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Nickel Chevrel phase supported on porous alumina

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Abstract

The objective of this work was the study of the hydrodesulphurization (HDS) catalytic properties of the nickel Chevrel phase $Ni_xMo_6S_8$ in a highly dispersed state. Since Chevrel phases are not soluble, new synthesis routes were developed on bulk materials from soluble precursors and then applied for the preparation on a porous support. The method is a two-step gas over solid thermal process: sulfurization under H_2S/H_2 and then reduction under H_2. The first step corresponds to the classical preparation of Ni_xMoS_2 on alumina industrial hydrotreating catalyst. XRD, TEM and catalytic activity measurements allowed us to determine the preparation parameters leading to the synthesis of $Ni_xMo_6S_8$ nanometric particles on alumina ($\phi < 5$ nm). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nickel Chevrel phases; Gas over solid reaction process; Hydrodesulfurization; Supported material; Nanocrystalline material; TEM studies

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1. Introduction

Chevrel phases are ternary molybdenum chalcogenides $M_xMo_6X_8$ (X = S, Se, Te and M is a metallic ion), very well known as high field superconductors [1]. More recently, these compounds were found to be active as hydrotreating catalysts. Hydrodesulfurization (HDS) is used to remove sulfur from the organic molecules contained in a crude oil. Schrader et al. reported that bulk Chevrel phases had intrinsic activities (expressed per m^2/g instead of g of catalyst) comparable to that of the conventional MoS_2 lamellar compound or Ni (or Co) promoted MoS_2 catalytic material, despite their low surface area (<1 m^2/g) [2–5]. However, for industrial application it is necessary to obtain a high specific surface area either by depositing the active phase on a support or with highly dispersed solids. Three routes for preparing dispersed Chevrel phases are described in the literature: an inorganic-organometallic molecular route [6,7], synthesis on a porous ceramic support [8] and a thin film route [9]. The second route was investigated by Rabiller-Baudry et al. [8] in order to test the oxychlorination catalytic properties of the copper Chevrel phase. In the present work, we applied this method to the nickel Chevrel phase to compare its hydrodesulfurization activity with the conventional industrial catalyst.

2. Synthesis

Usually, bulk Chevrel phases are prepared by the classical ceramic route: a stoichiometric mixture of elementary, binary, or multinary powdered compounds is heated at high temperature under an inert gas or static vacuum.

Another bulk synthesis route has been developed for the Ni–Mo–S system from the so-called HSP method [10]. Recently, it was demonstrated that sulfurization-reduction gas flow treatment of this powder led to the bulk nickel Chevrel phase [11]. This new route allowed the preparation of fine particles of 0.5 μm diameter. Because of the precipitation of transition metal sulfides, it cannot be applied to the preparation of supported material.

Up to now, no supported nickel Chevrel phase synthesis route has been perfected. In fact, the synthesis of a supported material requires several steps. First, impregnation of the support (alumina) with a solution containing the precursors is performed, followed by drying and calcination. The support (alumina + precursors) is then treated by an appropriate gas over solid reaction leading to the desired phase at a temperature which must avoid any sintering of the catalyst.

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2.1. Bulk synthesis

Taking the constraints due to the support into account, new different synthesis methods for the preparation of the bulk nickel Chevrel phase have been developed from soluble precursors. Because of the difficult characterization of the supported material, the synthesis parameters are first determined on bulk materials in order to be used as a model for supported material preparation.

The best choice turned out to be an aqueous solution of precursors $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (HMA) and $Ni(NO_3)_2\cdot 6H_2O]$ with a Ni/Mo ratio of 1:3. Then, after evaporation, the powder is dried and calcined. This oxide powder mixture ($NiO+MoO_3$ or $NiMoO_4+MoO_3$ according to the calcination temperature) is treated under gas flow by a two-step gas over solid process: first, a sulfidation reaction is carried out under a 10% H_2S/H_2 flow (flow rate 4 l/h) at 673 K for 4 h in order to prepare the Ni_xMoS_2 lamellar compound characterized by XRD (Fig. 1a, INEL CPS120 diffractometer). Then, a second reduction reaction under H_2 gas flow (flow rate 4 l/h) at 973 K for 8 h desulfurizes the lamellar compound to crystallized $Ni_2Mo_6S_8$ (Fig. 1b) according to the reaction

$$Ni_{0.33}MoS_2 \xrightarrow{H_2} Ni_{0.33}MoS_{1.33} + \tfrac{2}{3}H_2S$$

where $Ni_{0.33}MoS_{1.33}$ corresponds to the nickel Chevrel phase $Ni_2Mo_6S_8$.

