Nickel molybdate as precursor of HDS catalysts: effect of phase composition

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Sulfided α- and β-$NiMoO_4$ have been employed as model HDS catalysts, aiming to investigate the effect of phase composition of the precursor mixed oxide on the physicochemical characteristics and activity of the sulfides. Both sulfides are highly amorphous or microcrystalline, and could not be differentiated by means of XRD. The differences in BET area were also found to be minimal. However, it was found by means of TPR that the stable α-isomorph is reduced at lower temperatures than the unstable β-phase in both the oxidic and sulfided states. Sulfided β-$NiMoO_4$ was found to be a better catalyst for the HDS of thiophene than the sulfided α-isomorph. This could be related to the higher stability of the former in H_2, as decomposition of the active, amorphous Ni–Mo–S structures results in less active and more crystalline phases, as found by XRD.

Keywords: nickel molybdate; HDS catalysts; catalyst characterization (TPR)

1. Introduction

Nickel molybdate is a mixed oxide which can be potentially present in supported precursors of Ni–Mo hydrotreatment catalysts. Two normal pressure isomorphs are known of this compound, generally designated α- and β-$NiMoO_4$ [1]. The first one is stable at room temperature, while the β-isomorph is generated by heating α-$NiMoO_4$ at temperatures above 690°C [2] and is stable only if kept over 180°C [3]. Both phases are monoclinic, with space group C2/m. The main difference between them is the coordination of Mo^{6+} ions, octahedral in α-$NiMoO_4$ and tetrahedral in β-$NiMoO_4$. In both cases Ni^{2+} ions occur in sites with octahedral coordination.

Although pure β-$NiMoO_4$ is unstable below 180°C, it can be stabilized at ambient temperature after precipitation and calcination of mixed oxides in the composition range Ni/Mo (atomic ratio) > 1 [4], presumably by formation of a solid solution with

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the excess Ni oxide phases [4,5]. α-$NiMoO_4$ is always observed in bulk oxides with Ni/Mo $\leqslant 1$ [2,4]. However, β-$NiMoO_4$ has been positively identified *at room temperature* in the oxidic precursors of Ni–Mo/Al_2O_3 catalysts (Ni/Mo typically 0.5) by means of such characterization techniques as XRD [6–9] and laser Raman spectroscopy [10]. Note that, in some works [6–8], β-$NiMoO_4$ has been mistakenly described as the hydrate xNiO·MoO_3·$y H_2O$, as discussed elsewhere [11]. The possible presence of Ni–Mo mixed oxides in supported catalysts is interesting, as those compounds could be the precursors of active Ni–Mo–S structures [9].

Bulk Ni–Mo mixed oxides in a wide range of compositions have been employed as precursors for sulfided HDS catalysts [12,13], although no attention was given to the effect of the presence of either isomorph on the catalytic activity. It can be assumed that the stable α-isomorph is the Ni–Mo phase present in the oxides with Ni/Mo $\leqslant 1$, while β-$NiMoO_4$ could exist at room temperature for Ni/Mo > 1, as indicated above. Conspicuously, a maximum in HDS activity was reported precisely in the latter range of composition [12]. However, the stabilization of the β-phase by excess Ni oxide is a transient effect [4], and thus it is unknown whether this phase was actually present in these samples. Additionally, the contribution of sulfided products derived from the excess Ni and/or Mo oxides to the activity could obscure the assessment of the activities due to sulfided α- or β-$NiMoO_4$.

The objective of the present work is to compare pure α- and β-$NiMoO_4$ as precursors for sulfided HDS catalysts. Physico-chemical characteristics of the oxidic and sulfided materials are investigated by several techniques.

