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Addition of manganese to alumina and its influence on the formation of supported NiMo catalysts for dibenzothiophene hydrodesulfurization application

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ABSTRACT

The influence of adding manganese to NiMo/Al₂O₃ hydrodesulfurization (HDS) catalysts was studied by impregnation of manganese acetate at the surface of an Al₂O₃ support obtained by a sol-gel method. The as-obtained Mn-containing alumina supports were then impregnated with nickel nitrate, Ni(NO₃)₂·6H₂O, and ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄·4H₂O, dried at 120 °C for 12 h, and finally calcined in air at 400 °C for 4 h. The different solids were then sulfided using 10 mol.% H₂S in H₂ at 400 °C for 4 h and evaluated in the hydrodesulfurization of dibenzothiophene (DBT) at T = 300 °C and P = 30 bars H₂. Catalysts were characterized at each step of the preparation: after drying, after calcination, and finally in the sulfided state. Both the pH of the impregnation solution of Ni and Mo precursors and the Mn content (1 or 5 mol.% as MnO) strongly influence the nature of the Ni and Mo species formed. In this respect, the pH of the impregnation solution plays a critical role at low Mn content (1 mol.%). While impregnation at pH 7 results in well-dispersed molybdate species easily sulfided into a highly Ni-promoted MoS₂ phase, increasing the pH to 9 favors the formation of more polymerized Mo species and the loss of some nickel into a NiMnO spinel, leading after sulfidation to a lower promotion degree and a lower dispersion. At higher Mn content (5 mol.%), whatever the pH of impregnation, the formation of MoO₃ clusters and the loss of Ni into a NiMnO spinel phase leads to deleted HDS activity after sulfidation. Finally, our results also demonstrate a strong positive influence of manganese on the intrinsic activity of the NiMoS phase if conditions of preparation are optimized.

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1. Introduction

Fuel production with low emission of pollutants is one of the highest priorities for the oil industry to comply with environmental legislation. Hydrodesulfurization (HDS) has been and will remain the most effective technology for the production of ultralow-sulfur diesel (<10 ppm) [1]. Refineries can satisfy these very demanding specifications, but only through the use of new generations of more efficient HDS catalysts able to remove refractory molecules such as dibenzothiophene and alkyldibenzothiophenes [2].

Catalysts commonly used in hydrodesulfurization consist of MoS_2 or WS_2 clusters promoted by Co or Ni and supported on γ -Al₂O₃. Topsøe et al. [3] explained that the activity of Mo sulfide catalysts promoted by Ni or Co depends on the formation of the

* Corresponding author. Fax: +52 77 17 17 20 00x6501. *E-mail address:* guevaraa@uaeh.edu.mx (A. Guevara-Lara). so-called "CoMoS" or "NiMoS" active phases. In the CoMoS or NiMoS phases, the promoter Ni or Co atoms are located at the edge planes of MoS_2 layers [4,5]. However, only some Co or Ni atoms are involved in the Co(Ni)MoS phase. In fact, nickel or cobalt can also form additional inactive phases such as nickel (cobalt) sulfide or nickel (cobalt) aluminate, NiAl₂O₄ [6,7]. In addition, stable Ni and Mo oxide clusters may be formed and are difficult to transform into an active phase through sulfidation. These nonactive structures can be formed at each stage of the catalyst preparation: inside the impregnation by itself, or during the subsequent drying, calcination, and sulfidation steps [8,9]. The formation of active or nonactive species also depends on the nature of the salts, additives, or chelating agents used during the preparation of the impregnation solutions [10–13].

On the other hand, interactions with the support after drying and calcination steps can also influence activity. Main options to improve the activity of hydrodesulfurization catalysts consist of





JOURNAL OF CATALYSIS (1) the use of new active phases based on transition metals (for example, Ru, Fe, Rh, Pt) [14], carbides [15], or the quite active phosphides [16–23], (2) the use of new methods for preparing supported MoS₂ and WS₂ catalysts promoted by Ni or Co [1,24], (3) the use of new supports to replace the traditional γ -Al₂O₃ support such as SiO₂, Zr-TiO₂, C, MCM-41, or SBA-16, or (4) the modification of the γ -Al₂O₃ support by additives or other oxides (e.g.,TiO₂-Al₂O₃, SiO₂-Al₂O₃, P₂O₅-Al₂O₃, F-Al₂O₃, Ga-Al₂O₃, B-Al₂O₃) [25–31].

The ability to form the NiMoS phase also depends on the type of supported NiMo polyoxometalate [32]. Depending on the polyoxometalate and its interaction with the support, different NiMoS active species can be formed. Also, nonactive species can be obtained, such as Ni or Mo oxisulfides or nonpromoted Ni or Mo sulfides.

The objective of the present study is to evaluate the influence of adding manganese to Al₂O₃ on dibenzothiophene hydrodesulfurization activity of NiMo catalysts. Manganese oxide is used as a catalyst for industrial oxidation processes such as oxidation of CO [33], methanol [34], ethylene [35], or nitric oxide [36] and for combustion reactions [37]. This is due to the ability of Mn to present various oxidation states (II, III, IV, and VII) [38]. Particularly, manganese oxides are used to control the environmental pollution caused by volatile organic compounds (VOCs) [39]. In a study of postmetallocene catalysts, Fujisawa et al. [40] mentioned the importance of the oxidation state of transition metals in the catalytic activity. Catalysts based on Mn (II) present higher catalytic activity than catalysts based on Mn (III) and Mn (IV). On the other hand, Ban et al. [41] showed that complexes based on Mn (II) as [Mn^{II}(Cp)₂] can catalyze ethylene polymerization. Therefore, the oxidation state of manganese undoubtedly plays a major role in explaining catalytic behavior in many applications [42].

Manganese oxide is known to be unstable. However, manganese can be stabilized in NiMnMo clusters [43], or when supported on Al_2O_3 , ZrO_2 , TiO_2 , or SiO_2 . MnO_x/Al_2O_3 catalysts are used, for example, in ozone decomposition [44], for the reduction of benzaldehyde to ethanol [45], for the selective reduction of NO_x [46], and for the catalytic oxidation of toluene [38]. Nevertheless, manganese oxide catalysts supported on Al_2O_3 or ZrO_2 generally have low surface areas and can form spinels, as suggested by Polato et al. [47].

Pecoraro et al. [48] and more recently Chianelli et al. [49] reported the dibenzothiophene hydrodesulfurization activity of a series of transition metal sulfide catalysts according to their positions in the periodic table. Manganese sulfide catalysts have the lowest activity of the first series of transition metal sulfides. In another study, Villaroel et al. [50] showed for different series of promoters of MoS_2/γ -Al₂O₃ that manganese is the element that promotes the least molybdenum sulfide in dibenzothiophene (DBT) HDS. They concluded that manganese is not a good promoter. However, recently, Ho [43] reported that supported NiMnMo catalysts show high activity in hydrodesulfurization of sulfur compounds such as alkyldibenzothiophenes. This suggests that Mn is poorly active as the MnS phase and does not act as a promoter atom of MoS₂ for hydrodesulfurization. However, manganese seems able to increase the activity of already Ni-promoted MoS₂/Al₂O₃ catalysts.

Manganese has not yet been studied as a support in the hydrodesulfurization of dibenzothiophene. However, different oxidation states of manganese make it possible to obtain a reducing or oxidizing support that would influence the deposition of Ni and Mo species. In order to study the role of manganese, we synthesized two different Al₂O₃ supports covered with 1 and 5 mol.% of MnO, respectively. Supports have been impregnated with Ni/Mo precursor solutions at pH 7 or 9. The NiMo polyoxometalates were then

characterized at different steps of the preparation: after impregnation and drying, after calcination, and finally, in their sulfide state. The resulting NiMo catalysts were then evaluated in hydrodesulfurization, using dibenzothiophene as a representative sulfurcontaining screening molecule.

2. Experimental

2.1. Synthesis of the Al_2O_3 support covered with manganese

The reactants used for the catalyst synthesis were as follows: aluminum isopropoxide Al(OC₃H₇)₃ (Sigma–Aldrich, 98+%), 1propanol (Sigma Aldrich >99.8%), manganese(II) acetate tetrahydrate Mn(CH₃COO)₂·4H₂O (Sigma Aldrich, 99+%), nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O (J.T. Baker, ACS Reagent), ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O (Fluka, >99%), ammonium hydroxide NH₄OH (J.T. Baker, ACS reagent), and deionized water (18.2 M Ω cm).

The Al₂O₃ solid was prepared by the sol-gel method [8]. For this purpose, 40.85 g of aluminum isopropoxide was dissolved in 380 mL of 1-propanol. The gel was then obtained by hydrolysis with dropwise addition of deionized water (40 mL). The gel was dried at 100 °C for 12 h and calcined at 600 °C (5 °C/min) for 4 h.

Addition of manganese on the alumina surface was performed using the incipient wetness impregnation method. Al_2O_3 with 1 mol.% Mn as MnO was prepared by impregnating 1.0 g Al_2O_3 with a solution of 0.0243 g of manganese acetate dissolved in 1.8 mL of 1-propanol. The solid was then dried at 120 °C for 12 h and calcined at 550 °C (5 °C/min) for 4 h. This support is named RMn1. In the case of 5 mol.% of Mn as MnO, 1.0 g of Al_2O_3 was impregnated with a solution of 0.1215 g of manganese acetate dissolved in 2.5 mL of 1-propanol. The solid was then dried and calcined using conditions similar to those described before for RMn1. This support is called RMn5.

