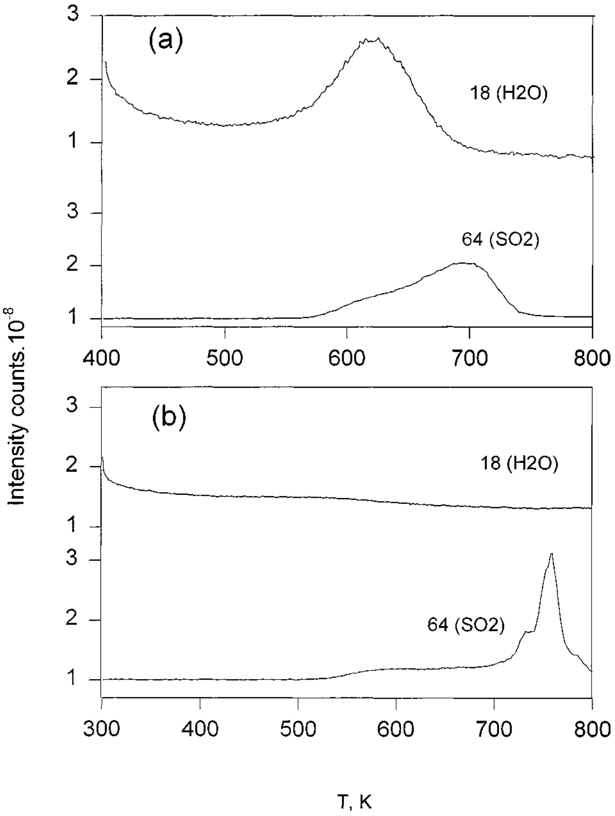

Figure 7. Mass spectra of the gases produced during thermoprogrammed oxidation of the solids treated with H_2S at 673 K for 4 h (a) and 873 K for 8 h (b). m/e values and the corresponding species are indicated over the curves.

Table 1
Thiophene HDS on the unsupported Nb, Mo and Nb–Mo sulfides at 573 K.

Catalyst	A_s[a] × 10^{-8} (mol/m^2 s)	% of butane
MoS_2	0.45	9
NbS_2	1.2	19
$Nb_2Mo_3S_{10}$	0.96	16

[a] A_s – specific activity at conversion of ca. 5%.

6. Catalytic activity

Catalytic activity of the $Nb_{0.4}Mo_{0.6}S_2$ phase was measured in the model reaction of thiophene hydrodesulfurization (HDS) at atmospheric pressure and 573 K. Unsupported MoS_2 and NbS_2 sulfides of low surface area were taken as the references to compare specific activity and selectivity. The results of measurements at equal conversion are shown in table 1. It follows from the data that the specific activity of mixed sulfide is about twice higher than that of unsupported MoS_2, whereas its selectivity was different, the butane share in the products being closer to that for pure Nb sulfide, which shows important hydrogenating activity. Specific values of catalytic properties of mixed sulfide lie between those of the individual sulfides, though closer to those of niobium sulfide.

The results presented here show that a mixed Nb–Mo sulfide can be obtained using a conventional sulfidation technique, but with a low surface area (ca. 4 m^2/g). However, if extended to the supported systems this approach may present real interest for catalytic applications.

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