Often, XRD patterns of $Ni_2Mo_6S_8$ so obtained also show the presence of metallic molybdenum. This impurity may originate from two processes. First, it arises from the reduction of MoO_2 created from MoO_3. During the sulfidation–reduction step (H_2S/H_2), a molybdenum disulfide layer forms on the surface of the MoO_3 grains preventing the core sulfurization of the grains, but not the reduction to MoO_2 [14]. Then, under H_2 at 973 K, MoO_2 is reduced to molybdenum metal. The formation of MoO_2 depends on the grain size of the oxides. This problem can be solved using the smallest particles of supported material. Secondly, molybdenum originates from the decomposition, under pure H_2, of $Ni_2Mo_6S_8$, which leads to nickel and molybdenum under further reduction. Due to our synthesis conditions, the reduction reaction does not give a compound under thermodynamic equilibrium. Therefore, this reaction slowly reduces the sulfide. This problem can be solved by adding a few ppm of H_2S to the H_2. According to this procedure, a nickel Chevrel phase powder with grain size <0.5 μm is obtained after only 8 h at 973 K instead of 4 or 5 days with the classical ceramic route (5–10 μm grain size).

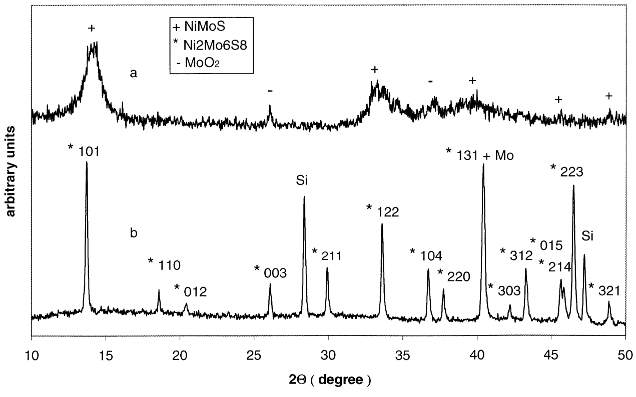

Fig. 1. XRD patterns (Cu $K\alpha_1$) of bulk materials arising from soluble precursors $[HMA+Ni(NO_3)_2\cdot 6H_2O]$: (a) Ni_xMoS_2, so-called NiMoS (673 K, 4 h, H_2S/H_2 10%); (b) $Ni_2Mo_6S_8$ (+973 K, 8 h, H_2) with hexagonal indexation, Si powder used as calibration sample.

2.2. Supported material

The support is a γ-alumina with a high specific surface area (270 m^2/g). A commercial porous alumina NiMo catalyst containing 14 wt% MoO_3 and 3 wt% NiO was used. The synthesis method described above is transposed to the preparation of a nickel Chevrel phase supported on alumina. The solid extrudates are placed in a U-tube on a sinter-silica filter and heated at 673 K for 4 h under a 10% H_2S/H_2 gas flow (flow rate 4 l/h) and then reduced under a flow of H_2 (4 l/h) at 998 K for 90 h. The first step of the procedure corresponds, in fact, to the standard activation of a Ni_xMoS_2 sulfide hydrotreating catalyst. Note that the $\alpha = Ni/(Ni+Mo)$ ratio is slightly higher in pre-impregnated commercial alumina ($\alpha = 0.3$) than in the nickel Chevrel phase ($\alpha = 0.25$).

For a better understanding, the syntheses of the supported and unsupported Ni Chevrel phases are shown schematically in Fig. 2.