2.2. Synthesis of the NiMo/RMn1 and NiMo/RMn5 catalysts

NiMo/RMn1 and NiMo/RMn5 catalysts were prepared by coimpregnation of nickel nitrate and ammonium heptamolybdate on the RMn1 and RMn5 supports using the incipient wetness method. Final loadings of 14 wt.% of MoO₃ and 3.1 wt.% of NiO were obtained, corresponding to a Ni/(Ni + Mo) molar ratio of 0.3.

Two different pHs (7 or 9) were used during the impregnation of the Ni and Mo precursor solutions. For the impregnation solution at pH 7, nickel nitrate hexahydrate (0.1412 g) and ammonium heptamolybdate tetrahydrate (0.1997 g) were dissolved in deionized water (1.5 mL) before impregnation onto 1.0 g of support. The same conditions were used for the impregnation at pH 9, except that the pH was adjusted with NH₄OH solution (0.5 M). Similar protocols using the same amounts of Ni or Mo precursors were used for preparing Ni-only or Mo-only catalysts supported on RMn1 or RMn5. After the impregnation step, catalysts were first dried at 120 °C for 12 h before being calcined at 400 °C (5 °C/min) for 4 h. Calcined catalysts were then ground and the 80–125 μm particle size range was selected. NiMo catalysts were called NiMo/RMn1 pH 7, NiMo/RMn1 pH 9, NiMo/RMn5 pH 7, and NiMo/RMn5 pH 9, respectively, and suffixes -D and -C were used to indicate dried and calcined samples, respectively.

The reference catalyst for activity measurements was a Ni–Mo/ γ -Al₂O₃ catalyst containing 3 wt.% NiO and 14 wt.% MoO₃. The solid presents a BET surface area of 250 m² g⁻¹ and a pore volume of 0.48 cm³ g⁻¹.

2.3. Catalyst characterization

RMn1 and RMn5 supports were characterized by zeta-potential measurements and N₂ physisorption. N₂ physisorption was carried out on an ASAP 2020 Micromeritics apparatus. Prior to measurements, the samples were treated at 300 °C for 4 h under vacuum at $P = 3.0 \times 10^{-5}$ mmHg. Specific surface area was obtained using the Brunauer–Emmet–Teller (BET) equation. Zeta-potential measurements were performed using a Malvern ZetaSizer Nano ZS90 apparatus. A quantity of 0.02 g of each support was dispersed in 200 mL of a 0.01 M NaNO₃ electrolytic solution at 25 °C. pH was adjusted with 0.01 M NH₄OH and 0.1 M HNO₃ aqueous solutions, respectively.

Catalysts in the oxide state were characterized by UV–vis diffuse reflectance (UV–vis DRS) and Raman spectroscopy. Raman spectra were recorded on two apparatus. The first spectrometer was a Perkin–Elmer GX Raman FT-IR apparatus equipped with a Nd:YAG laser (1064 nm) and an InGaAs detector. For each spectrum, an average of 10–60 scans was obtained with a laser power of 10–300 mW in the range 1500–100 cm⁻¹ with a 2 cm⁻¹ resolution. The second spectrometer was a BWTEK i-Raman Plus apparatus equipped with a microscope (100, 50, and $20 \times$), a 532 nm laser excitation, and an HQE-CCD detector. For each spectrum, an average of 10–50 scans was obtained with a laser power of 0–50 mW in the range 1500–100 cm⁻¹ and with 3 cm⁻¹ resolution. Attention was paid to avoiding any structural modifications induced by the Raman analysis.

UV–vis DRS spectra were obtained on a Perkin–Elmer Lambda 35 spectrometer equipped with an integration sphere. Spectralon SRS-99-010 (99% reflectance) tablets were used as UV–vis DRS reference. Data are shown using the Kubelka–Munk ($F(R_{\infty})$) function,

$$F(R_{\infty})=\frac{\left(1-R_{\infty}\right)^{2}}{2R_{\infty}},$$

in which R_{∞} is the reflectance at infinite depth. UV–vis DRS spectra were obtained at wavelengths between 200 and 1100 nm with a 1 nm resolution.

Catalysts in the sulfided state were characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), total combustion analysis, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission microscopy (HRTM).

ICP-OES analysis was performed to determine the Ni, Mo, and Mn amounts using a Horiba Jobin Yvon Activa spectrometer. Before analysis, samples were submitted to acid attack using a mixture of H_2SO_4 , HNO_3 , and HF (1:1:0.5, v/v/v ratio) followed by maximum evaporation. Sulfur amount analysis was performed through total combustion of samples using a Thermo Scientific Flash 2000 apparatus.

X-ray photoelectron spectroscopy (XPS) studies were performed on an Axis Ultra DLD (Kratos Analytical) spectrometer equipped with a dual Al/Mg anode. The spectra were excited using Al K α radiation (1486.6 eV). Peak shifts due to charging of samples were corrected, using as reference the Al2*p* line of Al₂O₃ at 74 eV. The sulfur samples were manipulated under inert atmosphere without contact with air. The samples were pressed on indium foil attached to the sample holder and placed in the XPS instrument. Binding energies were referenced to the C1*s* level of contaminating carbon at 284.6 eV.

Decomposition of the Mo3*d* and Ni2*p* XPS spectra was performed by curve fitting mixed Gaussian and Lorentzian lineshapes after the treatment of background by a Shirley-type baseline using CasaXPS software, version 2.0.71 [51,52]. The atomic percentage [*i*] of atoms was obtained from the measurement of the corresponding total peak area A_i and the use of appropriate sensitivity factors S_i :

$$[\mathbf{i}] = \frac{\frac{A_i}{S_i}}{\sum_{i=1}^n \left(\frac{A_i}{S_i}\right)}$$

Mo3*d* and Ni2*p* core level spectra can then be decomposed into three different contributions corresponding respectively to MoS₂, Mo_xOS_y, and MoO₃ species and to NiS_x, NiMoS, and NiO_x species [53–55]. The rules applied during the decomposition for the Mo3*d* spectra were the following: binding energy between the doublets as ΔE ($3d_{3/2}$ – $3d_{5/2}$) \approx 3.2 eV; ratio of the full width at half maximum FWHM $3d_{3/2}$ /FWHM $3d_{5/2}$ = 1.2, and relative area of doublet as $A(3d_{5/2})/A(3d_{3/2})$ = 1.5. Table S1 (Supplementary information) shows that the binding energies of Ni2*p*, O1*s*, C1*s*, and Al2*p* (reference) are similar on NiMo/Al₂O₃, NiMo/RMn1, and NiMo/RMn5 catalysts. This suggests that electronic effects from the support could be neglected.

The relative amount of the NiMoS phase is then given by

$$\% \text{NiMoS} = \frac{A_{\text{NiMoS}}}{A_{\text{NiMoS}} + A_{\text{NiO}_x} + A_{\text{NiS}_x}} \times 100,$$

with A_{NiMoS} , A_{NiO_x} , and A_{NiS_x} the experimental XPS areas of respectively NiMoS, NiO_x, and NiS_x species.

HRTEM results were obtained with a JEOL 2010 (200 kV) microscope. Freshly sulfided catalyst samples were ultrasonically dispersed in ethanol. The suspension was then collected on a carbon-coated copper grid. The NiMoS catalysts exhibit MoS₂ slabs, presenting a layered structure. Statistical analyses were performed on 15 different micrographs (2356 nm² for each one) taken from different regions of each studied sample, representing 600–800 counted particles. The average stacking number of layers per slab and the average slab length were obtained, using the equations [56]

$$\overline{N} = \frac{\sum_{i=1}^{n} n_i N_i}{\sum_{i=1}^{n} n_i},\tag{3}$$

$$\overline{L} = \frac{\sum_{i=1}^{n} n_i l_i}{\sum_{i=1}^{n} n_i},\tag{4}$$

with N_i and l_i representing respectively the stacking number and the length of a MoS_2 slab as determined directly on pictures. n is the number of particles measured in a size range or stacking number of index i.

2.4. Catalytic evaluation tests

Calcined catalysts were activated by sulfidation with a 4 L/h flow of 10 mol.% H_2S/H_2 gas mixture at 400 °C (5 °C/min) for 4 h. Catalysts were called NiMo/RMn1-S pH 7, NiMo/RMn1-S pH 9, NiMo/RMn5-S pH 7, NiMo/RMn5-S pH 9, respectively, where –S indicates sulfided samples.

Catalysts were tested in the hydrodesulfurization of a gasoline model (500 ppm S corresponding to a mixture of 0.37 M dibenzothiophene/n-heptane). Hydrodesulfurization tests were performed in a fixed-bed continuous microreactor with 0.01 g of catalyst at 30 bars. The reactor was fed with 0.3 cm³/min (STP) of liquid and 35 cm³/min (STP) of H₂. Heptane was selected as solvent because under these reaction conditions (P = 30 bars, T = 300 °C), all reactants are in the gaseous phase [57].

The reaction protocol is as follows: The stable activity of a freshly sulfided catalyst was obtained after 12 h of reaction at T = 280 °C with 0.12 cm³/min liquid flow. Immediately after the stabilization was achieved, the liquid feed was increased to 0.3 cm³/min for 2 h. The reactor temperature was then increased to 300, 320, and 340 °C every 2 h. Dodecane was added to the liquid feed in the same molar amount as DBT to serve as an internal standard. Liquid samples were analyzed by gas chromatography on

a Perkin–Elmer AutoSystem instrument equipped with a flame ionization (FID) detector and an HP Ultra 2 (30 m \times 0.32 mm i.d.) column.

