Nickel–Molybdenum–Tungsten Sulphide catalysts prepared by *in situ* activation of tri-metallic (Ni–Mo–W) alkylthiomolybdotungstates

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Unsupported nickel–molybdenum–tungsten sulphide catalysts were prepared from tri-metallic Ni–Mo–W alkyl precursors by *in situ* activation during the hydrodesulphurization (HDS) of dibenzothiophene (DBT). The tri-metallic Ni–Mo–W precursors were prepared by reaction of tetraalkylammonium thiomolibdotungstates salts, $(R_4N)_4MoWS_8$ (where R = H, methyl, propyl, butyl, cetyl-trimetyl), with $NiCl_2$ in water at a Ni/Mo(W) molar ratio of 2. These precursors are named $Ni/(NH_4)_4MoWS_8$, $Ni/[N(CH_3)_4]_4MoWS_8$, $Ni/[N(C_3H_7)_4]_4MoWS_8$, $Ni/[N(C_4H_9)_4]_4MoWS_8$, $Ni/[N(C_{19}H_{42})_4]_4MoWS_8$ to give NiMoW–H, NiMoW–C_1, NiMoW–C_3, NiMoW–C_4 and NiMoW–C_C catalysts respectively. These catalysts exhibit a "Swiss-cheese"-like morphology, a wide distribution of specific areas (from 46.9–194.07 m^2/g) and high content of carbon (C/Mo = 2.5–8.9). The *in situ* activation of these tetraalkylammonium thiotrimetallates precursors leads to a mesoporous structure with pore size ranging from 10–40 Å and type IV adsorption–desorption isotherms of nitrogen. X-ray diffraction showed that the structure of unsupported nickel–molybdenum–tungsten sulphide catalysts corresponds to a typical structure of 2H–MoS_2 poorly crystalline with low-stacked layers. The nature of the alkyl group strongly affects both the specific area and the HDS activity. The catalytic activity is strongly enhanced when using carbon-containing precursors; the NiMoW catalysts prepared by *in situ* activation present high HDS activity. The lowest specific area of the catalysts was observed for the NiMoW–H sample.

KEY WORDS: tri-metallic precursors; *in situ* activation; hydrodesulphurization; Ni–Mo–W catalysts.

1. Introduction

Transition metal sulphide (TMS) catalysts play an important role in the petroleum industry. Owing to their resistance to poisons, TMS are unique catalysts for the removal of heteroatoms (N, S, O) in the presence of large amounts of hydrogen. Hydrodesulphurization (HDS) of organic molecules as thiophene, benzothiophene and dibenzothiophene (DBT) is generally performed with molybdenum or tungsten sulphides supported on alumina and promoted by Group VIII elements as Cobalt or Nickel with a promoter atomic ratio Co(Ni)/[Co (Ni) + Mo(W)] of 0.3 for Co and 0.5 for Ni [1, 2]. Co-promoted catalysts are mainly used for HDS, whereas Ni-promoted catalysts are superior in hydrodenitrogenation (HDN) and hydrogenation (HYD) reactions. Ni-promoted catalysts have not been widely investigated and there is not enough understanding of the nickel-promoting effect [3].

The way in which promoter atoms are introduced on the MoS_2 catalysts, has an influence on the catalytic properties. Cobalt- or nickel promoted unsupported HDS catalysts has been prepared by different methods including, commaceration [4] and homogeneous sulphide precipitation [5].

Soled *et al.* [6] have synthesized catalytic trimetallic precursors (Ni–Mo–W) using several methods including direct precipitation, pH controlled precipitation among others. Thus when Mo is substituted at least partially for W, an amorphous phase is produced, whose decomposition and sulphidation produces catalytic active materials. These materials are decomposed *ex situ* in a tubular furnace under H_2S/H_2 10%. The final products are tested to have enhanced both HDS and HDN activity.

On the other hand, with the development of a new catalyst three times more active (NEBULA) [7] than the ones conventionally used in the industry, the research in new and improved catalytic materials for hydrotreatment it has become more important to petroleum industry.

