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Petroleum residue upgrading with dispersed catalysts
Part 1. Catalysts activity and selectivity

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Abstract

The results of a study aimed at the identification of the relevant chemical aspects involved in the process of upgrading heavy feedstocks in the presence of dispersed catalysts are discussed. The catalytic activity of different compounds was compared in terms of products yields and quality. Moreover, a detailed and systematic characterization of the catalysts recovered at the end of the reactions was achieved. The experimental work provided quite a large set of data, allowing to investigate the factors that may affect catalyst activity (precursor solubility, rate of activation, degree of dispersion, presence of promoters etc.). The results of this study demonstrate that the best performances are obtained by the microcrystalline molybdenite generated in situ by oil-soluble precursors. The nature of the organic ligand does not play a very relevant role in influencing the hydrogenation activity. The presence of phosphorus, however, significantly enhances hydrodemetallation, at least in terms of vanadium removal. Bimetallic precursors show a slight synergistic effect towards the hydrodesulfurization reaction. Microsized powdered catalyst precursors have a much lower catalytic activity compared to the oil-soluble ones.

Keywords: Residue hydroprocessing; Slurry process; Dispersed catalyst; Transition metal sulfide

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1. Introduction

The use of dispersed catalysts may offer an interesting solution for upgrading heavy feedstocks and petroleum residues [1]. In fact, the slurry processes combine the advantages of the carbon rejection technologies in terms of flexibility with the high performances peculiar of the hydrogen addition processes [2].

Very high levels of catalyst dispersion, which strongly affect the hydrogen uptake, can be achieved by introducing finely divided powders or water- or oil-soluble compounds into the feed. The active species of the catalyst is a metal sulfide, which is generated in situ by thermal decomposition of the precursor [3].

In the last few years, many aspects dealing with the use of dispersed catalyst have been explored rather extensively; nevertheless, the problems associated with the development of slurry processes are not completely solved [4]. Main limitations to their commercialization concern the high investment and operating costs due to the catalyst make-up and/or the severity of the process. At present, the most advanced slurry technologies [5–7] are based on the use of inexpensive additives, for instance Fe-based compounds, or carbonaceous material to control coke formation. It is well known that these additives show very low

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activity towards hydrogenation reactions compared to transition metals (molybdenum, nickel etc.); nevertheless, due to their lower cost, these materials can be used in a once-through mode. In this case, however, very high hydrogen pressures are necessary to counterbalance the scarce catalytic performance.

Based on previous observations, it follows that the development of an efficient hydroconversion technology depends on the identification of more effective/less expensive catalysts, as well as the optimization of operating conditions. Both objectives may be reached by a better understanding of the chemical and physico-chemical aspects of the process.

In the present paper (Part 1), we will extensively discuss the topics related to the catalytic activity of different materials. Then, in Part 2, attention will be focused on the kinetic aspects of the reaction, in order to study the effect of operating conditions on product yields and quality.

In the field upgrading heavy oils with slurry processes, as well as in direct coal liquefaction and coprocessing, a lot of precursors of different natures have been tested and patented, and several studies dealing with the identification of more active catalysts are available in the literature [1,8,9]. Nevertheless, a rationalization of the scientific knowledge is not as well established as in the field of hydrotreating reactions with conventional supported catalysts [10]. The objective of the present work was to understand the relation between catalyst properties and activity. The catalytic performances of a large number of materials of very different natures were evaluated. Beside several oil-soluble compounds (some of which synthesized by us according to literature procedures), we also tested powdered catalysts. These microsized materials can be obtained by various techniques, such as laser pyrolysis, plasma methods and also chemical synthesis. This novel approach, as reported by some authors [11–13], seems to provide a high degree of dispersion in the feedstock. Finally, the possibility of achieving a strong promotion of the catalyst activity by preparing bimetallic precursors was explored. In fact, it has been reported that two metals bonded together in a single cluster compound are substantially more active than the mixtures of different metal precursors [14,15].

Hydroconversion experiments performed in the presence of these catalytic systems provided quite a large set of data, which allowed gaining a deeper insight into the role played by many factors that may affect catalyst activity (i.e. solubility, rate of activation, degree of dispersion, surface area, presence of heteroatoms etc.).

