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Abstract

Unsupported and γ-Al_2O_3-, MCM-41-supported (Ni, Mo) carbides were
prepared and modified by '*in situ*' polymer (PAN: polyacrylonitrile)
pyrolysis. The supported catalysts were impregnated with Ni and Mo metals,
i.e. 2.8 atom Mo/nm^2, whose atomic ratio was $Ni/Ni + Mo = 0.5$. X-ray
diffraction (XRD) showed single NiC, MoC phases in all cases, with relatively
low surface areas, as verified by N_2 adsorption (BET). The catalytic behaviour
of the supported (Ni, Mo)C phases for n-C_8 hydrocracking depended on
the support type. (Ni, Mo)C/MCM41-PAN-P (P = pyrolyzed) showed a
total conversion of 40% while it was only 15% on Ni, MoC/γ-Al_2O_3. The
most active catalysts were (Ni, Mo)C unsupported catalysts, i.e., 90% total
conversion. In all cases the hydrocracking selectivity favoured lighter
hydrocarbons (C_1–C_4).

1. Introduction

The need for clean fuels for improving the quality of air has motivated the development of
new catalysts, which must have higher activity and more stringent properties to withstand
severe operation conditions. In particular, a new brand of ceramic nitrides and carbide phases
could present a combination of high catalytic activity together with high thermal stability
for some reactions of interest in the fields of oil refining and petrochemicals [1, 2]. Some
challenges are raised in order to deal with heavier oil fractions containing a higher proportion
of sulfur, nitrogen and metals (Ni, V) [3]. From this viewpoint, processes like FCC and
hydrocracking are becoming more important for upgrading residual feedstock and heavy oil

fractions while minimizing the barrel bottoms [4]. In both cases, the catalyst particles must withstand mechanical attrition and severe hydrothermal conditions that tend to destroy the particle integrity, their inner pore structure and other surface properties (acidity, active sites, etc), thus provoking deactivation and operation problems [5]. For these reasons, the search for more active phases with improved stability is a major issue. Thus, Ni and Mo carbides deserve further exploration to understand their basic properties and catalytic behaviour, which might be of interest for designing new catalytic materials for hydrocracking reactions [5]. In this study a series of supported and unsupported (Ni, Mo)C ceramic phases were synthesized and tested using n-octane conversion as a test reaction. An original point introduced in this study was the use of γ-alumina and mesoporous MCM41 as carriers to disperse the (Ni, Mo)C phases, with a previous treatment consisting of the impregnation and pyrolysis of a polymer (polyacrylonitrile), before the deposition of the metal precursors, in order to modify their structural stability and surface acidity. These properties are crucial for catalysis and to improve attrition resistance with less pore fouling, while withstanding the severe hydrothermal conditions prevailing in hydrocracking ebullient bed reactors [5].

2. Experimental details

Unsupported and Al_2O_3-supported Ni, Mo carbides were synthesized using precursor salts of nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich chemical Co., 99.97% purity) and ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, (Aldrich chemical Co., 99.97% purity). The MCM41 type materials were modified by means of '*in situ*' polymer (PAN: polyacrylonitrile) pyrolysis. After impregnation of the metal precursors by incipient wetness, drying followed at 383 K, then the samples were calcined in air at 773 K. Then, the materials were treated following the guidelines reported by Volpe and Boudart [6], which consisted of reducing the metal oxides with NH_3 (Anhydrous, 99.99% purity) and a mixture of CH_4/H_2 (2:1) at 923 K. Afterwards, the materials were passivated under an O_2/Ar flow (1 vol% O_2), in order to avoid pyrophoric outbursts. The unsupported catalysts had the same relative amount of metal, i.e., $Ni/Mo = 1$, while the supported catalysts contained 2.8 atoms Mo/nm^2, with an atomic ratio $Ni/(Ni + Mo) = 0.5$. The powder x-ray diffraction (XRD) patterns were obtained using a BRUKER (Axs) diffractometer (Model D8 ADVANCE). The textural properties were determined by nitrogen adsorption (BET) using a AUTOSORB-1, Model QUANTACHROME. The catalyst's performance was determined using a Varian 3300 GC, to follow the conversion of n-octane at 673 K and $P = 1$ atm (test reaction). In all cases the metal carbides were activated at 723 K under a hydrogen stream before carrying out the reaction.