Main reaction products were biphenyl (BP) and cyclohexylbenzene (CHB).

Conversion was calculated as

$$x_{\text{DBT}} = \frac{C_{\text{DBT}_0} - C_{\text{DBT}}}{C_{\text{DBT}_0}} = \frac{\sum A_i}{\sum A_i + A_{\text{DBT}}}$$

where C_{DBT_0} and C_{DBT} are the DBT molar concentration (mol L⁻¹) in the feed and at the outlet of the reactor, respectively. A_i = chromatographic areas of BP or CHB products.

Reaction rates were calculated assuming first-order kinetics and a differential reactor as follows:

$$r_{\text{DBT}} = kC_{\text{DBT}}$$
 and $C_{\text{DBT}} = C_{\text{DBTO}}(1 - x_{\text{DBT}})$.

The pseudo-first-order constant was then obtained as follows:

$$k = -\frac{F_{\text{DBT}_0}}{m_c C_{\text{DBT}_0}} \ln(1 - x_{\text{DBT}})$$

The pseudo-first-order reaction is

$$r_{\text{DBT}_0} = -\frac{F_{\text{DBT}_0}}{m_{\text{C}}}\ln(1-x_{\text{DBT}}),$$

where r_{DBT_0} is the reaction rate (mol s⁻¹ g⁻¹), *k* the rate constant (s⁻¹), *t* the time, F_{DBT_0} the molar flow of the DBT feed (mol s⁻¹), C_{DBT_0} the molar concentration of the DBT feed (mol s⁻¹), m_C the catalyst weight (g), and x_{DBT} the DBT conversion. Activation energies (E_a) were calculated assuming a first-order reaction, as

$$\operatorname{Ln} k = -\frac{E_{\mathrm{a}}}{R}\frac{1}{T} + \operatorname{Ln} A,$$

where *A* is the preexponential factor and *R* the universal gas constant (1.98717 cal mol⁻¹ K⁻¹).

Calculations of Thiele modulus ϕ and effectiveness factor η (0.99) show that intraparticle diffusion does not occur under our experimental conditions.

3. Results

3.1. Characterization of the RMn1 and RMn5 supports

3.1.1. N₂ physisorption

Fig. S1 in the Supplementary Information shows the N₂ adsorption-desorption isotherms of the alumina obtained by a sol-gel process and of the RMn1 and RMn5 supports. The isotherms of alumina, RMn1, and RMn5 present similar type IV profiles, associated with the presence of a mesoporous distribution. Moreover, H1 hysteresis loops are found in all cases, suggesting the presence of solids consisting of particles crossed by nearly cylindrical channels or made of aggregates or agglomerates of spheroidal particles [58]. In addition, a decrease in the N₂ amount adsorbed in the saturation region can be observed following the addition of manganese.

Table 1 shows the textural properties of the RMn1 and RMn5 supports and of the alumina used for the synthesis. BET measurement for the alumina indicates a specific surface area of 366 m²/g.

Table 1							
Textural	properties	of alun	nina, RMn	1, and	RMn5	supports.	

Support	Specific surface area (m²/g)	Porous volume (cm ³ /g)	Average pore size (nm)
Al_2O_3	366	1.7	18.4
RMn1-C	274	1.6	17.1
RMn5-C	217	1.2	30.4

After addition of manganese, the specific surface areas decrease. For the RMn1 support, the surface area decreases by 25% to $274 \text{ m}^2/\text{g}$, while the porous volume or the average pore size does not change, suggesting that addition of 1% Mn as MnO on the alumna surface results only in limited partial blocking of the alumina porosity. The situation is different for the RMn5 support. In this case, the surface area continues decreasing to $217 \text{ m}^2/\text{g}$ while the pore volume falls to $1.2 \text{ cm}^3/\text{g}$. This is accompanied by a clear increase of the average pore size to 30.4 nm. These results are characteristic of significant blocking of the smallest pores of the alumina support when 5% Mn is added as MnO.

3.1.2. Zeta-potential measurements

Fig. S2 in the Supplementary Information shows zeta-potential curves of the different supports. In the pH 1-7 range, the zeta potential tends to decrease with Mn addition, but slightly more rapidly for RMn1 than for RMn5. These curve evolutions suggest that the different supports remain structurally stable in this pH range. In the pH 9–12 range, the zeta potentials become negative and relatively similar for the three supports. Point-of-zero-charge values, obtained from the intersection of the zeta-potential curve with the pH axis, can be associated with the net surface pH of the oxide [59]. RMn1 and RMn5 supports have net surface pH values respectively of 8.4 and 8.3, slightly lower than for Al_2O_3 (8.6). This last value is similar to the one reported by Kosmulski et al. [60]. These results suggest only a slight modification of the surface charge of the alumina due to the presence of Mn shifting the PZC to lower values, as expected when an acid component such as MnO is added [45]. This effect remains weak, however.

3.1.3. UV-vis diffuse reflectance spectroscopy of the RMn1 and RMn5 supports

Manganese oxide can present different oxidation states such as Mn^{2+} , Mn^{3+} , Mn^{4+} , and even Mn^{7+} , making its characterization complicated [42]. In some cases, spin resonance spectroscopy and UV–vis reflectance spectroscopy make it possible to distinguish the oxidation states of Mn. Velú et al. [38] reported diffuse reflectance UV–vis spectra of Mn references with different oxidation states. Bands of manganese species reported in UV–vis reflectance spectroscopy studies are summarized in Table 2.

To study the influence of the Mn content during its impregnation on alumina, the supports were studied after impregnation and drying step at 120 °C (RMn1-D and RMn5-D), Fig. 1, and after the calcination step at 400 °C (RMn1-C and RMn5-C), Fig. 2. First of all, one should notice that bands corresponding to Mo charge transfer (255–320 nm) cannot be discerned because they overlap with stronger intense bands of the support.

Both RMn1-D and RMn5-D supports show a band at 255 nm associated with an $O^{2-} \rightarrow Mn^{2+}$ charge transfer and a shoulder at 320 nm associated with the $O^{2-} \rightarrow Mn^{3+}$ process. Moreover,

Table 2

Compound	Mn ⁿ⁺	λ (nm)	Assignment
MnO	Mn ²⁺	420	${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}$
		500	${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$
		610	$^6A_{1g} \rightarrow {}^4T_{2g}$
Mn ₃ O ₄	Mn ²⁺	255	$0^{2-} \rightarrow Mn^{2-}$
5.	Mn ³⁺	320	$0^{2-} \rightarrow Mn^{3-}$
Mn_2O_3	Mn ³⁺	370	${}^{5}B_{1\sigma} \rightarrow {}^{5}B_{2\sigma}$
2 3		485	${}^{5}B_{1\sigma} \rightarrow {}^{5}E_{\sigma}$
		755	${}^{5}B_{1g} \rightarrow {}^{5}A_{1g}$
Mn-Al ₂ O ₃	Mn ²⁺	422	${}^{6}A_{1\sigma} \rightarrow {}^{4}A_{1\sigma}$
	Mn ³⁺	485	${}^{5}E_{\sigma} \rightarrow {}^{5}T_{2\sigma}$
	Mn ⁴⁺	470	${}^{4}A_{2\sigma} \rightarrow {}^{4}T_{2\sigma}$



Fig. 1. UV-vis diffuse reflectance spectra of RMn1 and RMn5 supports after the drying step.



Fig. 2. UV-vis diffuse reflectance spectra of RMn1 and RMn5 supports calcined at 550 °C.

RMn1-D also presents a band at 485 nm due to Mn^{3+} in interaction with Al₂O₃ (Table 2). This band shifts to 500 nm and shows an increased intensity when the Mn content is increased, as in RMn5-D, showing in this latter case the presence of Mn^{2+} species as MnO. Since Mn^{2+} was present in the impregnation solution, the fact that both Mn^{2+} and Mn^{3+} species are detected indicates that the Al₂O₃ support influences the degree of oxidation for dried samples. Indeed, for RMn1-D, a stronger direct interaction of Mn with Al₂O₃ than for RMn5-D is found, leading to a higher proportion of Mn^{3+} . Increasing the Mn amount leads to a lower direct interaction between the covering Mn and the Al₂O₃ substrate, favoring the reappearance of the Mn^{2+} oxidation state.

Fig. 2 shows that the bands assigned to Mn^{2+} and Mn^{3+} for the dried RMn1-D support are preserved after the calcination step. The higher relative intensity of the band at 320 nm compared with the one at 255 nm in the RMn5-C support evidences a higher concentration of Mn^{3+} than in RMn5-D, suggesting that part of Mn^{2+}

was oxidized to Mn³⁺ during calcination. This result can be related to the study of Kijlstra et al. [42], who showed that only a small amount of Mn²⁺, with distorted octahedral symmetry, can be stabilized on the alumina surface. Therefore, the additional manganese present in a larger quantity on RMn5 remains free to be oxidized to Mn³⁺. This change is possible due to redox potential processes since oxidation reactions can be highly favored in basic medium [38], as expected here for alumina with a net surface pH of 8.6.