In this work were prepared tri-metallic Ni–Mo–W alkyl precursors by *in situ* activation during the hydrodesulphurization (HDS) of dibenzothiophene (DBT). The tri-metallic Ni–Mo–W precursors were prepared by reaction of tetraalkylammonium thiomolibdotungstates salts, $(R_4N)_4MoWS_8$ (where R = H, methyl, propyl, butyl, cetyl-trimetyl), with $NiCl_2$ in water at a Ni/Mo(W) molar ratio of 2. These precursors are referred as $Ni/(NH_4)_4MoWS_8$, $Ni/[N(CH_3)_4]_4MoWS_8$, $Ni/[N(C_3H_7)_4]_4MoWS_8$, $Ni/[N C_4H_9)_4]_4MoWS_8$, $Ni/[N(C_{19}H_{42})_4]_4MoWS_8$ to give NiMoW–H, NiMoW–C_1, NiMoW–C_3, NiMoW–C_4 and NiMoW–C_C catalysts respectively.

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2. Experimental

2.1. Trimetallic precursor preparation

The preparation of tetraalkylammonium thiometallates has been reported previously by Alonso and co workers [8–10].

Trimetallic precursors are prepared as follows: a solution containing equimolar quantities of Mo and W is prepared dissolving crystal ammonium thiomolybdate (ATM) and ammonium thiotungstate (ATT) in a minimum water volume at room conditions under stirring; once the solution is complete, an aqueous solution of tetraalkylammonium bromide (TAAB) is added at the same conditions, a suspension is immediately formed, the stirring is continued for about 20 min, after a solution of $NiCl_2$ dissolved in 10 mL of water is added at room conditions under continuous stirring a precipitate is rapidly formed. The final material is filtered and dried at room conditions. The general reactions take place as follow:

$$(R_4N)_2MoS_4 + (R_4N)_2WS_4 \longrightarrow (R_4N)_4MoWS_8$$

$$(R_4N)_4MoWS_8 + 2NiCl_2 \longrightarrow Ni_2/(R_4N)_4MoWS_8$$

The precursors were characterized by TGA–DTA analysis. All precursor materials are decomposed during the HDS reaction of DBT. After reaction all materials are characterized by SEM, N_2adsorption-desorption, elemental analysis and XRD.

The appropriate amount of thiomolibdotungstates precursors $(R_4N)_4MoWS_8$ to yield 1 g of Ni_2MoWS_6 [1 g of $(NH_4)_2MoS_4$, 1.3 g of $(NH_4)_2WS_4$, in 25 mL of water] was added under stirring conditions at room temperature to a second solution containing for each case 1.68 g of $(CH_3)_4NCl$ in 15 mL of water, 4.04 g of $[CH_3(CH_2)_2]_4NBr$ in 20 mL of water, 4.9 g of $[CH_3(CH_2)_3]_4NBr$, 5.5g in 25 mL of water, 5.5 g of $[(CH_3)_3CH_3(CH_2)_{15}]NBr$ in 30 mL of a 50:50 water-ethanol solution, a precipitate is immediately formed, this precipitate is impregnated with 1.8 g of $NiCl_2$ dissolved in 10 mL of water.

The five trimetallic precursors are dried at room temperature after filtering. These materials were amorphous and unstable in according with previous study by Pan *et al.* [11]. This instability could be related to on the formation of alkyl thiosalts which are unstable in air.

Owing to the amorphous character of these precursors, the analysis crystallographic are very difficult, in the present study these bimetallic thiosalts will only be labeled as $Ni/[(NR_4)_4MoWS_8$.

