Effect of Gallium and Vanadium in NiMoV/Al2O3-Ga2O3 Catalysts on Indole Hydrodenitrogenation

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Abstract
The effect of Ga as support modifier and V as second promoter on the NiMoV/Al2O3-Ga2O3 catalyst varying the synthesis method (SG: sol–gel synthesis vs I: impregnation synthesis) was studied. The catalysts were characterized by elemental analysis, textural properties, XRD, XPS, 27Al NMR, Raman, EDX elemental mapping and HRTEM. The chemical analyses by XRF showed coincidence between experimental and theoretical values according to stoichiometric values proposed to Mo/Ni = 6 and (V + Ni)/(V + Ni + Mo) = 0.35. The sol–gel synthesis method increased the surface area by incorporation of Ga3+ ions into the Al2O3 forming Ga–O–Al bonding; whereas the impregnation synthesis leads to decrease by blocking of alumina pores, as follows NiMoV/Al2O3-Ga2O3(I) < NiMoV/Al2O3-Ga2O3(SG) < Al2O3-Ga2O3(I) < NiMo/Al2O3 < Al2O3-Ga2O3(SG) < Al2O3. The values of BJH mesopores mean size between 6.13 and 7.68 nm. XRD and XPS confirmed a bulk structure typical of (NH4)4[NiMo6O24H6]·5H2O and the presence at the surface of Mo4+, Mo6+, NixSy, NiMoS, Ni2+, Ga3+ and V5+ species, respectively. Raman showed that the sol–gel synthesis method reduces the interactions Ni-Mo sulfide-support and improvement the sulfidation degree NiMoV/Al2O3-Ga2O3(SG) as showed sulfur analysis CHONS. The largest proportion of AlO4 content using the impregnation method to add Ga was verified by 27Al solid-state MAS NMR. The EDS elemental mapping confirmed that Ni, Mo, Al, Ga, V and S are well-distributed on support. The HRTEM analysis shows that the length and stacking distribution of MoS2 crystallites varied from 5.67 to 6.01 nm and 2.46 to 2.74 when using the sol–gel and impregnation synthesis method, respectively. The catalytic results revealed that the synthesis method induced the presence of gallium on the surface influencing the dispersion V5+ species, whose effect could have some relation with strength and density of acid sites that in turn influence the dispersion of the MoS2 phase, which correlates well with the indole HDN activities. The activities as indole HDN pseudo-first-order rate constants’ values (kHDN) from 0.29 to 2.78 mol/(m2·h): NiMoV/Al2O3 < NiMoV/Al2O3-Ga2O3(I) < NiMo/V/Al2O3 < NiMoV/Al2O3-Ga2O3(SG). Nevertheless, the nature of the active site can be related with reaction pathways, that is, NiMoV/Al2O3-Ga2O3(SG) and NiMoV/Al2O3-Ga2O3(I) catalysts produce ECH through HIND, while NiMoV/Al2O3 and NiMo/Al2O3 produce EB by hydrogenolysis of HIND to OEA. In the regard, the Ga and V act as structural promoters in the NiMo catalysts, allowing the largest generation of NiMoS M-edge-like and BRIM sites for HDN.
Graphic Abstract
The synthesis method influences the reaction pathways for indole HDN, suggesting that NiMoV/Al₂O₃-Ga₂O₃(SG) and NiMoV/Al₂O₃-Ga₂O₃(I) had the highest production of OEA suggesting that ECH derive from HIND, whereas NiMo/Al₂O₃ shows that OEA concentration is very low at short times, indicating that ECH derives of OEA

Keywords  Gallium · Vanadium · Modified al₂O₃ · Synthesis method · Indole hydrodenitrogenation

1 Introduction

The increase of activities that involving petroleum and its derivatives have caused a high energy consumption worldwide in an exaggerated way, leading to the depletion of light oil reserves; and therefore, the use of heavier oil fractions, which have high contents of refractory molecules with sulfur and nitrogen [1]. During the combustion of nitrogen and sulfur-containing fuels, it is produced SOx and NOx, which causes a great environmental impact by contributing to global warming, production of photochemical smog, acid rain, corrosive effects to industrial and architectural constructions, negative impact on the operability of the conversion and/or transport of crude oil plants [1, 2]. Based on the new regulations nowadays, which aim at a drastic reduction of sulfur and nitrogen emissions represent a challenging task for oil refineries [3]. In Colombia the Ministries of Mines and Energy, in 2014 issued regulations that lead to improved quality of diesel and gasoline in terms of sulfur and nitrogen content [4].