2. Experimental

2.1. CATALYST PREPARATION

The hydrated precursor $NiMoO_4 \cdot x H_2O$ was synthesized by coprecipitation from aqueous solutions of nickel nitrate (NN, Carlo Erba, rpe) and ammonium heptamolybdate (AHM, Merck, p.a.). As demonstrated by Mazzocchia et al. [2], careful control of the temperature and pH of solutions before and after mixing has to be carried out in order to obtain a precursor of the desired composition (Ni/Mo = 1). In our case, the temperature was thermostatized to 80 ± 1°C during coprecipitation, filtration and washings. The initial pH of the NN solution was 4.7 and that of the AHM solution 5.6. After mixing the thermostatized solutions, precipitation and ageing was allowed until the pH stabilized at 4.9. These conditions closely match those described by Mazzocchia and co-workers [2]. Drying at 100°C (2 h) and calcination at 550°C (2 h) produced α-$NiMoO_4$, as checked by XRD, IR and chemical analysis (atomic absorption).

The β-isomorph was generated in situ, as needed, by heating the 550°C precalcined α-$NiMoO_4$ sample at 760°C for 5 min. Afterwards, it was rapidly cooled to the desired temperature (always above ~ 250°C) to effect further treatments, reaction or characterization measurements. It is now well established [2] that this calcination procedure results in the complete transformation from α- to β-$NiMoO_4$. This process starts around 690°C and is completed at 760°C [2]. Long firing times at the higher temperatures produce decomposition of the molybdate and loss of MoO_3 by sublimation (see below). Thus, a special furnace was employed that allowed fast heating to the final desired temperature (about 10 min between ambient and 760°C, less than 2 min between 690 and 760°C), and also fast cooling.

In order to make valid comparisons between samples with similar areas (note that the area of the β-phase cannot be measured with the BET method), the samples of α-$NiMoO_4$ employed in the activity and characterization measurements were synthesized by cooling freshly prepared β-$NiMoO_4$ down to room temperature overnight before carrying out the desired experiment. It is assumed that the surface areas of the high temperature β-samples are similar to those of the α-samples resulting from this procedure. The latter were fully characterized by XRD, IR and chemical analysis, and demonstrated to be pure α-$NiMoO_4$.

2.2. PRESULFIDING

Samples for activity measurements or characterization were submitted to the following sulfiding protocol: After generation of the desired phase, the sample was stabilized at 400°C in helium for several minutes before admitting a 50 cm^3/min flow of pure H_2S. After 1 h, either the reactant mixture was admitted to the reactor or the sample was cooled down to room temperature in the H_2S flow to effect further characterization experiments.

2.3. CATALYTIC HDS ACTIVITY

Catalytic activity tests were carried out in a continuous flow microreactor, operating at atmospheric pressure. The conversion of thiophene was followed at 400°C after presulfiding 50 mg of sample. The reaction feed consisted of a mixture of 160 cm^3/min of H_2 and 7×10^{-5} mol/min of thiophene. The reproducibility between independent runs was better than 5%.

2.4. CATALYST CHARACTERIZATION

X-ray diffraction (XRD) was measured in a Philips PW 1730 instrument, employing Ni filtered Cu Kα radiation. *Temperature-programmed reduction* (TPR) was performed in a home made apparatus as described elsewhere [9], in a mixture of 15 vol% H_2 in N_2, and heating at 10°C/min. Samples of oxidic β-$NiMoO_4$ were measured between 300 and 900°C, in other cases the runs were followed from room temperature to 900°C. *BET surface areas* were measured using the BET method in an ASAP 2000 instrument from Micromeritics, employing N_2 as the adsorbate. *Scanning electron microscopy* (SEM) observations were made in a Philips PSEM-500 Electron Microscope. *Fourier transform infrared* (FTIR) spectra were measured with a Nicolet 5DXC instrument.

3. Results and discussion

3.1. CHARACTERIZATION OF CATALYST SAMPLES

3.1.1. XRD, colour and surface area

XRD traces of both α-NiMoO$_4$ samples – the one calcined at 550°C and that obtained by allowing the β → α transition at room temperature – were almost identical, the latter one showing slightly sharper peaks (figs. 1a, 1b). XRD of pure β-NiMoO$_4$ could not be measured, but is was found that this material presents a characteristic orange colour as opposed to the yellowish green of the α-phase. The orange colour appears in samples heated at 760°C, and changes back to green after cooling the sample below ca. 200°C. If the temperature is kept over 200°C the orange shade persists indefinitely. Thus, we conclude that this colour is characteristic of β-NiMoO$_4$.