3. Characterization methods of the supported material

Fig. 3a shows that the contribution of the support is only noticeable on the XRD pattern of the supported material. In order to obtain further information with this technique, a crystallization method was used. The sample was sealed in a silica tube under vacuum and heated at the same temperature as the reduction temperature (998 K) for 24 h. As shown in Fig. 3b, thermal treatment leads to a crystallized nickel Chevrel phase supported on alumina. Such a crystallization may be due to a chemical vapour transport phenomenon which occurs under static vacuum or static gas flow and not under dynamic gas flow. The phase identified by XRD could be synthesized during thermal treatment; this annealing treatment only allows us to determine if the stoichiometry required to form the phase is present in pores of the support. We then used TEM, one of the few techniques able to detect the presence of the phase before the annealing treatment.

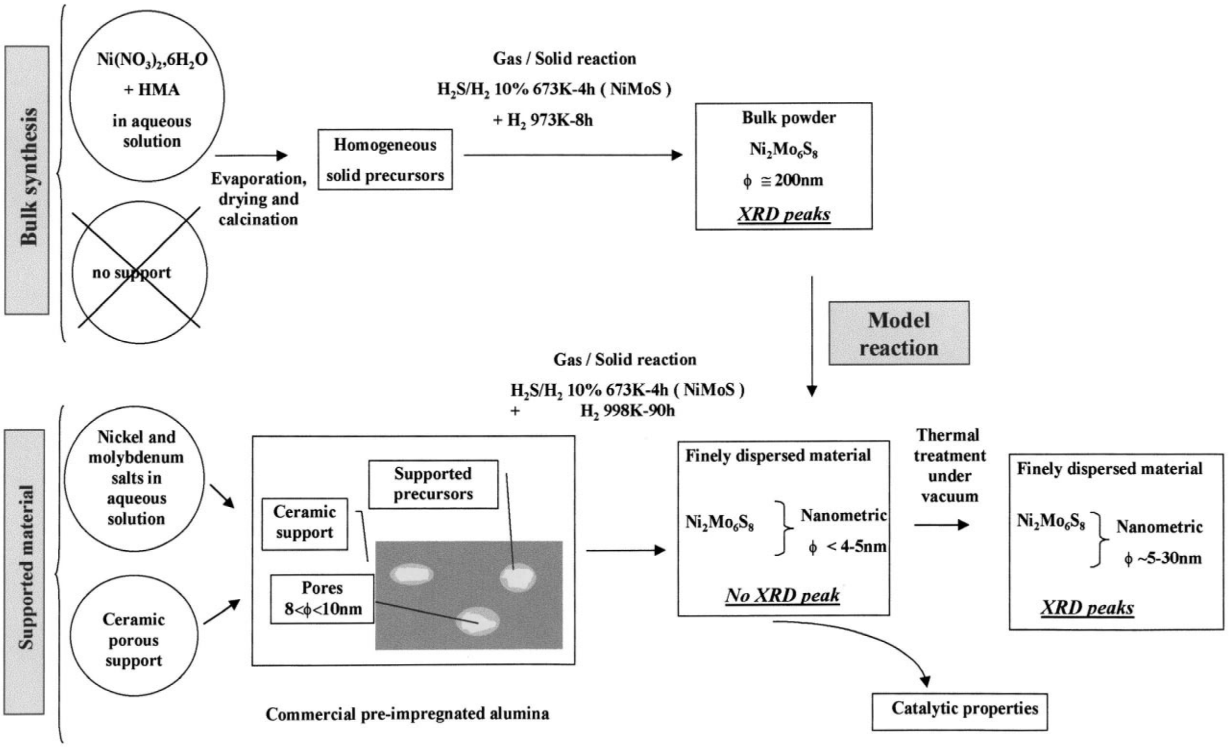

Fig. 2. Scheme for the preparation of a $Ni_2Mo_6S_8$ supported material. Bulk synthesis: research of new synthesis routes by gas over solid reactions from soluble precursors without ceramic support⇒XRD peaks. Supported material: transposition of these new synthesis routes to nanostructures on a ceramic support⇒no XRD peak.

3.1. TEM and XRD investigations

The particle sizes of the nickel Chevrel phases were determined by the use of either SEM (JEOL-JSM6301F) for sizes >100 nm or TEM for smaller particles. In the latter case, catalyst grains were dispersed in pure ethanol, the suspension stirred in an ultrasonic bath and one drop deposited on a carbon-coated copper grid. These grains were examined with a JEOL 2010 microscope (point-to-point resolution 0.192 nm) equipped with a Link Isis EDX detector.