2. Experimental

The hydrogenation reactions were performed on a vacuum residue of Belayim crude, used as a reference feedstock (Table 1). Various kinds of commercial compounds containing a transition metal were evaluated: molybdenum naphthenate (MoNaph), molybdenum acetyl acetonate (MoAA), phosphomolybdic acid (PMA), iron naphthenate (FeNaph), nickel naphthenate (NiNaph), cobalt resinate (CoRe), vanadium resinate (VRe), and ruthenium acetyl acetonate (RuAA). Some other precursors synthesized according to literature procedures were tested: two oil-soluble molybdophosphonic compounds [16], (MoO_2)–LA_2^* and (MoO_2)–LB_2^* (named, respectively, RMV6 and RMV12), where LA^* stands for $(O_2N$–Ph–$CH_2)_2$–$C(COOH)PO_3H_2$, and LB^* stands for $(Ph$–$CH)_2$–$C(COOEt)PO_3H_2$, and two bimetallic compounds, $Co(MoO_2)$–LB_2^* and $Ni(MoO_2)$–LB_2^*, named, respectively, RMV14 and RMV15 [16]; a dithiocarbamate complex [17] Mo_3S_7–$(dtc)_4$, where dtc stands for diethyl-dithiocarbamate (named SP2); a molybdenum carbide, Mo_2C, prepared by chemical synthesis [13]; an ultrafine molybdenum nitride, Mo_2N, obtained by laser pyrolysis [18] (provided by Kentucky University).

Table 1
Properties of Belayim vacuum residue

>500°C fraction (wt.%)	96.0
Density 15/4°C (g/cm^3)	1.016
Viscosity at 100°C (cSt.)	3600
CCR (wt.%)	20.7
C5-Asphaltene (wt.%)	21.6
C7-Asphaltene (wt.%)	14.4
Elemental analysis (wt.%)	
C	81.5
H	10.4
N	1.0
S	3.9
Ni (ppm)	130
V (ppm)	178

In order to obtain an effective dispersion of metals in the feedstock, both the catalyst precursor and the vacuum residue were dissolved in tetrahydrofuran (THF). The solutions prepared in this way were then sonicated; finally, the solvent was removed by rotary evaporation.

The conversion experiments were performed in a batch mode using a 30 ml autoclave with a 'swinging capillary' stirring device. In a typical experiment, the reactor was charged with 10 g of feedstock, pressurized with 9 MPa of hydrogen and heated to the reaction temperature for the desired reaction time. The reaction pressure was recorded during the experiments.

At the end of the run, the autoclave was rapidly quenched and vented; the gases were recovered into a gas-sampling bag for gas chromatographic (GC) analysis. The liquid and solid products of the reactions were recovered with THF. This mixture was stirred in an ultrasonic bath for 15 min and then filtered through a Millipore Teflon filter (0.5 μm) to separate THF-soluble material from the residues (coke and metal catalyst). The amount of coke was therefore calculated by subtracting the weight of the catalyst from the residue.

The THF-soluble product was deasphalted by addition of 40 volumes of *n*-pentane to produce a deasphalted oil (DAO) that was then analyzed by GC simulated distillation analysis (SIM-DIST) to obtain the distillation curves of volatile fractions. The conversion to distillate was therefore calculated by difference from the weight of the various residues (coke, asphaltenes and DAO >500°C fraction). The sulfur content of distillate was determined by chromatographic analysis of DAO, using a GC system equipped with Atomic Emission Detector (GC AED).

The residues of reactions containing the metal sulfides (together with coke) were characterized by X-ray diffraction (XRD) and electron microscopy.

2.1. XRD analysis

XRD data were collected using a Philips goniometer, step scan method and Ni-filtered Cu Kα radiation (λ=1.54178 Å). Crystalline phases were identified by search-match with standard phases using the DIFFRAC-500 computer package and the JCPD files. Crystal sizes were evaluated by the Scherrer method from line breadth without taking into account disorder effects. Owing to the lack of suitable pure reference compounds, quantitative analysis of the crystal phases in the mixture was not possible, and therefore, the variations in composition were simply related to the variations in intensity of selected well resolved diffraction lines.

2.2. SEM–AI analysis

The samples for scanning electron microscopy (SEM) and automated image (AI) analysis were prepared by dispersing the filtered dry powder of residue in isopropyl alcohol, sonicating and dropping the dispersion on a glass disk. Back-scattered images were collected with a Jeol JSM 840A microscope and processed using a Kontron IBAS 2000 automatic image analyzer to obtain the particle size distribution. The analysis was limited to the particles with diameter greater than 0.1 μm.

2.3. Transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) analysis was carried out using a Philips 420T microscope equipped with an EDAX PV9900 EDS apparatus and operating at 100 kV. Most of the samples were prepared starting from the reaction products without separation by filtration. A thin layer of product was spread on a glass and a suitably bent copper grid (300 mesh) was slightly brought into contact with the film. The very thin layer adhering to the grid was washed carefully with heptane in order to remove the soluble organic compounds, dried and analyzed by TEM–EDS. In some cases, TEM images were collected after shading the samples with tungsten by electron beam evaporation (angle 20°).