3.2. Characterization of the NiMo/RMnX (X = 1 or 5) catalysts after drying and calcination steps

3.2.1. Considerations about the species present in impregnation solutions

Ni and Mo species were analyzed after impregnation and calcination steps by Raman and UV-vis reflectance spectroscopies. Molybdenum and nickel species present in an impregnation solution can be predicted from predominance zone diagrams. These diagrams represent aqueous Ni²⁺ or Mo⁶⁺ oxo-species concentration as a function of solution pH [61]. In this respect, the Mo⁶⁺ diagram shows that a solution at pH 7 contains Mo70⁶⁺₍₂₄₁₎ ions whereas a solution at pH 9 contains mainly Mo0²⁺_(4a1) ions. Moreover, the Ni²⁺ diagram [62–65] shows that a solution at pH 7 contains Ni²⁺_(aq) ions, while a solution at pH 9 would lead to Ni(OH)₂ precipitation. These diagrams suggest that dissolutions at pH 7 or 9 would lead to impregnation solutions containing Ni²⁺_(aq)/Mo₇0⁶⁻_{24(aq)} or Ni (OH)₂/Mo0²⁺_(aq) combinations, respectively. However, these predominance zones diagrams are generally obtained using electrolytic solutions, i.e., NaCl, K₂SO₄, NaNO₃, as supporting electrolytes. The dissolution of ammonium molybdate and nickel nitrate salts in deionized water without a supporting electrolyte should favor the Ni²⁺/Mo⁶⁺ interaction:

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O_{(s)} + H_2O \rightarrow Mo_7O_{24(aq)}^{6-} + 6NH_{4(aq)}^+,$$

$$Ni(NO_3)_2 \cdot 6H_2O_{(s)} + H_2O \rightarrow Ni^{2+}_{(aq)} + 2NO^{-}_{3(aq)}$$

$$(NH_4)_6Mo_7O_{26} \cdot 4H_2O_{(s)} + Ni(NO_3)_2 \cdot 6H_2O_{(s)} + H_2O$$

 $\rightarrow MoO_{24(aq)}^{6-}/Ni_{(aq)}^{2+} + 6NH_{4(aq)}^{+} + 2NO_{3(aq)}^{-}.$

In addition, at pH 7, Ni can present both tetrahedral $[Ni^{2+}4O^{2-}]$ and octahedral $[Ni^{2+}6O^{2-}]$ local symmetries, while at pH 9, the Ni local symmetry is mainly tetrahedral [32].

Therefore, the impregnation solution at pH 7 could contain a combination of $[Ni^{2+}4O^{2-}]/[Ni^{2+}6O^{2-}]/Mo_7O_{24}^{6-}$ species. Increasing the pH solution to 9 with 0.1 M NH₄OH leads to the following reactions:

$$Mo_7O^{6-}_{24(aq)} + 4H_2O \rightarrow 7MoO^{2-}_{4(aq)} + 8H^+,$$

$$[Ni^{2+}40^{2-}] + [Ni^{2+}60^{2-}] + 4H^+ \rightarrow 2[Ni^{2+}40^{2-}] + 2H_20$$

Consequently, the solution at pH 9 could contain a combination of $[Ni^{2+}4O^{2-}]/MoO_4^{2-}$ species. The absence of precipitate suggests that $Ni(OH)_2$ is not formed.

3.2.2. UV-vis diffuse reflectance spectra of reference catalysts: Ni/ RMn1 and Ni/RMn5

During the preparation of the NiMo/RMn-X catalysts, it is essential to differentiate Ni-Mo interactions from Ni only-support interactions. For this purpose, Ni supported on RMn1 and RMn5 was prepared using impregnation solutions at pH 7 or 9. Fig. 3 shows the UV-vis reflectance spectra of the Ni/RMn1 catalysts impregnated at the two different pHs and calcined at the same temperature (400 °C). Both solids show bands at 255, 320, and 485 nm, which are characteristic of Mn²⁺ (255 nm) and Mn³⁺ (320 and 485 nm). Additionally, Fig. 3 shows a band at 380 nm that is related to the formation of the NiMnO spinel. In this spinel compound, Ni²⁺ strongly interacts with Mn³⁺ species from the support. Fig. 3 shows that the solid Ni/RMn1-C pH 9 presents more intense bands than the solid prepared at pH 7 at 320 nm and also at 380 nm. The impregnation at pH 9 therefore favors oxidation of Mn^{2+} into Mn³⁺ but also the formation of the NiMnO spinel in a higher proportion.

In the case of the Ni/RMn5 catalysts, Fig. S3 in the Supplementary Information shows that the UV profile of the RMn5 support is preserved after impregnation with Ni. The band at 380 nm associated with the formation of the NiMnO spinel is, however, more difficult to observe. This is due to the high intensity and width of the band at 500 nm, which does not allow the spinel band at 380 nm to be distinguished easily. A weak peak around 350–360 nm can also be observed, corresponding to a Mn^{3+} contribution due to the ${}^5B_{1g} \rightarrow {}^5B_{2g}$ transition. Both Ni/RMn1 and Ni/RMn5 also present a weak shoulder at 710 nm associated with Ni ${}^{2+}_{Oh}$. In contrast to Ni/RMn1 solids, no noticeable differences can be observed when the pH is increased from 7 to 9. Finally, comparison with the UV-vis profile of the RMn5 support (Fig. 2) also shows that the oxidation state of Mn is not modified after addition of Ni.

3.2.3. Characterization of Mo and NiMo catalysts supported on RMn1 impregnated at pH 7 or 9

3.2.3.1. UV-vis diffuse reflectance spectroscopy analysis. Figs. 4 and 5 show the UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn1, impregnated at pH 9 or 7, respectively. Fig. 4a shows UV-vis DR spectra of catalysts supported on RMn1 after impregnation at pH 9 and after the drying step. Results show



Fig. 3. UV-vis diffuse reflectance spectra of Ni/RMn1 catalysts, impregnated at pH 7 or 9, and calcined at 400 °C.



Fig. 4. UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn1, impregnated at pH 9, (a) dried at 120 °C and (b) calcined at 400 °C.

that the deposition of Mo species onto the RMn1 support followed by a drying step does not generally modify the UV-vis DR profile significantly, with bands at 255, 320, and 485 nm still corresponding to Mn²⁺ or Mn³⁺ species. However, the addition of Mo also leads to a higher relative contribution of the 320 nm charge transfer band attributed to Mn^{3+} and to the appearance of the small Mn^{3+} contribution due to the ${}^5B_{1g} \rightarrow {}^5B_{2g}$ transition, but shifting slightly around 370 nm. Therefore, the impregnation of Mo species (probably as MoO_4^{2-} , since the pH is equal to 9) influences the degree of oxidation of manganese. This result suggests a direct interaction between deposited Mo oxide species and the manganese recovering Al₂O₃. In the case of the NiMo/RMn1-D pH 9 solid, a slight decrease of the 485 nm band can be noticed, while the small contribution at 370 nm cannot be detected any more. This suggests a weaker interaction of manganese with the Al₂O₃ support, showing indirectly once again some kind of interaction of Ni with manganese.

The effect of the calcination step was also studied (Fig. 4b). Compared with the UV–vis DR profile of RMn1-C showing a strong contribution at 485 nm due to Mn³⁺ in interaction with Al₂O₃, the deposition of Mo for Mo/RMn1-C pH 9 leads both to a decrease of the intensity of this band and also to a shift to 470 nm, showing a further oxidation to Mn⁴⁺. Comparison with its dried analogue also confirms that the calcination of the Mo/RMn1 solid (Mo/RMn1-C pH 9) leads both to a weaker interaction of Mn with the Al₂O₃ support and to a further oxidation of some Mn³⁺ to Mn⁴⁺.

For NiMo/RMn1 solids prepared by impregnation at pH 9, comparison between the dried (NiMo/RMn1-D pH 9) (Fig. 4a) and the calcined sample (NiMo/RMn1-C pH 9) (Fig. 4b) shows a slightly higher intensity of the band at 320 nm due to Mn^{3+} after calcination. The shift to 470 nm of the band corresponding to Mn in interaction with Al_2O_3 is also confirmed, showing the appearance of the +IV oxidation state in this case. Moreover, the band at 380 nm due to the NiMnO spinel reappears. Comparison between NiMo/RMn1-C pH 9 and Ni/RMn1-C pH 9 (Fig. 3) also allows to evaluate the influence of Mo in NiMo precursors. NiMo/RMn1-C pH 9 presents lower intensity than Ni/RMn1-C pH 9 for the 320 and 380 nm bands due respectively to Mn^{3+} and NiMnO spinel, while the band at 485 nm shifts to 470 nm. This shows that molybdenum is responsible for the further oxidation of Mn^{3+} to Mn^{4+} , while the formation of the NiMnO spinel is still detected, but in a lower proportion.

Fig. 5a shows the UV–vis DR spectra of the solids impregnated at pH 7 after drying. When compared with their homologues impregnated at pH 9, there are no noticeable changes for the Mo/ RMn1-D and NiMo/RMn1-D samples impregnated at pH 7. After calcination, one can note, for NiMo/RMn1-C pH 7, a slightly lower intensity of the 320 nm band due to Mn³⁺ compared with NiMo/ RMn1-C pH 9, while the NiMnO spinel band at 380 nm is now hardly discernible. Therefore, changing the pH of impregnation from 9 to 7 leads to the almost complete disappearance of the signal due to the NiMnO spinel.