2.2. Catalytic activity and selectivity

The HDS of DBT was carried out in a Parr reactor type batch of high-pressure Model 4522. The appropriate amount of precursor was placed in the reactor with HDS reactant (5.0% vol. of DBT in decalin). Each trimetallic precursor was prepared in form of tablet by pressing and then crushed in a mortar before placing in the reactor. The reactor was pressurized to 3.1 MPa with hydrogen and heated to 623 K at a rate of 10 K/min. After reaching working temperature, sampling for chromatographic analysis was performed during the course of each run to determine the conversion *versus* time dependence. The reaction run time was 5 h. The reaction products were analyzed using a Perkin Elmer Auto-System chromatograph with a 9 ft × 1/8 i.d. packed column OV17 3% over Chromosorb uaw 800/100.

The main reaction products from the HDS of DBT are biphenyl (BP) and phenylcyclohexane (PCH). The selectivity for the main products (BP, PCH) was determinated for NiMoW–R catalysts prepared for each trimetallic precursor and was calculated for a given product in the product mixture. The mean deviation for catalytic measurements was about 2%.

2.3. Catalysts characterization

Catalysts characterization was performed on samples obtained after the catalytic test. These samples were separated from the reaction mixture by filtration then washed with 2-propanol to remove residual hydrocarbons and dried at room temperature.

A Jeol JSM 5800 LV scanning electron microscope was used to perform morphology an EDX elemental analysis. Several fields were analyzed at different magnifications in order to aid in recognition of the prevalent features. EDX analysis was performed using an eBX-ZAF system. MoS_2 reference compounds were used to deconvoluted L lines of sulphur and L lines of Molybdenum.

Specific area determinations were performed with a Quantachrome AUTOSORB-1 by nitrogen adsorption at 77 K using the BET isotherm. Samples were degassed under argon flow at 473 K for 2 h. before nitrogen adsorption. The pore size distribution was obtained from the desorption isotherm following the BJH method (see figure 1). The mean standard deviation for specific area measurements was about 2%.

X-ray diffraction (XRD) studies were carried out in a Phillips X Pert MPD diffractometer equipped whit a curved graphite monochromator using Cu Kα radiation ($\lambda = 1.54056$ Å) operating at 43 KV and 30 mA.

3. Results

3.1. TGA–DTA analysis

A TGA–DTA analysis was carried out on a TA instruments STD 2960 DTA–TGA from 27–800 °C at a range of 4 °C/min on N_2 atmosphere. The DTA–TGA

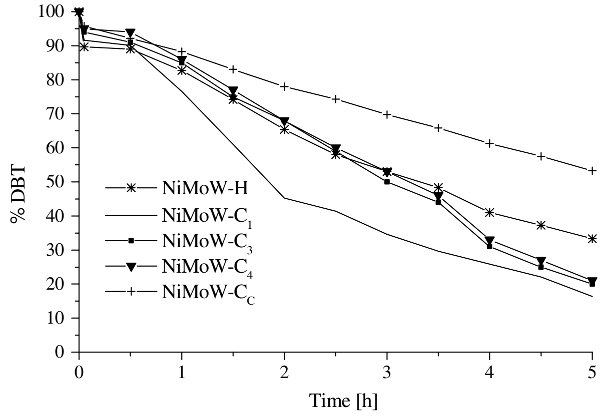

Figure 1. BJH pore size distribution of NiMoW–R catalysts formed after catalytic test.

analysis was used to determine the decomposition temperature of alkylthiometallate precursors.

The decomposition of all materials remains constant beginning at 200 °C and finishing at 300 °C, according to equation (1); after this temperature no change was observed.