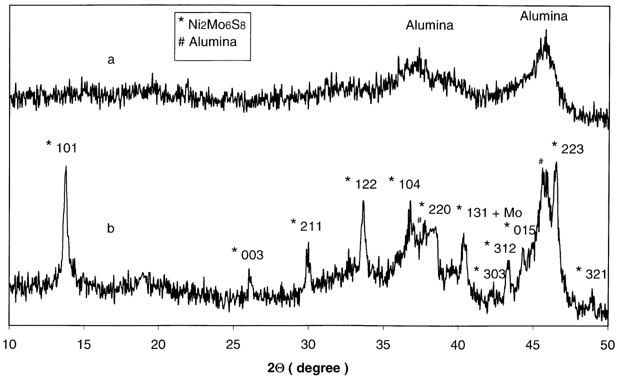

Fig. 3. XRD diagrams of the supported nickel Chevrel phase on porous alumina. (a) Catalytic material (998 K, 90 h, H_2); (b) catalytic material+ crystallization (annealing treatment 998 K, 24 h).

The three samples investigated were obtained according to the following methods: (i) sample A is a bulk material prepared by the new synthesis route described above; (ii) samples B and C are supported materials prepared from Ni–Mo supported commercial alumina treated by the gas over solid reactions described in Section 2.2. Sample B was intentionally reduced at 1048 K and annealed at 1048 K in order to increase the crystallites, whereas sample C underwent a reducing and annealing treatment at 998 K. TEM images and XRD patterns are shown in Figs. 4–6.

Sample A, identified by XRD as a well crystallized nickel Chevrel phase $Ni_2Mo_6S_8$, presents particle sizes in the range 200–300 nm (Fig. 4a,b). The TEM micrograph of sample B (Fig. 5a) shows a nanocrystalline $Ni_2Mo_6S_8$ particle (15 nm×25 nm size). The (100) rhombohedral plane is observed. The distance between two spots measures the rhombohedral parameter ($a_r \sim 6.5$ Å) and the angle between two rows determines the rhombohedral angle ($\alpha_r \sim 95°$). These parameters are characteristic of a $Ni_2Mo_6S_8$ phase. MoS_2 or NiMoS species are detected by XRD (Fig. 5b) and imaged on the TEM photograph on the upper right (fringes separated by 6.15 Å). Sample C underwent adequate heat treatment to prepare the supported material for catalysis except for an extra annealing treatment for 6 h. Contrary to previous samples, the XRD diagram of sample C is flat except for the alumina contribution. A small crystallite (4 nm×5 nm) of $Ni_2Mo_6S_8$ with the same orientation ([211] zone axis) and