The catalytic hydrotreating processes (HDT) depends largely on the origin of the feed, operating conditions and type of catalyst [3]. In regard to feed, the atmospheric gas oil (AGO, 300–400 ppm) and light cycle oil (LCO,
800–1000 ppm) are important in the production of gasoline and diesel; however, these have indoles and carbazoles that are organonitrogen compounds difficult to remove because they act as a poison for the HDT catalysts [5, 6]. Hence, the studies on HDN of 5-membered heterocyclic compounds are not very extensive [7]; in fact, the first kinetics studies of Indole HDN were conducted by Kim and Massoth, they elucidated the different types of sites present in the catalyst for this reaction, demonstrating that there are three types of sites present (i.e. two for the HYD and one for C–N rupture) [8]. Nguyen studied the kinetics of Indole HDN using Al2O3 and SiO2-Al2O3 supported NiMo(P), considering important the acidity of the support on the HDN, which occurs via aromatic ring HYD due to acidity promotes adsorption and removal of the nitrogen compound [9]. Recently, Ledesma used a series of mesoporous supports such as MCM-41 and SBAs modified with Ti, Al and F in the Indole HDN, its results revealed the presence of Bronsted sites in the catalyst more active and that the high strength of active phase–support interactions increased the dispersion and HDN [2]. However, relating to catalyst, the currently employed formulations have made it possible to meet environmental regulations, but only after significant modifications to the refining process that would cause negative effects on the catalyst life and additional costs of the refining processes [7]. Nowadays, the research is aimed at developing novel catalysts that could serve as an alternative to be able to fulfill these regulations [10]; also, it’s known that the activity and selectivity of the HDT catalyst are associated with the preparation methods. This involves an impregnation method to load the active components on the alumina [11, 12].

The preparation methods of the HDT catalyst involve, at least, impregnation of the support with active metals, making necessary a calcination step [13]. In first stages, the promoter reacts with the support to form Ni(0)Mo(W) aluminates, which is inactive in the HDT process due to the strong active phase–support interactions [10, 11]. In considering these limitations, studies have shown that modifying the surface properties of the alumina with boron, fluorine, phosphorus, silicon, zeolites [12, 14, 15], magnesium [16, 17], titanium [18], calcium [19] and zinc [14, 20] can adjust or aid in the redox properties, sulfur lability, mobility and stability of the corresponding metal site increase the dispersion of the active phase and decrease the interactions between active phase(promoter)–support [21, 22].

The use as alumina-modifier or promoter of gallium and vanadium for the preparation NiMo/Al2O3 catalysts has been reported. Recently, Jang reported the promotional effect of Ga for NiP catalyst on hydrodesulfurization of 4,6-DMDBT, showing that the Ga promote the DDS pathway via the formation of the σ-bond with the thienophenic S [23]. Zhou explained that Ga species located at the surface of NiMoS/ Yzeolite prevent the formation of strong Mo–O–Al bonds, which modulated acidity and weakened interactions between active metals and the support that allows it to play a very important role in the catalytic performance of DDT by the better accessibility of active sites [24]. Meanwhile, Zepeda et al. demonstrated that the addition of Ga has a strong effect on the morphology of tungsten sulfide, which modifies its CUS to improve the HYD mechanism in the DDS reaction (hydrocracking reactions of the aromatic rings prior to their hydrogenation) [25, 26]. De los Reyes suggested that the Ga3+ added to alumina before impregnation of the active components increased HDS activity [27, 28, 29]. Likewise, Rhe et al. showed that the Ga as promoter in the NiMo/ Al2O3 catalyst increased the HYD and HDN activity of pyridine (3%wt. Ga) [30]. Cimino and Lo Jacono reported the high affinity of Ga3+ to alumina tetrahedral sites, modifying the tetrahedral/octahedral ratio of Ni (Ni3+ Td/Ni3+ Oh) in the Ni/Al2O3 catalysts [31]. Petre et al. found that the acidity of the support decreased when Ga was incorporated into the alumina, increasing its HDS activity and modifying the DDS/HYD selectivity [32]. Altamirano et al. through several studies, they reported that the addition of Ga at low amounts (0.6–1.2%wt.) generates a positive effect on HDS activity of CoMo/Al2O3 and NiMo/Al2O3, due to the tetrahedral coordination of gallium on alumina, which led to the increase of Ni(Co) octahedral species that inhibit the formation of Ni(Co) Al2O4, improving the sulfiding of the active species [27, 33].

On the other hand, studies have shown that small amounts of vanadium to hydrotreating catalyst have to improve their performance the increase in the support acidity as reported have led to improve their performance as demonstrated De Jonghe et al. in his study on toluene HYD using NiMo catalysts promoted by V [34]. In this sense, Rankell and Rollman showed that VSx was active for HDT although less active than CoMoS [35]. Asaoka et al. affirmed that V3S4 functioned as anticatalyst during hydrodemetalization (HDM) [36]. Lacroix prepared VSx and it was more active in HDS than that MoS2 and WS2, respectively [37]. Paulino et al. have obtained NiV and VNiMo catalysts that exhibit 7 times greater activities than MoS2, promoting the HDS and HDN of LCO [38, 39].