$$Ni_2/(R_4N)_4MoWS_8 \rightarrow Ni_2/MoWS_6 \qquad (1)$$

3.2. Elemental analysis

The Ni/Mo, W/Mo, S/Mo and C/Mo atomic ratios determinated using EDX analysis and corroborated by A.A. spectroscopy (1% error), are reported in table 1. A crystalline MoS_2 flake was used for calibration of Mo and S signals, and known concentration standards for A.A. spectroscopy. The atomic ratio of Ni/Mo for most of the catalysts is of 2, except for NiMoW–C_4, where this ratio was 1, while W/Mo atomic ratio remains almost constant at a value of 1. On the other hand, S/Mo atomic ratio remains constant at 6 for all trimetallic (Ni–Mo–W) catalysts. High amounts of carbon ($2 \leq C/Mo \geq 9$) where detected on all catalysts prepared by *in situ* decomposition of trimetallic precursors during the HDS of DBT. Even for NiMoW–H catalyst, a certain amount of carbon is detected even though no carbon is present on the precursor salt. This result is observed previously for Co-promoted MoS_2 under the same conditions (C/Mo = 2.2) [12]. The amount of carbon increases as long as the carbon atoms increase on the alkyl chain. The high amount of residual carbon may be present in the structure and also on the surface of the catalysts.

3.3. Specific area and pore size distribution

The size of the alkyl group in the trimetallic precursor has an important effect on the specific area and the pore volume of the catalysts (cf. table 1.).

The pore volume exhibits a direct correlation with the length of the precursor organic chain this volume increases from 0.0164 cc/g for NiMoW–H to 0.095 cc/g for NiMoW–C_C.

As shown in figure 2, for NiMoW–H catalysts, a poorly developed porous system is observed whit a specific area low (33.8 m^2/g) and a type I adsorption isotherm. The presence of alkyl groups in the precursor lead to the development of a porous system with type IV isotherms.

However the NiMoW–C_1 presents an intermediate situation with a small hysteresis loop. Its specific area (46.9 m^2/g) is higher than the one for NiMoW–H catalysts but still much smaller than the one for NiMoW–C_3 catalysts. NiMoW–C_3 and NiMoW–C_4 presents a very similar form of isotherm. Finally NiMoW–C_C exhibits the higher specific area (194 m^2/g) and pore volume (0.095 cc/g), this could be related to the high amount of carbon.

All catalysts present a very similar pore size distribution with an average centered to 17–18 Å. The hysteresis loops shown by these catalysts corresponds mainly to cylindrical pores opened at both ends. However, some mesopores have narrow ends as an inkbottle pore shape particularly for NiMoW–C_3 and NiMoW–C_4 catalysts. NiMoW–C_C present a less step desorption branch.

3.4. Scanning electron microscopy

Images of NiMoW–R catalysts prepared from (a) $Ni/(NH_4)_4MoWS_8$, (b) $Ni/[N(CH_3)_4]_4MoWS_8$, (c) $Ni/[N(C_3H_7)_4]_4MoWS_8$, (d) $Ni/[N(C_4H_9)_4]_4MoWS_8$, and (e) $Ni/[N(C_{19}H_{42})_4]_4MoWS_8$ are reported in figure 3. All these materials appear to be very compact and disordered structure, with the exception of NiMoW–C_4, in this case, is observed a structure with many cavities around 5 μm, which could explain the increase in specific area but the main contribution to this may be

Table 1
Specific area, pore volume and elemental analysis for NiMoW–R sulphide catalysts

NiMoW–R Catalysts	Specific area (m^2/g)	Pore volume (cc/g)	Pore diameter Å	Elemental analysis (%atom)
NiMoW–H	33.8	0.0164	10–40	$Ni_2MoW\ S_6C_2$
NiMoW–C_1	46.9	0.0231	10–40	$Ni_2MoWS_6C_4$
NiMoW–C_3	108.1	0.0530	10–40	$Ni_2MoW\ S_6C_5$
NiMoW–C_4	165.1	0.0808	10–40	$Ni_1MoWS_6C_7$
NiMoW–C_C	194.1	0.0950	10–40	$Ni_2MoWS_6C_9$