It is important to emphasize that the material generated by cooling to room temperature samples calcined at 760°C during 5 min is pure α-NiMoO$_4$. Thus, according to the literature [2], the α → β phase transformation must have occurred with no decomposition of the high temperature phase. On the contrary, samples heated at temperatures in excess of 760°C or at 760°C for 15 min or more and cooled to room temperature showed a complex pattern, consisting of peaks due to both α- and β-NiMoO$_4$ (fig. 1c). In this case the β-isomorph is stabilized by excess Ni oxide resulting from decomposition of the mixed compound and sublimation of MoO$_3$ [5].

XRD of the sulfided samples cooled in H$_2$S to room temperature showed that these samples are essentially amorphous or microcrystalline (figs. 2a, 2b), and

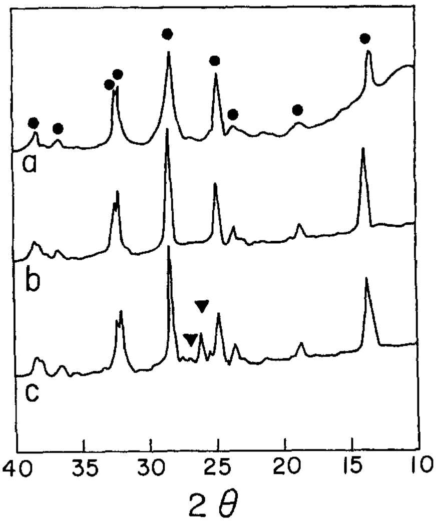

Fig. 1. XRD traces of oxidic NiMoO$_4$ samples, calcined at: (a) 550°C; (b) 760°C, 5 min; (c) 760°C, 15 min. (●) α-NiMoO$_4$; (▼) β-NiMoO$_4$.

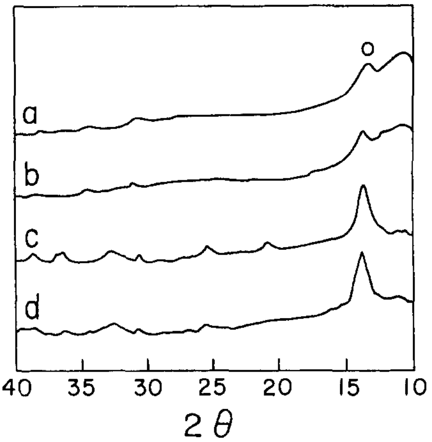

Fig. 2. XRD traces of sulfided $NiMoO_4$ samples: (a) α-$NiMoO_4$; (b) β-$NiMoO_4$; (c) α-$NiMoO_4$ after reaction; (d) β-$NiMoO_4$ after reaction. (○) MoS_2.

identical from the point of view of this technique. The broad signals at $2\theta \approx 14°$ can be assigned to very amorphous MoS_2 or MoS_3.

BET surface areas of the samples before and after sulfidation are reported in table 1. As anticipated, the sample of α-$NiMoO_4$ obtained by calcination of the hydrated precursor at 550°C showed a higher BET area (38 m^2/g) than the α-phase generated by cooling β-$NiMoO_4$ to room temperature (table 1). Note that the areas of both sulfided samples are quite similar. SEM observations (not shown) confirm that sulfides are very porous, in agreement with the magnitude of the BET measurements.