3. Results and discussion

3.1. Effect of metal

One of the most important advantages of the use of dispersed catalyst for the conversion of heavy feedstocks is the inhibition of coke formation. For this reason, in order to compare the activity of different

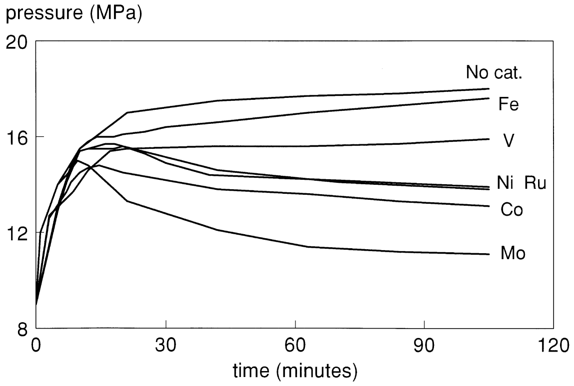

Fig. 1. Effect of active metal on hydrocracking performance: autoclave pressure vs. reaction time (460°C, 16 MPa H_2 initial pressure, 90 min).

metals, the oil-soluble compounds were evaluated under high severity conditions: 460°C, initial hydrogen pressure of 9 MPa and a reaction time of 90 min. The experiments were carried out in the presence of 1000 ppm of metal.

A first, immediate evaluation of the activity of the different catalysts is given in Fig. 1 that depicts the autoclave pressure profiles as a function of reaction time (including the heating-up period).

In a closed system such as the microautoclave, pressure evolution depends on the result of two opposite phenomena: hydrogen consumption, which reduces the pressure, and gas production, which tends to increase it. The catalysts which give the lowest final pressure should be preferable because they suppress the formation of hydrocarbon gases and promote hydrogen uptake. These results show that molybdenum is definitely more active than all other metals. Moreover, the shape of the corresponding curve suggests that MoNaph activation is very rapid because the reduction of autoclave pressure, and consequently, hydrogen uptake, start after about 11 min, that is substantially below the reaction temperature [19].

Table 2 summarizes the catalytic performances of the metals in terms of product yields and quality. As expected, molybdenum gave the best overall performance: compared to other metals, it shows the highest effectiveness for coke suppression as well as the best control on gas production. Consequently, the presence of this metal allows maximizing liquid yields. In fact, although vacuum residue conversion is thermally controlled, the addition of a very active catalyst significantly affects the product selectivity. In the absence of catalyst, or in the presence of less active metals, thermal cracking alone can achieve very high conversion, but it gives relatively low liquids yields because a significant amount of residue is rejected as coke.

Although at this stage of catalyst evaluation the highest importance was given to the suppression of coke and gas formation, the product quality in terms of removal of metals and sulfur was also considered as a significant parameter for ranking the performance of the metal compounds.

As can be noticed for the experiments carried out without additive or in the presence of a scarcely active metal (as iron), hydrodemetallation (HDM) generally increases with coke yields. However, Mo was found to achieve high degrees of demetallation even in the presence of very low coke yields. At last, as revealed by the sulfur content of distillate (Table 2), only Mo, Ni and Ru catalysts gave fairly good results in terms of hydrodesulfurization (HDS) activity.

Summarizing, on the basis of the overall performance, the comparison of the different oil-soluble precursors gave the following order of activity: Mo>Ni∼Ru>Co>V>Fe.

In particular, according to other studies [20–22], FeNaph data are very close to the results obtained in the uncatalyzed reaction. However, despite the low activity of iron sulfide being well known, Fe-based materials are often used in slurry processes because of their low cost. In such a case, thermal effects prevail over catalytic ones, and high hydrogen pressures are needed to control coke formation.

In addition to the above results, characterization of the solid samples recovered after hydroconversion experiments helps to rationalize the different catalytic performances.