3. Results and discussion

Figure 1 shows the diffraction patterns corresponding to the (Ni, Mo) carbides, both unsupported (A) and Al_2O_3-supported phases (B). A possible segregation of Ni carbide and Mo carbide phases is verified, and there are some traces of $NiMoO_4$ (18-0879, JCPDS). The values of $2\theta = 44.5°$, $51.9°$ and $75.5°$ correspond to the NiC phase, which has a cubic symmetry, in agreement with reference data reported in the JCPDS files (14-0020). The peaks appearing within the interval $35.5 \leqslant 2\theta \leqslant 75.3$ (figure 1(B)) correspond to the MoC phase, which has a hexagonal symmetry (JCPDS 08-0384). The peaks corresponding to the alumina phase are clearly outlined in figure 1(B).

The segregation of NiC and MoC phases may arise from the differences in metal–oxygen bond strengths and formation heats for each phase; thus the carburization conditions for Ni and Mo are rather different, especially for the latter case, which has a hexagonal framework that contributes further to those differences [7].
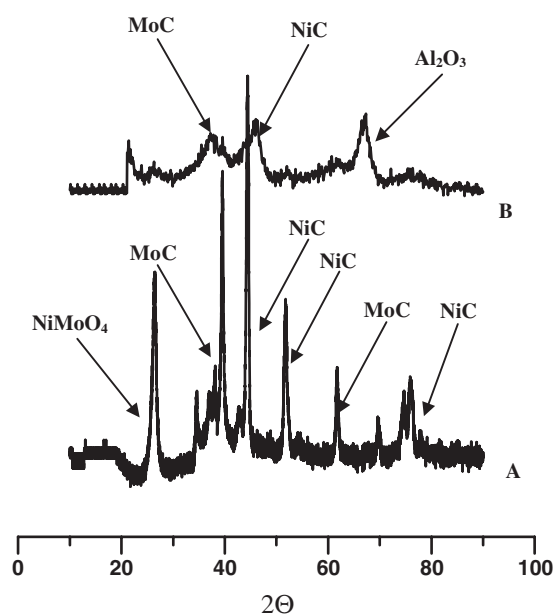
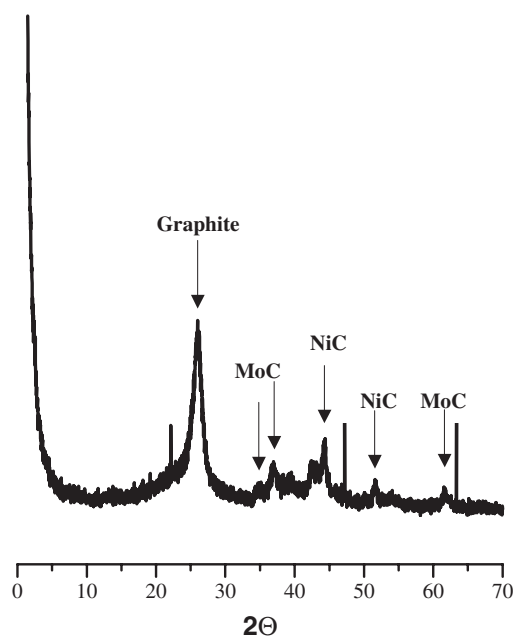**Figure 1.** Diffraction patterns of Ni, Mo carbides: unsupported (A) and Al$_2$O$_3$-supported phases (B).

Figure 2. XRD patterns of (Ni, Mo)C/MCM41-PAN-P samples.

Figure 2 shows the XRD pattern of the solids (Ni, Mo)C/MCM41-PAN-P (P = pyrolized), where the NiC and MoC phases segregate in a way similar to the Al$_2$O$_3$-supported monometallic solids. Some XRD peaks of graphite appear; these arise from hydrocarbon pyrolysis.

Table 1. Textural properties of the supports and catalysts.

Catalyst	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (Å)
MCM41	923	0.90	34
MCM41PAN-P	394	0.26	28
(γ-Al$_2$O$_3$)	259	0.73	72
NiMoC-50%[a]	51	—	—
NiMoC/(γ-Al$_2$O$_3$)	191	—	—
(NiMo)C/MCM41-PAN-P	166	0.35	84

[a] Wt% of Mo.