3.1.2. Temperature programmed reduction

TPR spectra of α- and β-$NiMoO_4$ (fig. 3) show a clear difference in reducibility between the two oxidic precursors. This is further evidence of the presence of the two distinct phases in either sample. Contrary to this, in the case of cobalt molybdates Haber and Janas found almost no differences between the two isomorphs while measuring the kinetics of reduction in hydrogen [14]. It should be noted, however, that in the $CoMoO_4$ system the temperature of $\alpha \rightarrow \beta$ transition (420°C) [15]

Table 1
BET area and quantitative TPR data of catalyst samples

Catalyst	State	BET area (m^2/g)	H_2 consumption (mmol H_2/g_{cat})	
			total	2nd peak
α-$NiMoO_4$	oxidic	26	18.3	3.5
β-$NiMoO_4$	oxidic	–	18.2	4.8
α-$NiMoO_4$	sulfided	28	5.7	–
β-$NiMoO_4$	sulfided	28	5.5	–

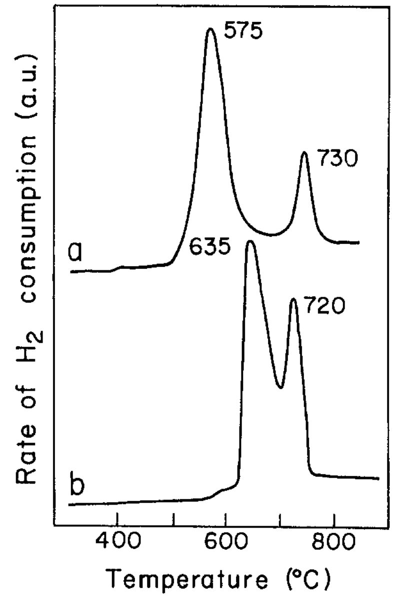

Fig. 3. TPR spectra of oxidic NiMoO$_4$ samples: (a) α-NiMoO$_4$; (b) β-NiMoO$_4$.

is lower than the temperature range studied in that work (480–560°C); thus, apparently what Haber and Janas measured as reduction of α-CoMoO$_4$ was that of β-CoMoO$_4$. In the case of NiMoO$_4$ the α → β transition occurs at temperatures well above those of reduction, and the differences among the isomorphs can easily be detected.

The higher temperature of reduction of β-NiMoO$_4$ as compared with α-NiMoO$_4$ agrees with what is generally observed in other Mo^{6+} oxidic compounds: as a general rule, Mo^{6+} tetrahedrally coordinated is more difficult to reduce than octahedral Mo^{6+} (see, e.g., ref. [9] and references therein). A simple explanation, based on purely electrostatic considerations, may be that removal of a single O^{2-} ligand from an octahedral environment corresponds to a change of 1 in oxidation state (OS) of the metallic center, while in a tetrahedral field the change in OS is formally 1.5. In the first case, there are five other O^{2-} ligands remaining to share the increased electron density on the metal, while in the tetrahedral coordination there are only three. Thus, Mo^{6+}[Oh] obviously requires less energy to become reduced than Mo^{6+}[Th], as observed.

Quantitative TPR (table 1) shows that both oxides are completely reduced to the metallic state. The extent of reduction after the first TPR peak amounts to 70–80% of the total H_2 consumption, and is interpreted, in agreement with previous results [16] to formation of alloys or intermetallic compounds – such as Ni_4Mo – dispersed on excess MoO_2. The latter is further reduced to metallic Mo under the second TPR peak; the amounts of MoO_2 remaining after the first TPR peak (reductive decomposition of the molybdate) are only marginally different (table 1).

A similar trend as in the case of the oxides is observed for the sulfided samples (fig. 4). Sulfided α-$NiMoO_4$ shows a sharp peak at ~ 333°C, while the sulfides derived from the β-phase produce a slightly broader signal at about 350°C. In the conditions of these experiments most of the reduction (roughly 75–80% of the H_2 consumption) occurs below 400°C, and it is essentially completed at about 550°C. These mild reduction temperatures suggest that, at variance with the case of the oxides, sulfides are not reduced to the metallic state under the present TPR conditions. The stability of, e.g., MoS_2 in H_2 under atmospheric pressure at temperatures up to 800°C is well documented [17].

The thermodynamically stable compounds of Ni and Mo in typical HDS conditions are Ni_3S_2 and MoS_2 [18]. Assuming that after H_2 reduction in TPR conditions the stoichiometry of the catalysts corresponds to a mixture of MoS_2 and Ni_3S_2, the quantitative data (table 1) is consistent with an overall composition "$NiMoS_4$" in the starting sulfides. This could correspond to unknown mixed sulfides with the same stoichiometry and/or MoS_3 plus NiS, MoS_2 plus NiS_2, etc.