3.2.3.2. Raman spectroscopy analysis. Mo species present on the Mo/ RMn1 and NiMo/RMn1 solids were also analyzed by Raman spectroscopy. The presence of some fluorescence due to manganese incorporated into the alumina support tends, however, to lower the signal-to-noise ratio, complicating the attribution of bands.

Fig. 6 shows the Raman spectra of the Mo and NiMo solids prepared by impregnation at pH 9 on the RMn1 support. First of all, one should note the absence of bands on the RMn1 support. The Mo/RMn1-D pH 9 catalyst presents a main band at 910 cm⁻¹, characteristic of MOQ_4^{2-} species. Also, two additional weaker bands at 950 and 985 cm⁻¹ are observed. They correspond respectively to the formation in low proportions of $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ species, respectively. Since the net surface pH of the RMn1 support is 8.4,



Fig. 5. UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn1, impregnated at pH 7, (a) dried at 120 °C and (b) calcined at 400 °C.

some MoO_4^{2-} species were probably polymerized to $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ species.

The NiMo/RMn1-D pH 9 catalyst also shows bands at 910 and 940 cm⁻¹ corresponding to MoO_4^{2-} and $Mo_7O_{24}^{6-}$ species, respectively [66]. The band due to $Mo_8O_{26}^{4-}$ species at 985 cm⁻¹ is hardly detectable in this case. This suggests that MoO_4^{2-} species in solution tend to be partly transformed into $Mo_7O_{24}^{6-}$ species after impregnation. A band at 1048 cm⁻¹ characteristic of nitrate species coming from the nickel nitrate salt is also observed.

After calcination, the Raman spectra tend to simplify and to show a stronger fluorescence interference, lowering the sensitivity of the technique (Fig. S4 in the Supplementary Information). However, the Mo/RMn1-C pH 9 solid still presents a detectable band at 945 cm⁻¹ associated with $Mo_7O_{24}^{6-}$. Comparison with its dried homologue suggests that calcination causes further polymerization of some MoO_4^{2-} species to $Mo_7O_{24}^{6-}$. In the case of NiMo/RMn1-C pH 9, a wide band from 910 to 990 cm⁻¹ with a maximum at 945 cm⁻¹ is found. In this case, a shift to higher wavenumbers is observed from Mo/RMn1-C pH 9, confirming results obtained in the dried state about the higher polymerization degree of Mo species, mainly as $Mo_7O_{24}^{6-}$ and $Mo_8O_{46}^{4-}$ species in interaction with Ni.

In the case of impregnation at pH 7 (Fig. 7), the Mo/RMn1-D pH 7 solid shows a broad band with a maximum at 930 cm^{-1} and a contribution at 910 cm^{-1} corresponding mainly to MOQ_4^2 species. No clear contribution can be noticed at higher wavenumbers, showing in this case that decreasing the pH from 9 to 7 leads to a lower polymerization degree of the Mo species.

In the case of NiMo/RMn1-D pH 7, the main band is located at 926 cm^{-1} , with shoulders at 900 and 940 nm, showing the presence of both MoQ_4^{2-} and $Mo_7O_{24}^{6-}$ species. This result confirms that Ni favors the polymerization of Mo species. A weak contribution at 990 cm⁻¹ can also be observed due to MoO_3 clusters. However, compared with the pH 9 case, impregnation at pH 7 partly limits the polymerization of Mo species.

After calcination (Fig. S5 in the Supplementary Information), the Mo- and NiMo/RMn1-C pH 7 solids present a similar band at 945 cm^{-1} due to $Mo_7O_{24}^{6-}$ species. One should note here that Ni does not influence the degree of polymerization of the Mo species, since the 945 cm⁻¹ band does not shift or shows contributions at higher wavenumbers following the addition of Ni. Interestingly, a weak band is found around $810-823 \text{ cm}^{-1}$ due to stretching vibrations of Mo–O–Mo entities [67]. However, this band is not accompanied by a contribution around 990 cm⁻¹ due to MoO₃ clusters, ruling out the presence of MoO₃ clusters on those solids. Finally, bands around $460-480 \text{ cm}^{-1}$ due to stretching vibrations of Mn–O are also observed [68].

A summary of the results about the series of catalysts supported on RMn1 using UV–vis DR and Raman spectroscopies is shown in Table 3. About Mn species, calcination leads systematically to a further oxidation of Mn to the +IV oxidation degree. Moreover, calcination at pH 9 leads to some loss of Ni inside a NiMnO spinel, in contrast to the case at pH 7. About Mo species, the addition of Ni favors the polymerization of Mo after calcination if impregnation is performed initially at pH 9, while this effect is less obvious after



Fig. 6. Raman spectra of Mo and NiMo catalysts supported on RMn1, impregnated at pH 9, and dried at 120 °C.

calcination in the pH 7 impregnation case. The effect of increasing the pH from 7 to 9 also leads to a higher polymerization of Mo species for unpromoted Mo/RMn1 solids, but only in the dried state. On NiMo/RMn1, increasing the pH from 7 to 9 leads to higher polymerization after calcination.

3.2.4. Characterization of Mo and NiMo catalysts supported on RMn5 and impregnated at pH 9 or 7

3.2.4.1. UV-vis diffuse reflectance spectroscopy analysis. Fig. 8 shows the UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn5, impregnated at pH 9, dried (Fig. 8a) and after calcination (Fig. 8b). These samples present the same bands at 255, 320, and 500 nm characteristic of Mn²⁺ and Mn³⁺ as for the RMn5 support alone, after the drying and calcination steps. In this respect, the 500 nm band due to Mn²⁺-Al₂O₃ interaction does not change significantly for any samples. This band is accompanied on dried and calcined Mo/RMn5 pH 9 solids by a weak band at 370 nm due to the ${}^{5}B_{1g} \rightarrow {}^{5}B_{2g}$ transition of Mn³⁺ species. The addition of Ni leads in the dried state to a slightly higher relative intensity of the 320 nm band due to Mn^{3+} , while a small signal at 380 nm due to the NiMnO spinel appears. In the calcined sample (NiMo/RMn5-C pH 9), the addition of Ni does not modify the proportion of Mn³⁺ from its nonpromoted homologue. However, in the NiMo/RMn5-C pH 9 case, a contribution at 380 nm due to the NiMnO spinel can still be noted.

Fig. 9a and b show the UV-vis DR spectra of the dried and calcined catalysts impregnated at pH 7 on RMn5, respectively. After drying and calcination, the same triplet of main bands at 255, 320, and 500 nm as for the pH 9 case are present, showing a predominance of Mn^{2+} with some Mn^{3+} species. Here, a clear band at 380 nm can be observed on the NiMo/RMn5-D pH 7 sample after the drying step. However, after calcination, this band is still present but becomes less detectable.

3.2.4.2. Raman spectroscopy analysis. The effect of the Mn amount added to the support can also be evidenced by Raman spectroscopy after the drying state (Fig. 10). The Mo/RMn5-D pH 9 solid shows bands at 930 and 990 cm⁻¹ associated with MOO_4^{2-} and MOO_3 clusters, respectively. After addition of Ni, the NiMo/RMn5-D pH 9 sample shows a poorly defined and broad band comprising contributions at 930, 945, and 966 cm⁻¹ and corresponding to MOO_{2-}^{4-} , $Mo_7O_{2-}^{6-}$, and $Mo_8O_{2-}^{46}$ species. Compared with the RMn1 case, Mo species appear more polymerized in the present case.

After calcination (Fig. S6 in the Supplementary Information), Raman spectra show that the Mo/RMn5-C pH 9 and NiMo/RMn5-C pH 9 samples present a band at 930 cm⁻¹ due to MoO_4^{2-} and a clear band at 990 cm⁻¹ due to MoO_3 clusters. Compared with the RMn1 case (Fig. S5), the presence of clear, relatively strong contributions at 990 cm⁻¹ shows here that the higher polymerization degree of Mo species in the drying state can lead to the formation of MoO_3 clusters after calcination.

In the case of impregnation at pH 7 (Fig. 11), the Mo/RMn5-D pH 7 solid mainly presents bands at 910 and 920 cm⁻¹, which are associated with MoO_4^{2-} species. Similarly, the NiMo/RMn5-D pH 7 solid shows bands at 910 and 930 cm⁻¹ associated with MoO_4^{2-} species. Compared with the impregnation at pH 9, decreasing the impregnation pH to 7 leads to less polymerized Mo species.

Fig. S7 in the Supplementary Information shows that after calcination, on the Mo/RMn5-C pH 7 sample, MOQ_4^{2-} is polymerized to $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ species, as confirmed by the 940 and



Fig. 7. Raman spectra of Mo and NiMo catalysts supported on RMn1, impregnated at pH 7, dried at 120 °C.

Table 3

Summary of the Mn and Mo species present in Mo/RMn and NiMo/RMn catalysts, impregnated at pH 7 or 9, dried, and calcined, as determined by Raman and UV-vis DR spectroscopy.