Similarly to Al$_2$O$_3$-supported (Ni, Mo)C phases (figure 1(B)), the XRD patterns of the (Ni, Mo)C/MCM41-PAN-P solids present peaks attributed to the single phases NiC and MoC, which are known to have cubic and hexagonal symmetries (after files JCPDS 14-0020 and JCPDS 08-0384), respectively, with peaks in the interval $44.5 \leqslant 2\theta \leqslant 75.5$ for NiC and $35.5 \leqslant 2\theta \leqslant 75.3$ for MoC.

Table 1 shows the textural properties, i.e., surface area, pore volume and mean pore diameters, of the supports and supported catalysts. In all these cases the surface area of the solids was modified drastically as a consequence of the synthesis conditions. For example, the surface area of (NiMo)C/MCM41-PAN-P is about one third of the pyrolyzed support (MCM41-PAN-P), or only 17% of the area of the initial MCM41 support (table 1). In contrast to this behaviour, the alumina-supported carbides keep about 73% of the original area, with respect to the former support (γ-Al$_2$O$_3$). Also, other textural properties, as for example the total pore volume of (NiMo)C/MCM41-PAN-P materials, show a decrease down to about one half of the initial support (MCM41), while the pore size increased up to about three times. Again, the surface area of the supported metal-loaded materials decreased in the same proportion after impregnation and carburization.

The catalytic hydrocracking reaction of n-octane was carried out over unloaded- and metal-loaded solids. Figure 3 shows a relatively high activity of the metal-loaded solids, with respect to the initial supports (figure 3). Unsupported Ni, Mo carbides were the most active and stable catalysts, i.e. almost 90% conversion was maintained for a period of 3 h. This behaviour has been observed before for ceramic Mo nitrides [1, 2, 8] used as catalysts for HDS/HDN reactions, for which the activity seems linked to the crystallite size of the ceramic phases. The present study confirms this result, because the unsupported (Ni, Mo)C phases have only a small fraction of surface sites available for the reactants (n-C$_8$, H$_2$) but n-octane conversion (figure 3) proceeds further on those crystallites. Also, the initial support materials, MCM41 and MCM41PAN-P, showed a marginal conversion of less than 10%, which is about 4–9 times lower than the activity of the metal carbide phases loaded on those supports. This results confirms that the site of the catalytic activity is the (Ni, Mo)C phase.

Figure 4 shows the selectivity pattern for (Ni, Mo)C/MCM41PAN-P catalysts, which is mostly orientated towards C$_1$–C$_4$ lighter products, without significant changes after 3 h on stream.

Similarly, figure 5 shows the selectivity pattern for the NiMoC/Al$_2$O$_3$ catalyst, which is equivalent to the previous case, except for smaller variations of the lighter products' (C$_1$–C$_4$) proportion (i.e., 8%) and the C$_5$–C$_6$ fraction (figure 5). Also, the Al$_2$O$_3$-supported (Ni, Mo)C catalyst showed a deactivation rate slightly higher than (Ni, Mo)C/MCM41PAN-P, in spite of having a similar metal content (i.e., about 18 wt%) and a similar Ni/Mo ratio (i.e., 0.5).
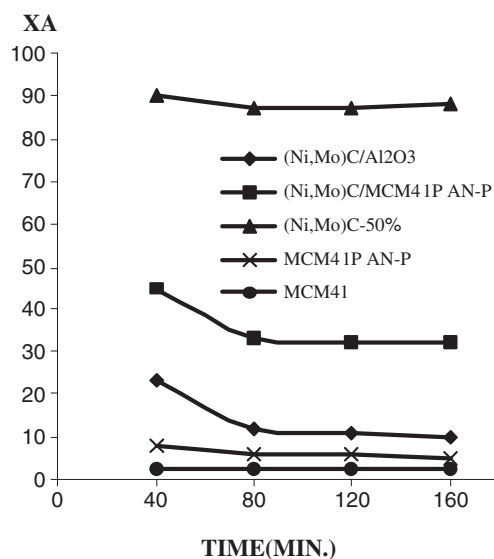
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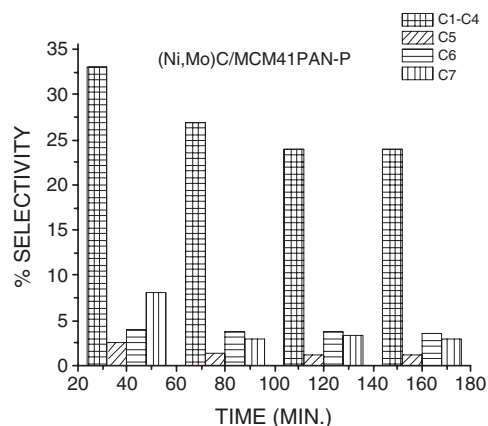**Figure 3.** The conversion of n-octane at 673 K, $P = 1$ atm.