X-ray diffraction (XRD) analysis of Mo-based catalyst shows the presence of an MoS_2 microcrystalline phase with the layered structure of molybdenite [23]. The lack of the *0 0 1* diffraction lines in the XRD patterns (Fig. 2) suggests the presence of monolayers or crystallites with a stacking limited to a few layers (maximum two to three). The average radial dimension of the layers, evaluated by profile analysis of *1 1 0* diffraction line and applying the Scherrer equation, is 20–40 Å. TEM–EDS analysis evidences slabs of MoS_2 isolated or, less frequently,

Table 2
Effect of active metal on product yield and quality[a]

Catalyst precursor	No catalyst	MoNaph	FeNaph	NiNaph	CoRe	VRe	RuAA
Feedstock conversion (wt.%)	89.6	84.9	87.6	83.2	83.7	85.2	81.4
Product distribution (wt.%)							
C1–C4	10.9	7.3	10.0	12.6	11.7	13.2	11.7
C5-200°C	33.5	38.5	35.3	32.9	35.4	32.0	30.7
200–350°C	16.6	23.8	16.2	21.2	19.2	19.6	21.8
350–500°C	6.7	12.0	6.9	11.5	9.4	8.2	11.8
>500°C	10.4	15.1	12.4	16.8	16.3	14.8	18.6
Coke	21.9	3.3	19.2	5.0	8.0	12.2	5.4
C5-Asphaltene	8.9	14.3	10.5	13.5	14.1	13.9	15.3
Product quality							
HDM (%)	>99	82	98	87	89	93	78
S in 200–350°C (wt.%)	3.2	1.9	3.2	2.3	3.0	2.9	2.3
S in 350–500°C (wt.%)	4.9	2.6	4.8	3.3	4.5	4.4	3.3

[a] 460°C, 16 MPa H_2, 90 min, 1000 ppm of metal.

grouped in sheaves, in which the slabs are almost parallel and regularly spaced 25–30 Å (Fig. 3). Furthermore, TEM micrographs show that the molybdenite crystallites tend to aggregate in micronic loose particles, which appear as irregular clusters with a mean diameter of 0.5–2 μm (Fig. 4). In addition to the catalyst, the elements recovered from the feed by demetallation (V, Ni, Fe, ...) crystallize as sulfides with a pyrrhotite-like structure (Fig. 5), which disperse rather homogeneously in the same aggregates of molybdenite. Unlike Mo-based catalytic systems, the sulfides derived from the other metals (Ni, Co, Fe, ...) generally form a three-dimensional pyrrhotite-like crystalline structure with a crystal size of 200–300 Å (Scherrer method). Compared to MoS_2, this means a significantly lower specific surface area, which can partially explain the lower activity of these elements.

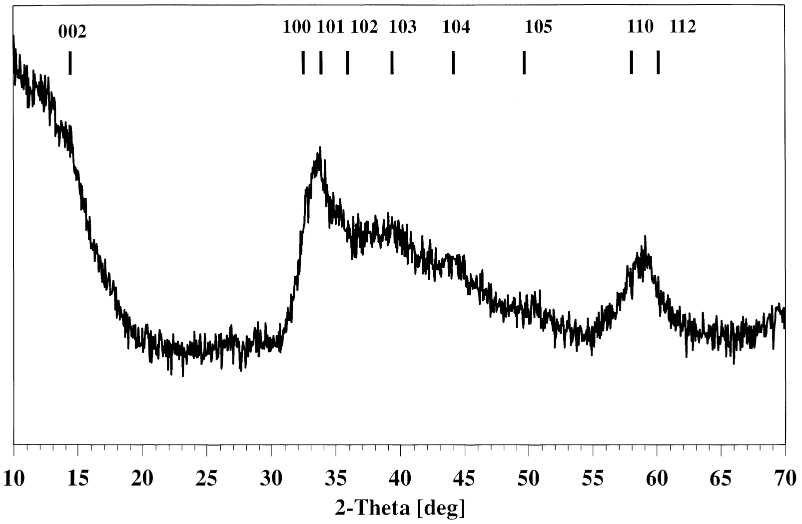

Fig. 2. XRD pattern for the catalyst recovered after activation of molybdenum naphthenate.