Catalyst	Impregnation at pH 9		Impregnation at pH 7		
	Dried	Calcined	Dried	Calcined	
Mo/RMn1	$\begin{array}{l} Mn^{2+},Mn^{3+}\\ MoO_4^{2-},Mo_7O_{24}^{6-}\\ Mo_8O_{26}^{4-}\end{array}$	Mn^{2+}, Mn^{3+} Mn^{4+} $Mo_7O_{24}^{6-}$	Mn^{2*} , Mn^{3*} MoO_4^{2-}	Mn ²⁺ , Mn ³⁺ Mn ⁴⁺ Mo ₇ O ^{6_} 24	
NiMo/RMn1	$\frac{Mn^{2^{+}}, Mn^{3^{+}}}{MoO_{4}^{2^{-}}Mo_{7}O_{24}^{6^{-}}}$	Mn ²⁺ , Mn ³⁺ Mn ⁴⁺ , NiMnO Mo ₇ O ⁶ ₂₄ , Mo ₈ O ⁴ ₂₆	Mn^{2+}, Mn^{3+} $MoO_4^{2-}, Mo_7O_{24}^{6-}$	Mn ²⁺ , Mn ³⁺ Mn ⁴⁺ Mo ₇ O ⁶ ₂₄	
Mo/RMn5	Mn ²⁺ > Mn ³⁺ MoO ₄ MoO ₃	Mn ²⁺ > Mn ³⁺ MoO ₄ ^{2−} MoO ₃	$Mn^{2+} > Mn^{3+}$ MoO_4^{2-}	$Mn^{2+} > Mn^{3+}$ $Mo_7O_{24}^{6-}, Mo_8O_{26}^{4-}$	
NiMo/RMn5	$Mn^{2+} > Mn^{3+}$ MoQ_4^{2-} $Mo_7O_{24}^{6-}, Mo_8O_{26}^{4-}$	$Mn^{2*} > Mn^{3*}$ NiMnO $MoO_4^2^-$ MoO ₃	$Mn^{2+} > Mn^{3+}$ Ni MnO MoO_4^{2-}	Mn ²⁺ > Mn ³⁺ NiMnO MoO₄ [−] , MoO₃	

980 cm⁻¹ bands, respectively. For NiMo/RMn5-C pH 7, a maximum around 925 cm⁻¹ due to MoO_4^{2-} species can still be observed, while an intense distinct band due to MoO_3 clusters at 990 cm⁻¹ is also present.

A summary of the results about Mn and Mo species for the series of catalysts supported on RMn5 is shown in Table 3. The main change resulting from the increased loading of manganese is the stabilization of Mn, mainly in the Mn^{2+} oxidation state with some Mn^{3+} contribution. The formation of the NiMnO spinel also appears

to occur whatever the pH of impregnation. A stronger tendency to form MoO₃ clusters can be noticed here than in the RMn1 case.

This modification in the nature of the Mn and Mo species according to the Mn loading suggests a strong influence of manganese on the Mo species formed. In this respect, Mn (IV) is known to be a poor reductant and a strong oxidant, so that Mn (IV) species are rarely stable. Mn (III), as an intermediate between Mn (II) and Mn (IV), can act as an oxidant or a reductant. This behavior is due to its d^4 electronic configuration. In the case of Mn (II), the d^5 elec-



Fig. 8. UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn5, impregnated at pH 9, (a) dried at 120 °C and (b) calcined at 400 °C.

tronic configuration leads to poor reducing ability, as explained by the ligand field stabilization energy (LFSE) theory [40]. In a support containing Mn (III) species (as for the RMn1 support), Ni and Mo surface species can be reduced or oxidized. In this case, the pH of impregnation plays a significant role by controlling the dispersion of Mo species. Above the net pH surface of RMn1-C (8.4), as for the impregnation at pH 9, basic conditions weaken the interaction between molybdate species and the support, partly hampering the dispersion of Mo species and leaving some Ni available to interact with Mn to form a spinel. On the other hand, impregnation at pH 7 favors a higher dispersion of Mo species and avoids the formation of a spinel phase.

In contrast, on RMn5 support, Mn (II) predominates. Mn (II) is more stable than Mn (III) and (IV) and cannot be oxidized or reduced. This leads to a lower interaction of Ni and Mo species with the RMn5 support since they are inert. Therefore, this also favors the formation of higher polymerized molybdate species or even MoO_3 clusters after calcination. Similarly, the lower dispersion of Mo species leaves some Ni available to form the NiMnO spinel.

Therefore, taking into account in a simple way the degree of polymerization of molybdate species, as well as the tendency to form MoO₃ clusters or NiMnO spinel, as the main parameters susceptible to influence catalytic properties, one would expect that final HDS activities would be higher on RMn1 than on RMn5, while impregnation at pH 7 would more favorably influence activity than impregnation at pH 9. To confirm this point, the different NiMo catalysts supported on RMn1 or RMn5 and impregnated at pH 7 or 9 will be studied in the next section in their sulfided states.

3.3. Catalyst characterization in the sulfide state

3.3.1. ICP-OES and total combustion analyses

Ni, Mo, and Mn content was first determined by ICP-OES, while the S amount was obtained by total combustion analysis. The different amounts are reported in Table S2 in the Supplementary Information. Results show good agreement between theoretical and experimental values, particularly for the Mn content, reaching weight percentage values corresponding nearly to 1 mol.% (0.9) for the NiMo/RMn1-S catalysts and to 5 mol.% (5.3) for the NiMo/ RMn5-S catalysts. The resulting Mn/Mo and Mn/Ni molar ratios are therefore respectively 0.1 and 0.25 for the NiMo/RMn1 catalysts and 0.6 and 1.45 for the NiMo/RMn5 catalysts. The addition of manganese also results in better sulfidation of the NiMo catalysts than of the NiMo/Al₂O₃-S reference. This S amount even tends to increase with increasing amounts of Mn. However, its exact location, on the support or on the active phase, cannot be determined easily based only on elemental analysis. Further characterization by XPS is mandatory in this case.

3.3.2. X-ray photoelectron spectroscopy (XPS) of the NiMo sulfide catalysts

The influence of Mn on the nature of Mo and Ni oxide species suggests that the addition of manganese could also modify the formation of Ni and Mo sulfide species. These modifications were analyzed by XPS in order to study (1) the effect of the Mn amount and (2) the influence of the pH of impregnation. Table S3 in the Supplementary Information shows the surface atomic concentrations obtained from XPS analysis. On NiMo/RMn5-S, the atomic percent-



Fig. 9. UV-vis diffuse reflectance spectra of Mo and NiMo catalysts supported on RMn5, impregnated at pH 7, (a) dried at 120 °C and (b) calcined at 400 °C.

age in sulfur is higher than on NiMo/RMn1-S catalysts, in agreement with elemental analysis results. NiMo/RMn1-S and NiMo/ RMn5-S catalysts show Mn/Al atomic ratios around 0.011 and 0.020, respectively. The comparison between these ratios and the theoretical values expected for RMn1 and RMn5 suggests that Mn is quite well dispersed on the Al₂O₃ surface in the RMn1 case, but much less on RMn5. On the other hand, Ni/(Ni + Mo) atomic ratios determined from XPS values are slightly higher than the theoretical value of 0.3, suggesting that Ni is also quite well dispersed on the surfaces of the NiMo/RMn1-S and NiMo/RMn5-S catalysts.

Table 4 shows the results obtained from the decomposition of Mo3*d* and Ni2*p* core level spectra. The Mo3*d* spectra decomposition procedure has been reported previously [53–55,69,70]. The Mo3*d* spectral region contains Mo3*d*_{5/2} and Mo3*d*_{3/2} contributions. Three Mo3*d* doublets are found as follows: (1) a Mo3*d*_{5/2} and Mo3*d*_{3/2} doublet with binding energies respectively at 229.0 and 232.0 eV associated with Mo⁴⁺ species of the MoS₂ phase, (2) a doublet with binding energies at 230.0 and 233.4 eV correlated with Mo⁵⁺ species of a MoOS_x oxysulfide phase, and (3) finally, the doublet with binding energies at 232.1 and 235.3 eV related to Mo⁶⁺ oxide species. In addition, this spectral region contains additional peaks at 223.0 and 227.6 eV corresponding to the S2*s* core level and attributed respectively to S²⁻ of MoS₂ and to S²⁻ species from MoO_xS_y oxysulfide.

Results reported in Table 4 shows that both Mn addition and the pH of impregnation clearly influence the formation of the MoS₂ phase. First of all, the addition of Mn to Al₂O₃ leads to a lower

formation of the MoS₂ phase, whatever the amount of Mn added. This result seems contradictory to the previous elemental analyses. However, one possible reason for such a result could come from the fact that part of the sulfur was used during the sulfidation process to sulfide manganese preferentially, forming MnS at the expense of molybdenum. The increase of the total S amount observed would therefore be insufficient to compensate for the loss of sulfur remaining available for sulfiding molybdenum. The exact state of manganese can be more clearly ascertained if one considers the $Mn2p_{1/2}$ binding energies reported in Table S1 in the Supplementary Information. These values range between 653.3 and 653.8 eV, showing the formation of the α -MnS phase after sulfidation [71,72]. Note that under our experimental conditions, the $Mn2p_{3/2}$ contribution cannot be determined since it overlaps with the Ni LMN Auger peak. Therefore, XPS confirms the sulfidation of manganese under the H₂/H₂S activation conditions used here.

If one now considers the influence of the pH of impregnation, for the RMn1 series, impregnation at pH 7 leads to a greater formation of the MoS₂ phase than at pH 9. This result can be understood if we refer to the nature of the Mo oxide species formed before sulfidation (Table 3). Indeed, the degree of polymerization of the molybdate species is greater after impregnation at pH 9, suggesting a direct relationship between the degree of polymerization of the molybdate species and their ability to be sulfided into MoS₂. One should note (Table 4) that the lower tendency to form MoS₂ in the case of impregnation at pH 9 leads to a higher proportion of



Fig. 10. Raman spectra of Mo and NiMo catalysts supported on RMn5, impregnated at pH 9, dried at 120 $^\circ C.$

Mo oxysulfides, while the percentages of Mo oxides remain similar whatever the impregnation pH.