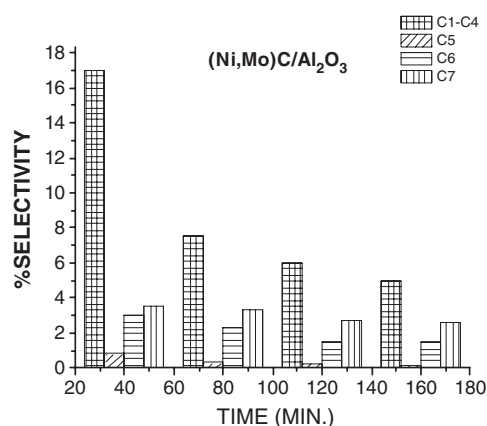**Figure 4.** The selectivity pattern of the NiMoC/MCM41PAN-P catalyst.

Figure 5. The selectivity pattern of the NiMoC/Al$_2$O$_3$ catalyst.

This indicates a significant difference of the active phase distribution or its chemical state on one support with respect to the other. Also, under the reaction conditions here described the selectivity patterns (figures 4 and 5) only reflect the consequence of sequential reactions, at least up to a secondary level. However, these conditions were adopted in this study to evaluate the relative activity of the supports.

Therefore, the most active catalysts were the unsupported (Ni, Mo)C solids, which present 100% selectivity towards the lightest fraction (C_1–C_4).

4. Main conclusions

As shown by the XRD characterization of the solids, under the conditions used in this study the formation of single bimetallic (Ni, Mo)C phases does not occur, but the formation of separated

NiC and MoC phases (figures 1 and 2) seems more favourable. This was expected from the bases of significant differences existing between the formation heats of both phases [1, 9] and also from their distinct structural symmetry and metal–oxide bond strengths. On the other hand, the surface area of the metal carbides supported on alumina diminished 27% with respect to the former support, while the solid (Ni, Mo)C/MCM41-PAN-P showed a porous structure that was drastically affected by the combination of pyrolysis at 773 K and reducing treatments at 923 K. Under these conditions, additional release of heat occurs, due to the metal–oxygen bond breaking and formation of the metal carbide phases. Thus, these conditions induce the collapse of the support porous structure, as shown by the surface area loss of about 58 and 83% with respect to the MCM-PAN-P and initial MCM41 support materials, respectively. The total conversion of n-octane over the unsupported metal carbides was higher than with their supported counterparts; however, the latter were more diluted, i.e., about 18 wt%, which leads us to conclude that in fact the activity of (Ni, Mo)C/MCM41-PAN-P, expressed as conversion by metal (Ni + Mo) atoms, was 2.2 times superior than by unsupported (Ni, Mo)C. Also, from the present results it seems that the BET surface areas are unsuitable for describing the activity of the ceramic type catalysts, as reported earlier [1, 2], but the catalytic activity of (Ni, Mo)C catalysts could be related to the crystallite size and their morphology. However the preliminary results of the present study demonstrate the inherent activity of (Ni, Mo)C/MCM41PAN-P and (Ni, Mo)C/γ-Al$_2$O$_3$ materials for hydrocracking of intermediate linear chain hydrocarbons, i.e. n-octane. Also, this study demonstrates the validity of the former hypothesis on the catalytic stability of the ceramic carbide phases, which is illustrated by a minimum variation of their catalytic activity during periods of several hours.

However, further studies under less severe reaction conditions must be performed to obtain a better evaluation of the primary selectivity, without interference of secondary reactions. In summary, this study presents original results regarding the synthesis methods for obtaining active and stable ceramic-type carbide phases for the catalytic hydrocracking of n-paraffins. Also, the original hypothesis on stability to withstand high temperature conditions under reducing atmospheres was demonstrated in this study.

Acknowledgment

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