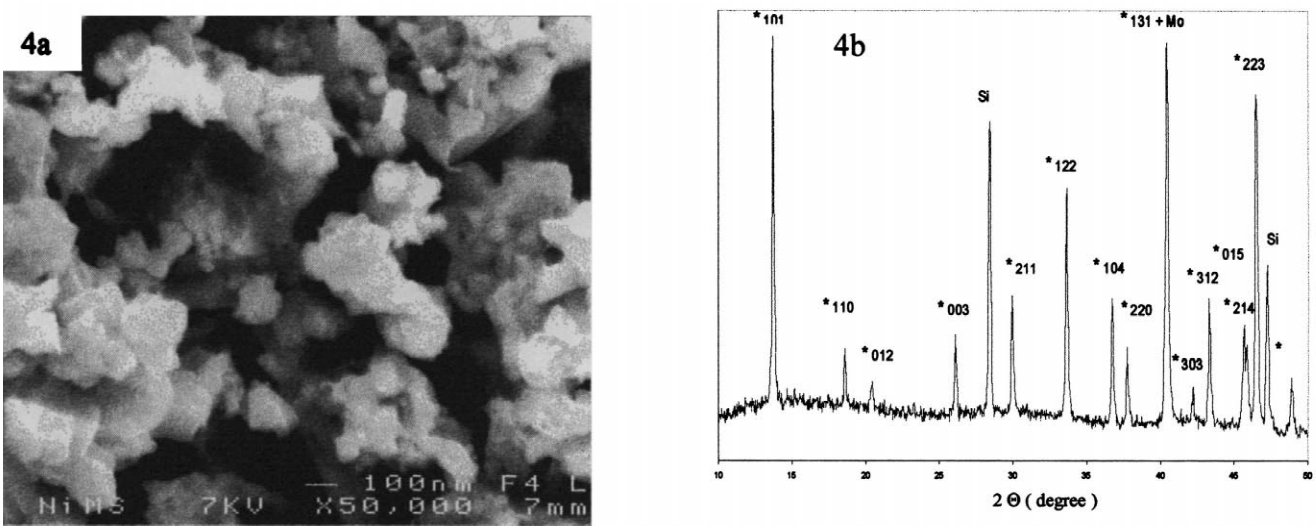

Fig. 4. Sample A: bulk nickel Chevrel phase obtained from sulfurized and reduced soluble precursors. (a) SEM photograph, grain size ~200 nm; (b) XRD pattern with hexagonal indexation.

corresponding parameters as that previously observed for sample B is observed (Fig. 6a,b).

In spite of the high dispersion (1.8 mol.% Mo_6/Al_2O_3), a supported material with a grain size of about 20 nm exhibits a relatively well-defined XRD diagram and this kind of material can be characterized by XRD. The characterization of smaller particles ($<$10 nm) is more difficult. Without annealing treatment, the particles of the nickel Chevrel phase catalyst are smaller than 5 nm. TEM studies of unannealed samples do not exhibit a network of nickel Chevrel phase. Therefore, HRTEM investigations will be necessary to observe these particles.

This new synthesis route allows the preparation of the nickel Chevrel phase on the nanometric scale and, thus, testing of the catalytic properties of these new supported materials.

3.2. Catalytic activities as a function of reduction treatment

The catalysts were tested in the hydrodesulfurization of dibenzothiophene (HDS of DBT). DBT is a model molecule used to evaluate the HDS catalytic properties. Experiments were carried out in microreactors operated in the dynamic mode in the vapor phase. The operating conditions were: temperature 523 K, total pressure 30×10^5