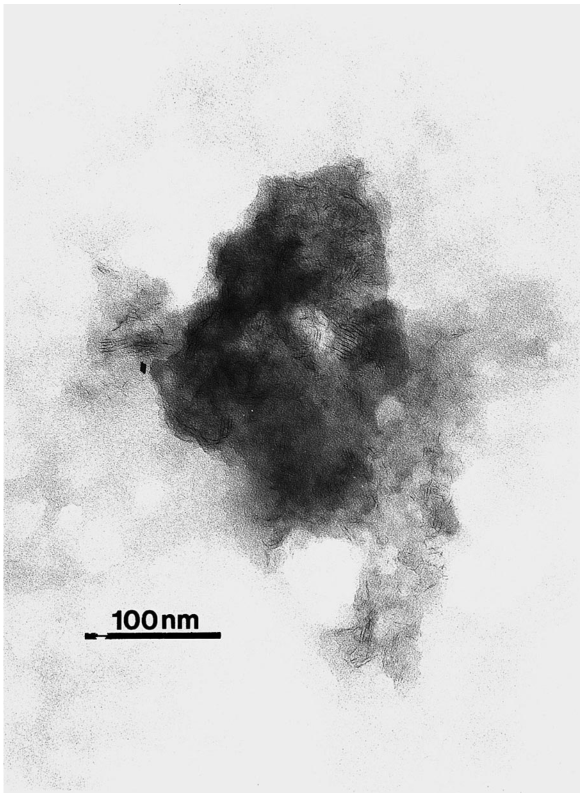

Fig. 3. TEM micrograph of molybdenite particles from the decomposition of molybdenum naphthenate. The lamellar structure is well evidenced (405 000×).

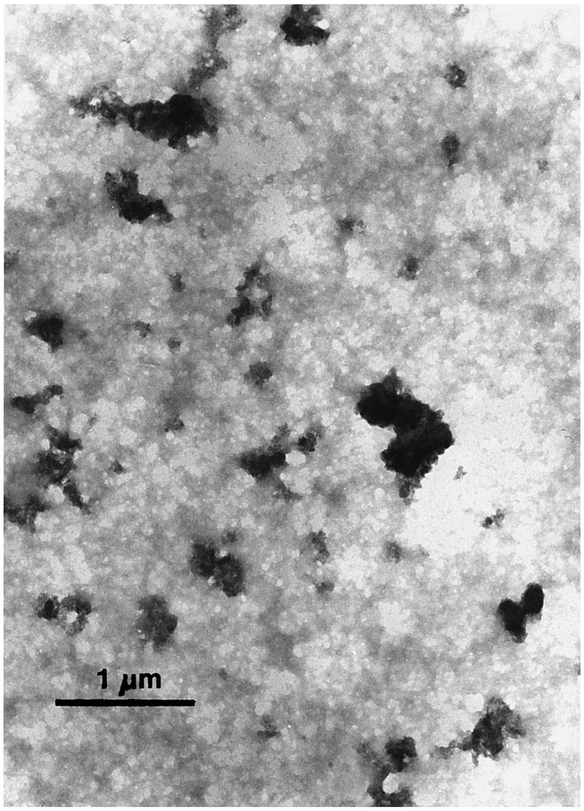

Fig. 4. TEM micrograph of molybdenite particles from the decomposition of molybdenum naphthenate (40 500×).

3.2. Effect of catalyst formulation

The aim of this work was also to understand the role played by the organic portion of the molecule, and to determine whether the presence of a particular element (such as phosphorus or sulfur) had any significant influence on the catalyst performance. For this purpose, we prepared and evaluated two oil-soluble precursors: a molybdophosphonic compound, RMV6 and a dithiocarbamate complex, Mo_3S_7–$(dtc)_4$ (named SP2). These catalyst precursors were compared with three commercially available compounds (MoNaph, MoAA and PMA).

Moreover, in order to better understand the effect of dispersion on catalyst activity, Mo-based ultrafine materials were also tested: molybdenum nitride, Mo_2N, synthesized by laser pyrolysis, and molybdenum carbide, Mo_2C, prepared by chemical synthesis.

Fig. 6 shows the autoclave pressure profiles recorded during the experiments carried out in the presence of the different Mo-based compounds. At a first comprehensive sight, the trends of these curves show that no significant difference can be found among the soluble precursors in terms of hydrogen consumption and gas production. On the other side, the higher final pressure related to the testing of Mo_2N and Mo_2C suggests a lower catalytic activity of these powdered materials. The data reported in Table 3 confirm this initial interpretation.

All these compounds were tested at two different levels of severity: 460°C for a residence time of 90 min and 410°C for a residence time of 240 min. At the lower temperature (Table 4), the thermal effects become less important, and this fact allows emphasizing the differences in terms of catalyst activity.