The NiMo/RMn5-S catalysts present a stronger tendency to form MoS_2 than the catalysts supported on RMn1. This result shows that a further increase in Mn content can better favor the sulfidation of both Mn and Mo than in the RMn1 case, in agreement with elemental analysis results. Moreover, the pH of impregnation does not significantly influence the proportion of MoS_2 to be formed. This result, once again, can be understood if one considers the Mo oxide species formed before sulfidation (Table 3). In both cases, whatever the impregnation pH, similar Mo oxide species are formed, leading after sulfidation to similar proportions in MoS_2 .

Results about the decomposition of the Ni2p core level spectra are also reported in Table 4, while Ni2p decomposition spectra are presented in Fig. 12. The Ni $2p_{3/2}$ spectra contain three contributions with their respective satellites [8,55,73-76]. The peak at binding energy 853.1 eV is related to NiS_x species. The signals at 854.1 and 856.1 eV are associated respectively with the NiMoS phase and NiO_x species. A smaller tendency to form the promoted phase is observed on Mn-containing catalysts than on NiMo/Al₂O₃-S, even if NiMo/RMn1-S pH 7 exhibits a NiMoS percentage close to the one found for the reference catalyst. Increasing the pH of impregnation from 7 to 9 or increasing the Mn content leads to a net decrease of the proportion of the promoted phase. These results can be well explained by assuming the presence of a NiMnO spinel phase in the oxide state. For the RMn1 series, the impregnation at pH 9 induces the formation of a NiMnO spinel phase that is not observed for the pH 7 case (cf. Table 3). This spinel leads after sulfidation to an increase of the proportion of the nonpromoted NiS_x at the expense of the NiMoS phase while similar proportions



Fig. 11. Raman spectra of Mo and NiMo catalysts supported on RMn5, impregnated at pH 7, dried at 120 $^\circ C.$

of Ni oxides are observed whatever the pH of impregnation (Table 4).

Increasing the Mn content leads systematically to the formation of a NiMnO spinel phase for the RMn5-supported catalysts. This fact coupled with a loss of dispersion of Mo species characterized by the formation of MoO_3 clusters makes it even more difficult for Ni to locate at the edges of MoS_2 layers. This leads to an even lower propensity to form the promoted NiMoS phase for NiMo/ RMn5 catalysts compared with the RMn1 series. This situation seems even aggravated if impregnation is performed at pH 9. One should note that the proportion of Ni oxides (similar once again whatever the pH) is lower on the RMn5 series, in agreement with the better sulfidation degree of these catalysts as determined by elemental analysis.

3.3.3. Transmission electron microscopy

TEM analyses were performed in order to evaluate the influence of Mn and the impregnation pH on the morphology of the MoS₂ slabs. Representative images of NiMo/Al₂O₃-S, NiMo/RMn1-S pH 7 and NiMo/RMn1-S pH 9 catalysts are shown in Fig. 13A–C. NiMo/Al₂O₃-S catalyst presents typical fringes of the MoS₂ phase (Fig. 13A) with a relatively homogeneous dispersion of MoS₂ particles formed from two to three stacked slabs and with a superficial density of 17.4 stacks per 1000 nm² (Table 5). NiMo/RMn1-S pH 7 (Fig. 13B) contains a relatively homogeneous dispersion of MoS₂ particles principally formed of single and short slabs with a density of 18.8 stacks per 1000 nm². NiMo/RMn1-S pH 9 catalyst (Fig. 13C) also shows high dispersion with a density of 18.5 stacks per 1000 nm² but with longer slabs than those observed on NiMo/ RMn1-S pH 7.

Table 4

Mo and Ni proportions obtained from the decomposition of XPS Mo3d and Ni2p core level spectra, respectively, for the different series of catalysts. Binding energy (BE) values are given for the Mo3d_{5/2} and Ni2p_{3/2} contributions.

) %
12.5
22.0
21.8
15.3
14.0



Fig. 12. Ni2p XPS decomposition spectra of the NiMo/Al₂O₃-S reference and of the different NiMo/RMn1-S and NiMo/RMn5-S catalysts obtained by impregnation at pH 7 or 9.



Fig. 13. TEM pictures of (A) NiMo/Al₂O₃-S, (B) NiMo/RMn1-S pH 7, (C) NiMo/RMn1-S pH 9, (D) NiMo/RMn5-S pH 7, and (E) NiMo/RMn5-S pH 9 catalysts.

Statistical determination of the stacking number and slab length of MoS_2 particles were performed on several TEM images taken on different regions of micrographs. The addition of 1 mol. % Mn for the NiMo/RMn1-S pH 7 catalyst leads to a better dispersion on the RMn1 support characterized by smaller and less stacked slabs than for the reference catalyst. The average stacking number for NiMo/RMn1-S pH 7 is 1.45 vs 1.72 for the reference catalyst. Impregnation at pH 9 does not lead to any change in slab length from the pH 7 case, while the average stacking number tends to increase again to 1.66.

Figs. 13D and E show respectively TEM representative images of NiMo/RMn5-S pH = 7 and NiMo/RMn5-S pH = 9 catalysts. NiMo/ RMn5-S pH 7 and pH 9 catalysts show typical fringes of MoS₂ with a similar homogeneous dispersion of MoS₂ particles mainly formed of single slabs and with superficial densities of 17.8 and 17.4 stacks per 1000 nm² (Table 5).

Statistical determination of average slab length and stacking number for the RMn5 series shows that in contrast to NiMo/ RMn1-S catalysts, further addition of Mn did not lead to any decrease of the average slab length compared to the NiMo/Al₂O₃-S reference. On the contrary, the slabs appear less stacked than for the reference, showing values (whatever the pH of impregnation) similar to those for the NiMo/RMn1-S pH 7 solid.

3.4. Dibenzothiophene hydrodesulfurization on NiMo catalysts supported on RMn1 and RMn5

A clear influence of manganese on the nature of the Mo and Ni species has been elucidated in the oxide and sulfide states. In order to determine how the presence of manganese influences hydrodesulfurization properties, the NiMo catalysts in their sulfide state were evaluated in the HDS of dibenzothiophene (DBT). The

Table 5

Density of stacks per 1000 nm^2 , average stacking number $(\overline{N}),$ and average stack length (\overline{L}) of catalysts.

Catalyst	Stacks per nm ²	\overline{N} (nm)	$\overline{L}(nm)$
NiMo/Al ₂ O ₃	17.4	1.72	2.75
NiMo/RMn1 pH 7	18.8	1.45	2.58
NiMo/RMn1 pH 9	18.5	1.66	2.59
NiMo/RMn5 pH 7	17.8	1.46	2.84
NiMo/RMn5 pH 9	17.4	1.49	2.77

HDS of DBT leads to two products, biphenyl (BP) and cyclohexylbenzene (CHB), obtained respectively through two parallel reaction pathways, the so-called direct desulfurization (DDS) route and the hydrogenating (HYD) route [77]. Under our conditions, BP is not hydrogenated into CHB.

Results are reported in Table 6 and show a clear influence of adding manganese to an Al_2O_3 support on HDS efficiency. Indeed, all the NiMo catalysts supported on either RMn1 or RMn5 exhibit higher activity than the NiMo/Al₂O₃-S reference, while selectivity results show a very high selectivity to biphenyl through the so-called direct desulfurization route in all cases. However, depending on the impregnation pH and the Mn loading, strong variations can be observed among the NiMo catalysts supported on RMn1 and on RMn5 supports. Comparison with results reported in Tables 3–5 can help to distinguish causes explaining such activity variations.

First of all, the highest activity at 320 °C is found for the NiMo/ RMn1-S pH 7 catalyst with a reaction rate of 40.4×10^{-7} mol/s g_{cat}, 84% higher than for the NiMo/Al₂O₃ reference. Raman and UV-vis DRS results show that this catalyst does not present the NiMnO spinel and shows the best Mo dispersion with only Mo₇O₂₄⁶ species

Table 6

DBT hydrodesulfurization results (P = 30 bars H₂, 500 ppmS) of the NiMo catalysts supported on RMn1 and RMn5 supports: comparison with a NiMo/Al₂O₃ reference. *T* reaction: 320 °C, LHSV = 4.2 h⁻¹.

Catalyst	$r imes 10^{-7} \text{ (mol/s } g_{cat})$	BP selectivity (%)	E_a (kcal/mol)	TOF (h^{-1})	[NiMoS] $(10^{-4} \text{ mol}_{Ni}/g_{cat})$	Ni (in NiMoS)/Mo (edge)
NiMo/Al ₂ O ₃ -S	21.9	95	16	31.7	2.49	0.77
NiMo/RMn1-S pH 7	40.4	97	16	71.3	2.33	0.71
NiMo/RMn1-S pH 9	24.1	96	12	47.9	2.02	0.61
NiMo/RMn5-S pH 7	25.5	97	14	44.5	1.72	0.57
NiMo/RMn5-S pH 9	22.5	95	14	37.3	1.60	0.49

at the oxide state. XPS and TEM results show that this catalyst presents the highest proportion of the NiMoS phase of all the NiMo catalysts supported on Mn-containing Al_2O_3 supports (even if lower than for the reference) and the highest dispersion of MoS_2 particles with short and less stacked MoS_2 slabs.