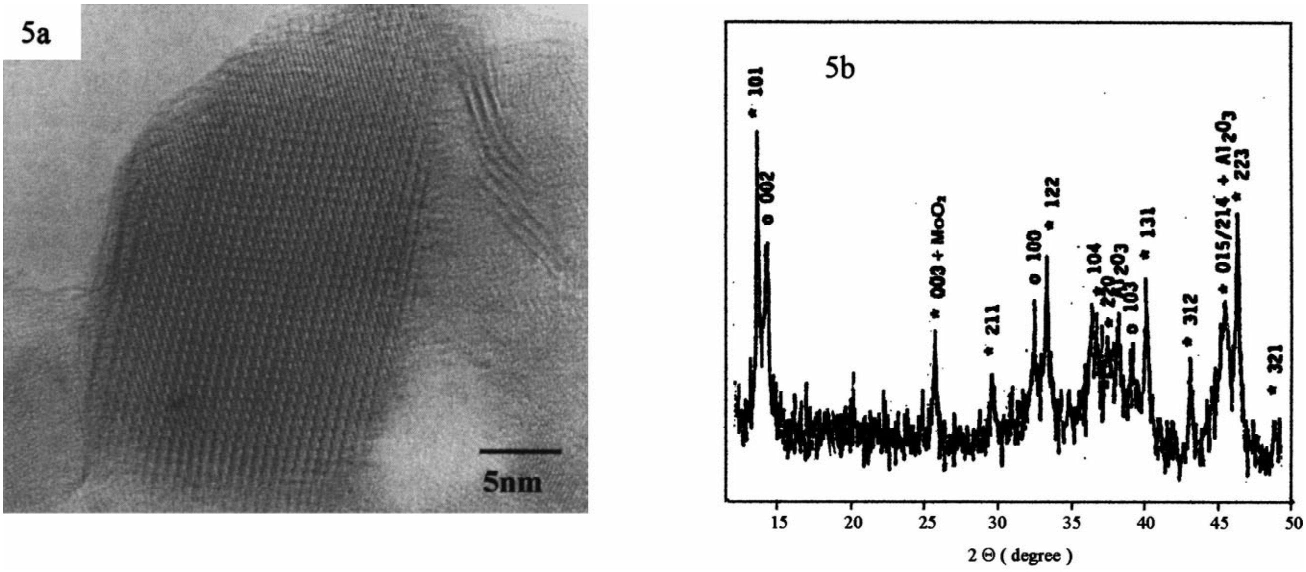

Fig. 5. Sample B: $Ni_2Mo_6S_8$ supported on porous alumina (1048 K, 48 h, H_2) annealed at high temperature (1048 K, 24 h). (a) TEM photograph ([211] zone axis) projection on the 100 rhombohedral plane, grain size ~20 nm; (b) XRD pattern with hexagonal indexation [(*) $Ni_2Mo_6S_8$; (○) NiMoS].

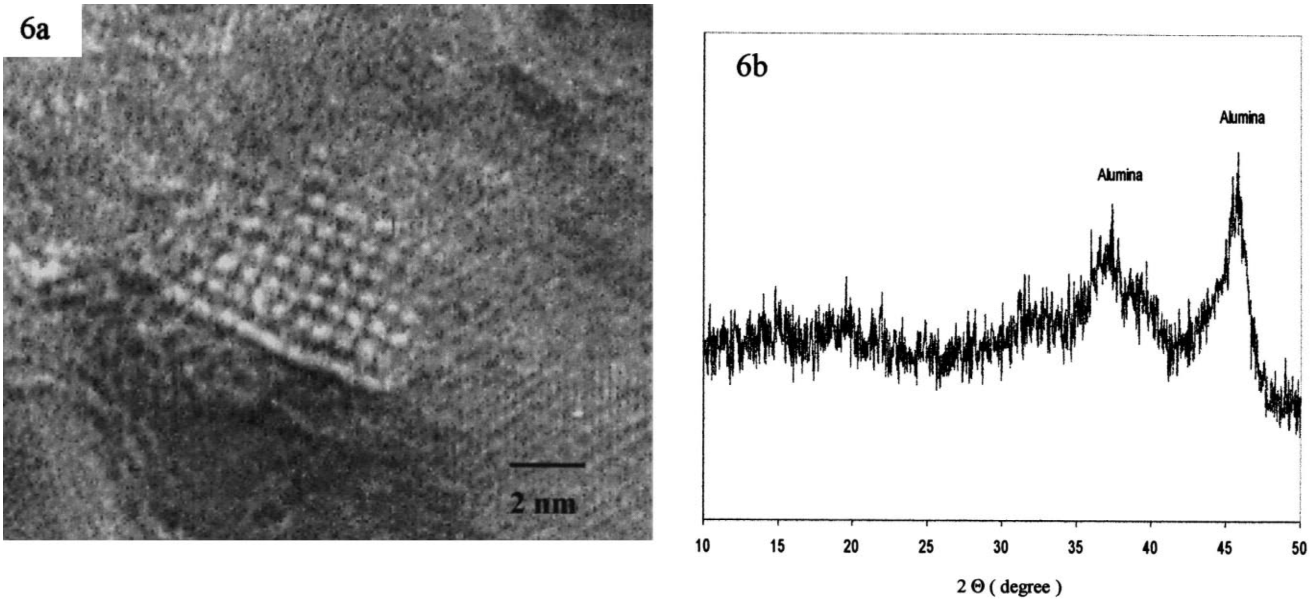

Fig. 6. Sample C: $Ni_2Mo_6S_8$ supported on porous alumina (998 K, 90 h, H_2) and annealed (998 K, 6 h). (a) TEM photograph ([211] zone axis), grain size 4×5 nm; (b) flat XRD pattern reflecting the nanometric size of the $Ni_2Mo_6S_8$ particles.

Pa, DBT partial pressure 577 Pa, and no H_2S added. After equilibrium has been attained, and according to the model of the integral reactor, the rate constant k of a reaction can be expressed as

$$k = \frac{F_0}{m \times C_0} \ln(1 - \tau) \ \ (\mathrm{l/(s \cdot g)})$$

where τ is the conversion rate, m the mass of the catalyst (g), F_0 the molar flow of reactant (mol/s) and C_0 the concentration of reactant (mol/l).