3.2. CATALYTIC ACTIVITY

A significant difference between the sulfides obtained from either precursor was observed, the β-phase producing a more active catalyst than the α-isomorph (fig. 5). Initial activity is highest, and decreases monotonically with reaction time. This most likely is due to structural changes and/or coking. However, coke deposition has been demonstrated to be less important in the case of sulfided samples, as

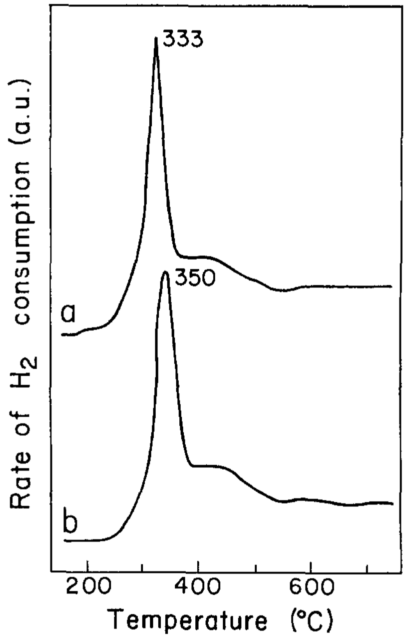

Fig. 4. TPR spectra of sulfided $NiMoO_4$ samples: (a) α-$NiMoO_4$; (b) β-$NiMoO_4$.

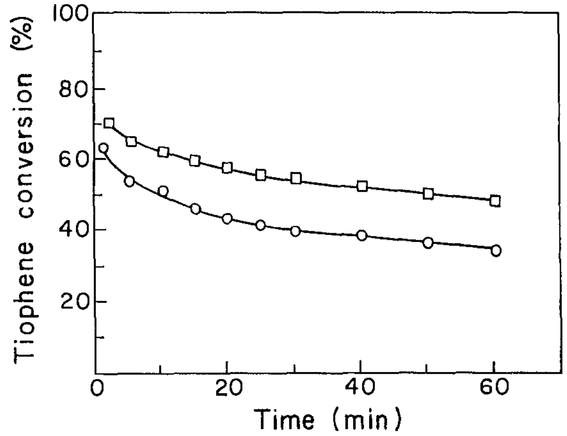

Fig. 5. Thiophene HDS activity of sulfided $NiMoO_4$ samples. (○) α-$NiMoO_4$; (□), β-$NiMoO_4$.

compared to the oxidic precursors [19]. Therefore, it can be assumed that a significant proportion of the highly active but unstable Ni–Mo–S type phases generated by sulfiding decompose to the separated MoS_2 and Ni_3S_2 sulfides under the reductive conditions of the reaction environment. Indeed, XRD analysis of the reacted samples show increased crystallinity, specially in the peak around $2\theta \approx 14°$ (MoS_2). Although no clear differences among the sulfided samples are clearly seen by XRD (figs. 2c, 2d), the higher stability of β-$NiMoO_4$ in H_2, as compared with the α-phase, could be related to the higher activity of the former, favouring more incorporation of Ni in the Ni–Mo–S structures.

In connection with the present results, Melo et al. [7] found a fair correlation of the amount of "xNiO·MoO_3" in the oxidic precursor with HDS activity of the sulfided catalyst. These authors based their claim on the ASTM card file No. 12-348 [20]; as previously demonstrated [11] the phase erroneously described as "xNiO·MoO_3·$y$$H_2O$" is in fact β-$NiMoO_4$. Thus, it is possible that phases resembling the β-isomorph are present in industrial-type Ni–Mo/Al_2O_3 catalysts, and are convenient precursors of very active sulfided catalysts.

4. Conclusions

β-$NiMoO_4$ has been found to be a better catalytic precursor than α-$NiMoO_4$ for the HDS of thiophene at normal pressure. As no structural differences among the sulfides were found from XRD, it is concluded that the active phases are microcrystalline or amorphous.

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