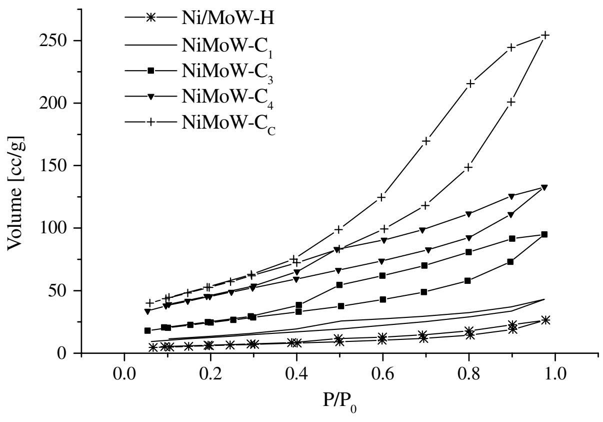

Figure 2. Adsorption–desorption isotherms for NiMoW–R catalysts formed by *in situ* decomposition of different thiotrimetallates precursors.

the development of macropores. The increased degree of disorder respect to the other materials, and the appearance of cavities in NiMoW–C_4, may be attributed to the gas products during the decomposition *in situ*. The resulting structure is formed by agglomeration of small particles.

3.5. X-Ray diffraction

Figure 4 show the XRD patterns of the NiMoW catalysts prepared from different Tetraalkylammonium thiomolibdotungstates, these patterns are in agreement for those poorly crystalline MoS_2 and WS_2 structures [13] (ICDD 17–744) with a weak (002) diffraction peak at $2\theta = 14°$ except for NiMoW–H where this peak is very sharp. Accordingly, the *c* direction layer stacking for catalysts formed from alkyl precursors is representative of partly exfoliated materials. In addition, All catalysts presents a Ni_3S_2 phase (ICDD 27–341) with weak diffraction peaks at $2\theta = 30°$, 45° and 54°, and a Ni_9S_8 (ICDD 22–1193) at $2\theta = 23°$ for NiMoW–C_3 only.

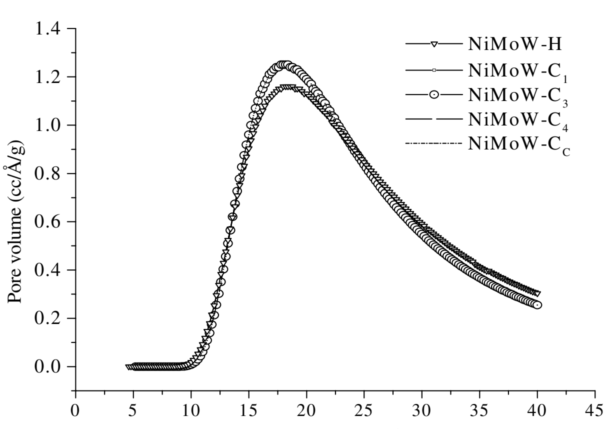

Figure 3. Scanning electron microscopy images of the NiMoW–R catalysts prepared from: (a) $Ni/(NH_4)_4MoWS_8$, (b) $Ni/[N(CH_3)_4]_4MoWS_8$, (c) $Ni/[N(C_3H_7)_4]_4MoWS_8$, (d) $Ni/[N(C_4H_9)_4]_4MoWS_8$ and (e) $Ni/[N(C_{19}H_{42})_4]_4MoWS_8$.

3.6. Catalytic activity and selectivity

The HDS of DBT yield two main products: Biphenyl (BP) through the so-called direct desulphurization pathway (DDS) and cyclohexilbenzene (CHB) and tetrahydrodibenzothiophene (THDBT) through the hydrogenative pathway (HYD). Phenylcyclohexane is a secondary product along this pathway obtained by C–S bond breaking reaction from THDBT, an intermediate product formed by hydrogenation of one of the aromatic rings of dibenzothiophene. Since these two pathways occur in parallel [14], the ratio between HYD and DDS can be approximated in terms of experimental selectivity by means of the equation (2).

$$\frac{(\mathrm{HYD})}{(\mathrm{DDS})} = \frac{(\mathrm{PCH} + \mathrm{THDBT})}{(\mathrm{BP})} \qquad (2)$$

Table 2 summarizes the activity results and selectivity for BP and PCH through (HYD)/(DDS) ratios measured for different NiMoW–R catalysts formed by *in situ* decomposition of Tetraalkylammonium thiotrimetallates. Initial rate constants were determinated, as for alkyl thiomolibdotungstates, a complete decomposition of these precursors before 623 K for the HDS of DBT [8]. The higher reactivity and tendency for decomposition of Ni-containing alkylammonium thiomolibdotungstates compared with no carbon containing.