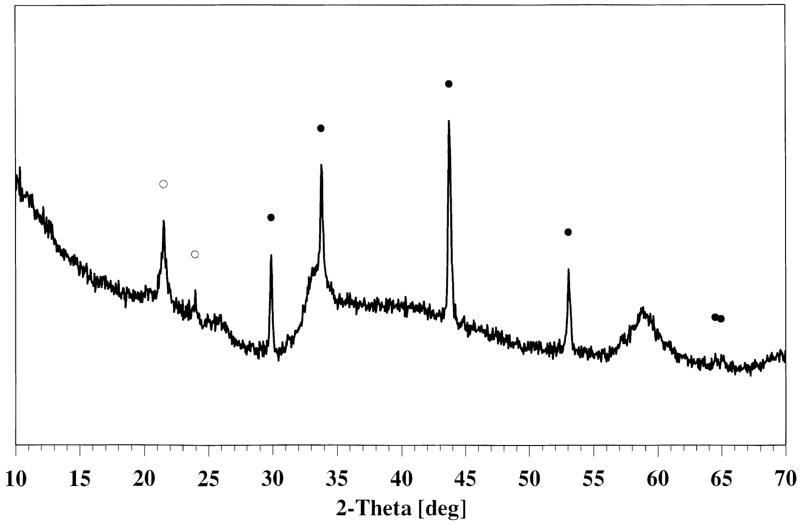

Fig. 5. XRD pattern for the catalyst recovered after catalytic test. The pattern shows the diffraction lines of a pyrrothite-like structure crystal phase (●); the lines of a fraction of crystalline paraffins are evidenced (○).

Concerning the effect of the presence of sulfur on catalyst performance, no difference was observed between the dithiocarbamate precursor and the other compounds. This result suggests that the sulfur compounds present in the feedstock provide a sufficient amount of sulfur for catalyst activation. Consequently, an additional source of this element (introduced as elemental sulfur, hydrogen sulfide or present in the organic portion attached to molybdenum) has no effect on favoring sulfided active species formation [1].

The effectiveness of phosphorus addition for sulfur and metal removal in upgrading heavy feedstocks has already been reported [24–26]. Our experiments carried out with a large number of molybdophosphonic compounds [16] confirm the beneficial effect of phosphorus on vanadium removal. Fig. 7 shows the results obtained in the presence of our compound RMV12 compared to MoNaph. This enhancement of HDM activity might be related to the formation of oil-insoluble P–V compounds [25]. No significant improvement was observed in the HDS activity of phosphomolybdic compounds, although a slight increase in sulfur conversion was found for bimetallic phosphonic precursors, as reported in the following paragraph.

Summarizing, catalyst performances of the oil-soluble compounds seem to be nearly independent of the organic group bonded to the metal. The small variations may be attributed to the different thermal liability of the precursors. If the rate of precursor decomposition and sulfidation is slow, the reaction is thermally controlled, despite the additive being present. In this case, the parameters which are more sensitive to the presence of a well-activated catalyst (such as coke formation and sulfur removal) are strongly affected.

This effect is well evidenced by the experiments performed in the presence of powdered materials. In

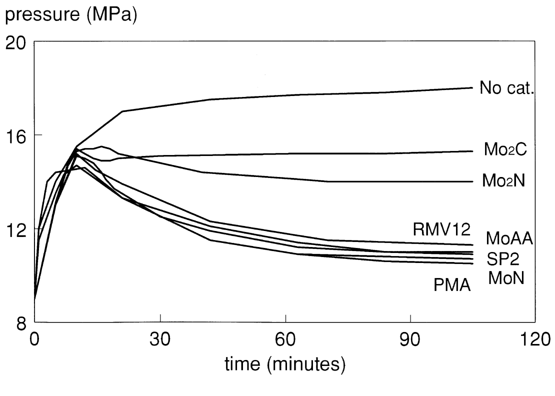

Fig. 6. Effect of compound type on Mo-based catalyst performance: autoclave pressure vs. reaction time (460°C, 16 MPa H_2 initial pressure, 90 min).

Table 3
Effect of compound type on product yield and quality[a]

Catalyst precursor	MoNaph	PMA	MoAA	SP2	RMV6	Mo_2C	Mo_2N	Mo_2N[b]
Feedstock conversion (wt.%)	84.9	85.0	85.2	84.0	83.1	87.6	83.1	84.2
Product distribution (wt.%)								
C1–C4	7.3	10.2	10.5	10.0	10.1	10.7	11.1	10.5
C5-200°C	38.5	34.1	33.9	36.0	27.7	36.7	35.0	32.6
200–350°C	23.8	24.2	24.3	22.5	26.2	16.6	19.6	23.4
350–500°C	12.0	12.7	13.8	11.7	16.2	7.3	10.0	13.8
>500°C	15.1	15.6	14.8	16.0	16.9	12.4	16.9	15.8
Coke	3.3	3.2	2.7	3.8	2.9	16.3	7.4	3.9
C5-Asphaltene	14.3	12.2	11.1	13.3	10.9	9.2	12.8	11.3
Product quality								
HDM (%)	82	80	75	79	94	95	79	79
S in 200–350°C (wt.%)	1.9	1.8	1.8	2.1	1.7	n.a.[c]	2.4	2.1
S in 350–500°C (wt.%)	2.6	2.7	2.6	3.0	2.4	n.a.[c]	3.7	2.8