Catalytic activity measurements were used to optimize the reduction parameters for the synthesis of $Ni_2Mo_6S_8$ supported on alumina from NiMoS. Furthermore, this reduction process has also been followed by an EXAFS investigation [14]. Different supported materials were first sulfided under H_2S/H_2 at 673 K and reduced under H_2 at 998 K for 50, 75, 80, 90 and 100 h. The catalytic results are reported in Fig. 7 and XRD patterns of the samples after annealing treatment at 998 K for 24 h are reported in Fig. 8.

After 50 h reduction time, the NiMoS phase was still identified from the XRD pattern. This means that the reduction time is too short. After 75 h under H_2, in spite of the annealing treatment, no diffraction peaks were observed. The NiMoS phase is degraded into small particles of nanometric size which are not detectable by XRD and very difficult to observe by TEM. In contrast to the two previous samples, the XRD diagram of the 90 h reduced sample exhibits the occurrence of the pure nickel Chevrel phase on the support. The sample reduced for 10 h more is also composed of the nickel Chevrel phase. However, only the more intense $Ni_2Mo_6S_8$ peak is detected for the last

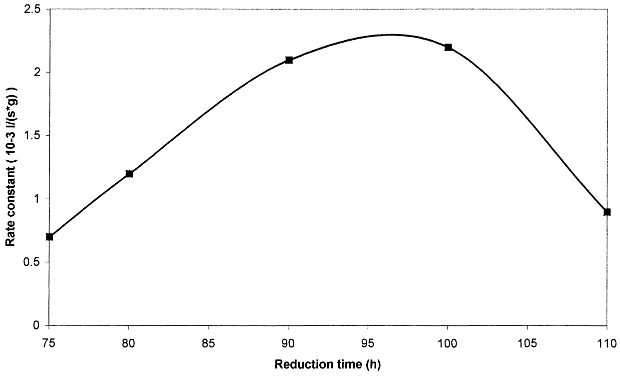

Fig. 7. Catalytic activity of DBT hydrodesulfurization as a function of the NiMoS reduction time (998 K, H_2).

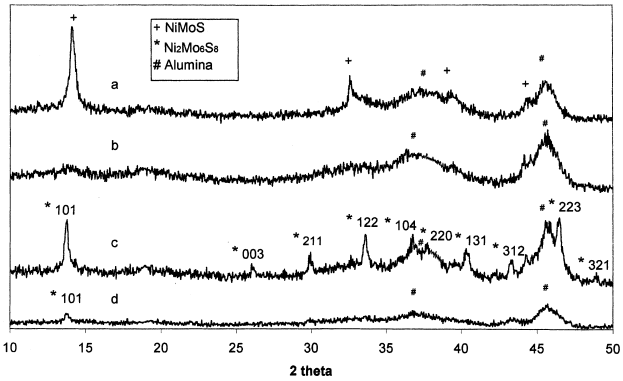

Fig. 8. XRD patterns of the products from the reduction under H_2 of supported NiMoS at 998 K for 50 h (a), 75 h (b), 90 h (c) and 100 h (d). Samples (a), (b), (c), and (d) were annealed at 998 K for 24 h before X-ray diffraction.

sample, showing that the $Ni_2Mo_6S_8$ phase begins to decompose after 90 h under H_2 at 998 K.

The catalytic activity measurements versus reduction time show a maximum of activity around 100 h of reduction and then drastically decreases.

Note that a NiMoS catalyst reduced at 998 K for 8 h has a half of the initial catalytic activity [12–15]. From 8 h to about 70 h reduction time, the activity decreases then remains constant. Above 70 h, it increases again. This confirms that a new hydrodesulfurization material is synthesized during the reduction process: the nickel Chevrel phase supported on alumina. Thus, according to these results, 90–100 h reduction at 998 K seems to be the conditions required for reducing the so-called 'NiMoS' phase to $Ni_2Mo_6S_8$.

4. Conclusion

A new synthesis route from liquid precursors was implemented to prepare bulk nickel Chevrel phases with grain sizes of 200–300 nm. This new synthesis route was transposed to a porous supported material. The nickel Chevrel phase supported on alumina was synthesized and characterized by TEM. This is the first time that a nickel Chevrel phase has been obtained with a grain size on the nanometric scale, <5 nm diameter. The first HDS catalytic tests are very encouraging and more investigations will have to be carried out.

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