Compared with the NiMoW–H catalyst formed from $Ni/(NH_4)_4MoWS_8$, presence of alkyl groups in the precursor leads to a strong activity increase with a maximum of activity for NiMoW–C_1 catalyst (cf. table 2).

In general these trimetallic catalysts presents higher activity than commercial catalysts $NiMo/Al_2O_3$ with $k = 12 \times 10^{-7}$ mol/g*s.

4. Discussion

The *in situ* activation of tetraalkylammonium thiometallates during the hydrodesulphurization of dibenzothiophene has been used to generate non-promoted active MoS_2-based catalysts [8]. This preparation method leads to materials with high specific area, mesoporosity, large amounts of carbon and increased catalytic activity. In this work, such method was extended to prepare NiMoW sulphides through the use of tetraalkylammonium thiotrimetallates precursors. In agreement with previous results for MoS_2 and $CoMoS_2$ catalysts, high specific, mesopore size distribution and high C/Mo ratios (from 2 to 9) are also obtained.

The alkyl group presented in the tetraalkylammonium precursor has a direct influence on specific area, total

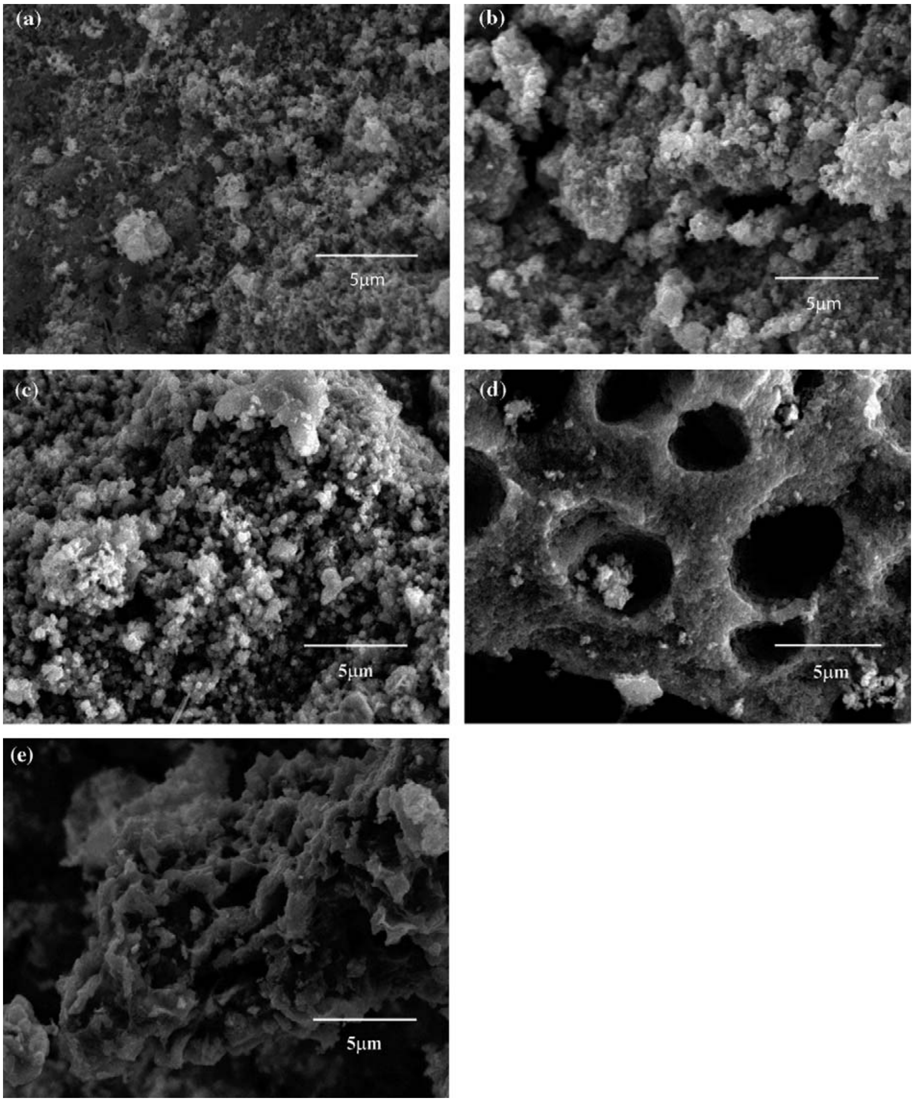

Figure 4. XRD patterns of NiMoW–R catalysts formed by *in situ* decomposition of different molibdotungstate precursors.

pore volume and HDS activity. Increasing the alkyl chain length from methyl to cetyl-trimetyl results in a marked increase in both specific area from 46.9 to 194.07 m^2/g and the total pore volume from 0.0231 to 0.095 cc/g. this increase in specific area is accompanied by the