[a] 460°C, 16 MPa H_2, 90 min, 1000 ppm of metal.
[b] 90 min at 410°C plus 90 min at 460°C.
[c] n.a.: Not analyzed.

particular, Mo_2C shows a very poor activity under high severity conditions, as displayed in Table 3: the results are very similar to those obtained in the absence of the catalyst or in the presence of scarcely active metals. This great difficulty in activation seems to be overcome at low severity. Also, molybdenum nitride is relatively inactive for coke suppression under high severity conditions. In this case, we tried to improve the activation of catalyst precursor by carrying out a relatively low severity step (410°C, 90 min) followed by a high temperature reaction (460°C, 90 min). This two-step experiment led to a significant improvement in controlling coke formation (3.9% versus 7.4% of coke) as well as in sulfur removal. The data demonstrate that the performances of ultrafine particle catalysts are worse than those of oil-soluble compounds, although a suitable pre-treatment stage seems to be beneficial. The results obtained by characterization of

Table 4
Effect of compound type on product yield and quality[a]

Catalyst precursor	MoNaph	PMA	MoAA	SP2	RMV6	Mo_2C	Mo_2N
Feedstock conversion (wt.%)	56.9	53.8	53.7	54.0	58.1	64.1	61.9
Product distribution (wt.%)							
C1–C4	3.2	3.7	3.3	4.0	2.9	4.6	3.5
C5-200°C	11.0	11.0	8.7	9.8	11.8	15.0	17.0
200–350°C	16.1	13.0	14.5	14.4	16.5	17.9	16.7
350–500°C	25.7	24.8	25.7	24.3	25.5	25.5	23.7
>500°C	43.1	46.2	46.3	46.0	41.9	35.9	38.1
Coke	0.9	1.3	1.5	1.5	1.4	1.1	1.0
C5-Asphaltene	10.2	11.0	8.6	9.8	10.7	11.9	12.6
Product quality							
HDM (%)	82	40	80	79	63	n.a.[b]	37
S in 200–350°C (wt.%)	1.7	1.3	1.5	1.4	1.9	2.2	2.5
S in 350–500°C (wt.%)	1.8	1.5	1.6	1.4	1.9	2.4	2.5

[a] 410°C, 16 MPa H_2, 240 min, 1000 ppm of metal.
[b] n.a.: Not analyzed.

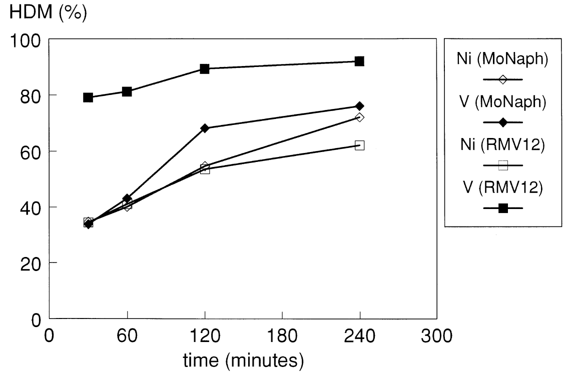

Fig. 7. Effect of phosphorus on Ni and V removal: a comparison between MoNaph and a molybdophosphonic compound (RMV12) (410°C, 16 MPa H_2 initial pressure).

the recovered catalysts are in excellent agreement with the above conclusions. In fact, XRD and TEM analyses do not evidence any significant structural and morphological difference between the MoNaph-derived molybdenite crystallites and those derived from the other oil-soluble precursors (MoAA, PMA, RMV6). On the contrary, the XRD pattern of MoS_2 obtained by the activation of Mo_2N ultrafine powder indicates a short-range order in the stacking direction also (*0 0 l*); the average number of layers stacked was estimated at five to six by profile fitting methods. The stacking of molybdenite layers, which means lower surface area and worse dispersion, may be the cause of the lower performance observed for ultrafine particle catalysts.

3.3. Bimetallic catalysts

The results reported above, in addition to the literature data published on this subject, suggested that the most promising approach for the development of new catalysts could lie in the utilization of multi-component systems.

It is well known that the addition of a second transition metal (Co, Ni etc.) to a sulfide such as MoS_2 or WS_2 can lead to a significant enhancement of hydrogenation and hydrodesulfurization activity [10,27,28]. Such promotional effect occurs in either supported or unsupported catalysts [29,30]. As concerns dispersed catalysts, most of the previous work on bimetallic systems has involved the mixture of two precursors [20,31]. However, it has been reported [14,15,32] that better results can be obtained by using two different metals bound together in a single molecule.