The NiMo/RMn1-S pH 9 catalyst presents an activity much less important than after impregnation at pH 7 (24.1 \times 10⁻⁷ mol/s g_{cat}). In the oxide state, this sample exhibits several parameters affecting negatively its final HDS activity: (1) the presence of highly polymerized Mo species due to the use of basic conditions for impregnation and (2) formation of the NiMnO spinel with the highest proportion of all the solids studied here leading to a loss of nickel unable to interact positively with Mo to improve activity (Table 4).

The NiMo/RMn5 catalysts obtained by impregnation either at pH 9 or 7 exhibit lower HDS activities than NiMo/RMn1-S pH 7, respectively 22.5×10^{-7} mol/s g_{cat} and 25.5×10^{-7} mol/s g_{cat} . This result looks reasonable since, according to Table 3, RMn5 solids present similar kinds of Mo and Mn species in the oxide state. In both cases, MoO₃ clusters are formed in a significant way, impacting the degree of dispersion of Mo species in the oxide state negatively. This leads after sulfidation to a lower dispersion with longer MoS₂ layers. This situation is also worsened by the presence of the NiMnO spinel. The spinel formation leads after sulfidation to a high proportion of nonpromoted NiSx species as observed by XPS (Table 4), a proportion even higher if the impregnation is performed at pH 9.

The whole results acquired here therefore emphasize the beneficial effect of adding manganese to an Al₂O₃ support, but only if the pH of impregnation and the oxidation degree of Mn are precisely controlled to avoid loss of dispersion and of Ni promoter.

4. Discussion

The addition of Mn to Al_2O_3 deeply influences the HDS catalytic properties of supported NiMo catalysts. Both the Mn loading and the impregnation pH modify the nature of the Ni/Mo oxide species, which directly impacts the proportion of promoted phase and the final HDS activity.

Results clearly emphasize that a Mn loading of 1 mol.% leads to the incorporation of manganese into alumina and to the most beneficial effects in terms of dispersion of Mo oxide species (Tables 3 and 5). However, the pH of impregnation also has to be optimized. Impregnation under basic conditions does not allow Mn to influence the nature of Mo oxide species in a positive way, favoring in this case a higher degree of polymerization of the molybdate species (Raman, Table 3) and therefore a lower propensity to form a MoS₂ phase after sulfidation (XPS, Table 4). It also leads to a lower dispersion of the active phase, as shown by TEM (Table 5). Basic conditions of impregnation also induce the formation of a NiMnO spinel, which after sulfidation decreases the proportion of the promoted phase and the final HDS activity (Tables 3, 4 and 6).

Increasing the Mn loading, as in the RMn5 series, negatively influences the catalytic properties by favoring direct interaction of Mn with Ni and the formation of a NiMnO spinel whatever the pH of impregnation. After sulfidation, this leads to a lower proportion of the promoted phase (Table 4), particularly if impregnation is performed under basic conditions. The use of an RMn5 support also induces a stronger tendency for Mo to form agglomerated MoO_3 clusters (Table 3) instead of well-dispersed molybdate species, suppressing any gain in dispersion of MoS_2 particles, at least in terms of slab length (Table 5).

Combining TEM and XPS characterization results with DBT HDS activities can help analyze the consequences of the addition of Mn to Al_2O_3 towards HDS catalytic properties of NiMo/RMnX (X = 1 or 5) catalysts more deeply.

First, turnover frequency (TOF) values have been calculated for all the different catalysts by applying the geometrical model proposed by Kasztelan et al. [78]. This model helps to access the atomic ratio between the total number of Mo atoms in the slabs (Mo_t) and the number of Mo edge atoms (Mo_e), the only ones catalytically active in HDS. Therefore, correlation with XPS Mo3*d* decomposition results allows determining the number of sulfided Mo^{IV} edge sites using the equations

$$Mo_t = 3n^2 + 3n + 1$$
,

 $Mo_e = 6n$,

with n (Å) = $\frac{L}{2 \times 3.2}$ (L = slab length, and d_{Mo-Mo} = 3.2 Å).

Turnover frequency (TOF) values (in h^{-1}) (Table 6) are then retrieved thanks to the equation

TOF
$$(h^{-1}) = r \cdot N/n_{(MoS2e)}$$
,

with *r* the DBT activity at 320 °C, *N* the Avogadro number, and $n_{(MoS2e)}$ the number of Mo edge atoms as MoS₂.

The TOF value of the NiMo/RMn1-S pH 7 catalyst is 2.2 times higher than that for the NiMo/Al₂O₃-S reference (Table 6), showing that the intrinsic activity of the catalytic sites on the best optimized NiMo catalyst supported on Mn–Al₂O₃ is strongly increased due to the addition of Mn compared to the NiMo catalyst supported on Al₂O₃ only. Increasing both the pH to 9 and the Mn loading leads to a strong decrease of the TOF values, even if they are still higher than for the reference catalyst, the lowest turnover frequency being obtained on NiMo/RMn5-S pH 9. Therefore, determination of TOF results emphasizes the direct relationship between the types of Ni or Mo oxides initially formed, their propensity to form a sulfided promoted phase, and their intrinsic activity.

XPS, TEM, and elemental analysis results can also be combined to determine the number of moles of Ni engaged in NiMoS moieties by multiplying the percentage of NiMoS found using XPS by the Ni content determined using ICP-OES (Table 6). Results do not show a large variation in the number of moles of Ni in NiMoS entities between the reference and the NiMo/RMn1-S pH 7 catalyst. Inversely, a monotonic decrease of the NiMoS amount can explain correctly the variations of HDS activity among the different NiMo catalysts supported on Mn–Al₂O₃.

Similarly, the proportion of Ni in NiMoS entities in decoration of Mo edge atoms can be determined by dividing the moles of Ni in NiMoS entities as determined by the Mo edge amount obtained by TEM measurements (Table 6). Once again, the proportions of Ni in decoration of Mo edge atoms remain relatively similar between the reference catalyst and NiMo/RMn1-S pH 7, while a continuous decrease of this Ni/Mo ratio explains variation in activity among the NiMo/RMnX (X = 1 or 5) catalysts.

The whole results therefore strongly suggest that if Mn is incorporated into a NiMo/Al₂O₃ catalytic system in an optimized way, a strong increase in intrinsic HDS activity can be achieved. Two different hypotheses can be considered here to explain the beneficial effect of Mn on the intrinsic activity of the active phase. The first hypothesis is related to direct interaction of Mn at the support surface with the NiMoS phase through modification of the electronic properties of the promoted entities. However, XPS results (Tables 4 and S1) did not show any significant changes in binding energies for Ni2p, Mo3d, or Mn2p core level spectra. An electronic interaction can therefore be ruled out. The second hypothesis is related to a modification of the active phase-support interaction increasing the intrinsic activity of highly HDS active type II sites and/or decreasing the proportion of low active type I sites [79,80]. This explanation seems more reasonable since as shown by Raman spectra, increasing the Mn content leads to the formation of more polymerized Mo oxide species suggesting that the presence of Mn at the support surface directly influences the active phase-support interaction. The highest activity of the NiMo/RMn1 pH 7 catalyst may therefore correspond to the best compromise between decreasing the support interaction (and therefore increasing the intrinsic activity of the NiMoS phase) and not losing dispersion.

This result must also be analyzed by comparison to the only study concerning NiMnMo/Al₂O₃ catalyst by Ho [30,43], who reported that the addition of Mn to Mo in conjunction with Ni led to a strong synergetic effect in HDS, particularly for dibenzoth-iophene conversion. Unfortunately, the absence of characterization data in these publications from industry did not allow the causes for such a synergetic effect to be determined. However, the present study tends to confirm the results acquired in this previous work about a strong positive effect of Mn on final HDS properties of NiMo/Al₂O₃ catalysts if properly implemented. Further studies will be carried out to determine more deeply how Mn is able to modify the catalytic properties of NiMo/Al₂O₃ HDS catalysts.

5. Conclusions

The present study shows a beneficial effect of adding manganese to an Al_2O_3 support for dibenzothiophene hydrodesulfurization applications. Both the pH of the impregnation and the Mn loading strongly influence the nature of the Mn oxidation state and of the Ni and Mo species formed during drying, calcination, and sulfidation steps.

The use of a Mn loading of 1 mol.%, if combined with impregnation under neutral conditions, can lead to well-dispersed molybdate species without formation of a NiMnO spinel phase. This leads to the formation of a well-promoted NiMoS phase with short and less stacked MoS₂ particles. Impregnation at pH 9 can, however, influence final HDS catalytic properties negatively by favoring more polymerized molybdate species and the formation of a NiMnO spinel, decreasing the proportion of promoted phase and leading to a loss of dispersion of MoS₂ particles.

Increasing the Mn loading further, as in the RMn5 series, favors a direct interaction of Mn with Ni with the presence of a NiMnO spinel hampering the formation of a promoted phase after sulfidation. It also induces the formation of agglomerated MoO₃ clusters, which after sulfidation limits the dispersion of MoS₂ particles.

Results also emphasize that if optimized, the incorporation of Mn into a NiMo/Al₂O₃ catalytic system strongly increases the intrinsic activity of HDS catalytic sites.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.08.015.

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A. López-Benítez et al./Journal of Catalysis 344 (2016) 59-76

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