progressive formation of a mesoporous organization with an average pore diameter from 10 to 40 Å with a maximum at 20 Å for all tested materials. More interesting, tetraalkylammonium trimetallic precursor leads to an increase in HDS activity compared with non-carbon-containing ammonium trimetallic precursors, except for cetyl-trimetyl ammonium precursor, which presents a highly decreased HDS activity. There is no relationship between specific area and HDS activity. Also there are changes in the DBT conversion, while the presence of alkyl groups leads to an increase of DBT conversion as shown in figure 5. On the other hand an increment on alkyl chain length leads to a less DBT conversion as shown in catalytic activity also. The DBT conversion decreases after 3 h; this may is attributed to a decrease in DBT. For instance, the NiMoW–C_1 catalysts presents low specific area (46.9 m^2/g), but highly increased HDS activity ($k = 27.6 \times 10^{-7}$ mol/g*s). In the same way, the development of a mesoporous organization could not be invoked since the high HDS activity is observed for the NiMoW–C_1 catalysts, which possesses a modest mesoporous organization in compar-

Table 2
Initial rate constants, selectivity (HYD/HDS) of NiMoW–R catalysts

Catalysts	$k \times$ 10E−07 Mol/g s	$k \times$ 10E−07 Mol/s m^2	HYD/HDS
NiMoW–H	17.2	0.51	1.19
NiMoW–C_1	27.6	1.70	0.93
NiMoW–C_3	18.6	0.17	1.14
NiMoW–C_4	20.4	0.12	1.31
NiMoW–C_C	10.3	0.05	4.13

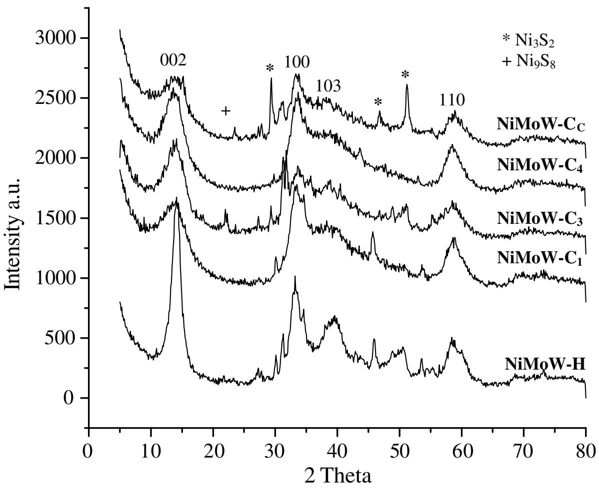

Figure 5. DBT conversion curves for trimetallic NiMoW catalysts.