The objective of our work was to prepare bimetallic precursors, which could generate finely dispersed binary sulfides upon thermal decomposition.

In order to point out the effect due to the presence of the second metal, we compared two phosphonic Co–Mo and Ni–Mo precursors (respectively, RMV14 and RMV15) to the molybdophosphonic compound RMV12. These three precursors contain the same organic function. In this way, the comparison is practically free from effects due to the kinetics of decomposition of the molecules. Fig. 8 shows the sulfur content of the THF soluble fractions at four different reaction times. After 30 min of reaction, MoNaph gave the best HDS activity; this fact can be explained by the lower activation rate of these phosphonic compounds. However, at longer reaction times, the Co–Mo compound achieved a slight increase in sulfur removal, compared to Mo and Mo–Ni precursors. Nevertheless, the results obtained with bimetallic catalysts were much below expectation; this fact could again be partially explained by characterization of the catalytic residues recovered.

For both Co–Mo and Ni–Mo catalytic systems, XRD analysis indicates the presence of an MoS_2 molybdenite and an MS_x pyrrhotite-like phase (M is Co or Ni). The molybdenite phase has the same structural and morphological characteristics as observed previously in catalytic systems based on oil-soluble precursors, whereas the pyrrhotite-like phase is well

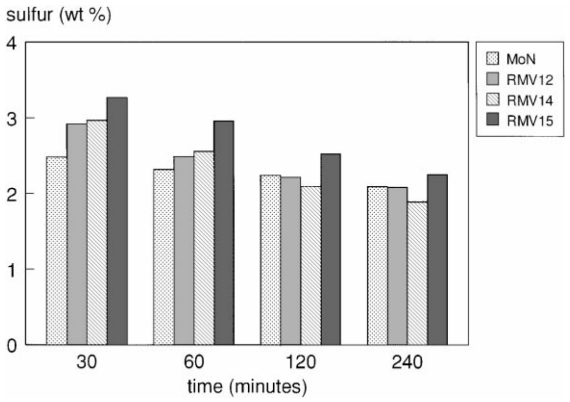

Fig. 8. HDS activity of different Mo-based precursors: effect of the second metal (410°C, 16 MPa H_2 initial pressure).

crystallized. Even though we cannot exclude that some substitution of Mo in molybdenite with Co or Ni may occur, it is difficult to hypothesize the presence of Co or Ni cations in the prismatic-trigonal coordinative sites of the molybdenitic lattice, octahedral and tetrahedral coordination being preferred by these metals. Clearly, since the molybdenite crystallites are largely more active than those of the other sulfides, the catalytic bimetallic system does not differ significantly from a monometallic Mo-based one with comparable structural peculiarities and dispersion.

4. Conclusions

The results of this work confirm the effectiveness of the slurry technology for the conversion of heavy feedstocks.

The experimental work has been performed with a large number of catalyst precursors of different natures, and a careful evaluation of catalytic performance has been made. A detailed characterization of the solids recovered at the end of the reactions has been carried out, in order to better understand the correlation between catalyst properties and its activity. Based on the results of our study, the following conclusions can be drawn:

1. The comparison of catalytic performances of the metals tested gave the following order of activity: Mo>Ni∼Ru>Co>V>Fe.
2. Mo-based oil-soluble precursors generate a microcrystalline sulfide dispersed in the feedstock as irregular clusters with a mean diameter of 0.5–2 μm; the crystallites consist of a stacking of a single layer or of a few layers, and have a crystal size of 20–40 Å.
3. The catalytic performances are nearly independent of the organic group bonded to the metal, provided that it ensures the oil-solubility as well as the thermal liability of the precursor.
4. Powdered materials gave results below expectation and inferior to oil-soluble compounds. A suitable pre-treatment step could partially improve their performance.
5. The presence of phosphorus remarkably enhances vanadium removal; this effect could be related to the formation of P–V insoluble compounds.
6. Compared to the analogous Mo-based compound, the bimetallic Co–Mo precursor seems to present a slight synergistic effect in terms of hydrodesulfurization. No evidence for the formation of bimetallic sulfide was found by using the available characterization techniques.

Based on the knowledge acquired with this study, it can be concluded that it seems hard to imagine a novel catalyst which may improve significantly the high catalytic performances of the most common Mo-based precursors (MoNaph, PMA etc.) [1,2]. Furthermore, it must be taken into account that the more exotic the preparation, the higher will be the cost, and this fact could limit the commercial use of promising materials. Thus, our object was devoted to the kinetic aspects of the reaction, in order to better investigate the effect of the operating conditions on product yields and quality [33].

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