ison with the NiMoW–C_3, NiMoW–C_4 and NiMoW–C_C (see figure 2). On the other hand, a positive role of carbon in hydrotreatments demonstrated by Chianelli and Berhault [15] could not be established in this work, since the high HDS activity corresponds to NiMoW–C_1 which has a low amount of carbon, compared with all carbon-containing ammonium precursors. Indeed, in typical hydotreating conditions, carbide and sulphide catalysts would tend to common active specific presenting both S and C moieties, as already has been reported by different authors [8–10, 16, 18–20]. The formation of surface carbide-like entities was clearly observed by Berhault and co-workers [17] using NEXAFS on MoS_2 catalyzing the HDS of DBT. Consequently, the formation of "structural" carbon replacing surface sulphur atoms at the edges of the layers and taking part in the active phase may be envisaged in the present case.

It should be empathized that the amount of carbon detected could be presented either at the surface of the catalysts (structural carbon) or as a support (excess carbon). Then, differentiation between structural or morphological role of the carbon in this situation is not possible.

NiMoW Catalysts (Ni/Mo molar ratio = 2) present higher catalytic activities than their $CoMoS_2$ counterparts prepared from the equivalent bimetallic tetraalkylammonium precursor. This demonstrates that when, Mo is substituted partially for W in the catalysts structure; a strong synergic effect is created.

The HDS of DBT process occurs along two parallel pathways, the so-called direct desulphurization route (DDS) leading to biphenyl and the so-called hydrogenative route (HYD) leading to phenyl cyclohexane via tetra-hydrodibenzothiophene. The HYD/DDS ratio for NiMoW sulphide catalysts prepared by *in situ* decomposition of different Thiosalts precursors remains almost constant around 1 (see table 2) except for NiMoW–C_C which presents a highly selectivity for hydrogenative route.

The HYD/DDS ratio for all catalysts is similar, except for NiMoW–C_C showing a marked selectivity to HYD, these results are in agreement with Kabe *et al.* in Ni systems [21]. Therefore, Ni promotion modifies the selectivity comparated with CoMoS systems.

The alkyl group does not appear to affect selectivity, except for NiMoW–C_C catalyst. As revealed by the XRD, the evolution of the (002) peak intensity indicates a marked decrease in the stacking along the *c* direction when a hydrocarbon chain is incorporated to the precursor salt (see figure 4). According to the "Rim-Edge" model [22,23], a slightly more DDS favored selectivity would be expected since "rim" sites at the exterior of the stacked layers would be responsible for both C–S bond breaking and hydrogenation whereas "edge" sites located on internal stacked layers is only active for C–S bond breaking reactions. However this can not be assumed for these catalysts, it should be emphasized that the "rim-edge" model was proposed for non-promoted unsupported MoS_2 catalysts, and should not be applied to other systems like trimetallic (Ni–Mo–W) catalysts. The extension of this selectivity/stacking correlation to Ni–Mo–W catalysts has still to be done. However, applicable or not in this case, a selectivity/stacking correlations in the "rim-edge" model is not responsible for selectivity behavior observed in this work. The absence of selectivity variations between NiMoW–H and NiMoW–C_1, while the stacking decreases definitely is not selectivity/stacking causality.

5. Conclusions

Ni–Mo–W sulphide catalysts (NiMoW–R where R = H, C_1, C_3, C_4 and C_C) were prepared by *in situ* decomposition of different tetraalkylammonium thiotrimetallates precursors. The materials obtained using this procedure presents interesting morphological properties with high specific area and characteristic type IV isotherms with a sharp mesoporous distribution and the presence of various active phases. A hydrogenative effect of Ni is observed and an enhanced HDS activity compared with other Mo systems supported or unsupported (commercial NiMo/Al_2O_3 $k = 12 \times 10^{-7}$ mol/g*s, CoMo $k = 17.4 \times 10^{-7}$ mol/g*s) [12].

The nature of the alkyl group strongly affects both specific area and the HDS activity, since when carbon-containing precursors are used; it is observed that the catalytic activity is strongly enhanced.

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