In this regard, given that the addition of Ga and V may change the product selectivity of the HDN. It is thus a major goal of the present work to investigate the effect of gallium and vanadium addition on the physical properties of NiMo/ Al2O3 catalysts and on the catalytic activity in the HDN of indole.

2 Experimental

2.1 Preparation of Alumina Modified with Gallium

Mesoporous Al2O3 was synthetized by the sol–gel synthesis traditional [40]. Appropriate amounts of aluminum (III)
isopropylate (Al[OCH(CH₃)₂]₃, 99.8%, Sigma-Aldrich) was dissolved in 50 mL of isopropanol ((CH₃)₂CHOH, 98%, Sigma-Aldrich) under magnetic stirring at about 75–77 °C for 4 h, then it was slowly added to the surfactants solution obtained by homogenizing 56.5 mmol of tetramethylammonium hydroxide (TMAOH, 25% in H₂O, Sigma-Aldrich) in 30 mL of deionized water with 18.1 mmol of hexadecyltrimethylammonium bromide (CTMAB, 99%, Sigma-Aldrich), until complete dispersion. After that, the pH was adjusted at 8–10 with diluted ammonium hydroxide (NH₄OH, 28.0–30.0% NH₃ basis, Sigma-Aldrich), keeping under stirred for 2 h. The resulting mixture was aged for 48 h without stirring, filtered, washed, dried at 393 K for 12 h, pulverized and calcined at 883 K for 6 h.

The Al₂O₃-Ga₂O₃ catalytic supports with 3 wt% as Ga₂O₃ was prepared by two different methods that will be identified as Al₂O₃-Ga₂O₃(SG) and Ga₂O₃/Al₂O₃(I). The Ga₂O₃/Al₂O₃(I) was prepared by impregnation in excess of pore volume adding dropwise to a flask containing 5 g of above-mentioned Al₂O₃ an aqueous solution of [CH₃COCH=C(O-)CH₃]₃Ga at 353 K, under stirring and pH 5–6. The impregnation step was until removal of the solvent by evaporation. Then, the as-made sample was dried at 383 K for 12 h and then it was calcined at 883 K for 6 h. In the other hand, Al₂O₃-Ga₂O₃(SG) was prepared by the sol–gel synthesis traditional [41, 42]. In a typical experiment, appropriate amounts of Al[OCH(CH₃)₂]₃ and gallium(III)acetylacetonate ([CH₃COCH=C(O-)CH₃]₃Ga, 99.9%, Sigma-Aldrich) were dispersed in 50 mL of (CH₃)₂CHOH under magnetic stirring at about 75–77 °C until obtaining a homogeneous solution (4 h). Simultaneously, a surfactants solution was obtained, homogenizing 56.5 mmol of TMAOH in 30 mL of deionized water followed by addition of 18.1 mmol of CTMAB, until complete dispersion. After that, the polymerized solution of [CH₃COCH=C(O-)CH₃]₃Ga/Al[OCH(CH₃)₂]₃ in alcoholic medium was slowly added to the surfactants mixture and the pH was adjusted at 8–10 with NH₄OH, keeping under magnetic agitation for 2 h. The resulting mixture was aged for 48 h without stirring and the gel formed was washed with deionized water until neutral pH and vacuum-filtered. The solid obtained was dried at 393 K for 12 h and the sample was calcined at 883 K for 6 h and then it was calcined at 773 K for 4 h. Finally, 3 g of above-mentioned supports and Al₂O₃ were impregnated in excess of pore volume with aqueous solution of Anderson ammonium salt ([NH₄]₄[NiMo₆O₂₄H₆]·5H₂O, 20 wt% Mo and 2.04 wt% Ni), under stirring at 323 K and pH around 5–6. The impregnation step lasted until removal of the solvent by evaporation and the mass obtained was further dried at 378 K for 12 h [43].

The ([NH₄]₄[NiMo₆O₂₄H₆]·5H₂O supported on alumina modified with gallium and vanadium will be identified as NiMoV/Al₂O₃-Ga₂O₃(x), where x is the support synthesis method (SG: sol–gel and I: impregnation).

### 2.3 Catalyst Characterization

The elemental analysis for NiMoV/Al₂O₃-Ga₂O₃(x) was determined by X-ray fluorescence using a MagixPro PW–2440 Philips instrument. The textural properties were determined by means of the physisorption technique of N₂ at 77 K using a Micromeritics 3FLEX™ instrument. Prior to the measurements the samples were degassed at 300 °C for 16 h in vacuum of 10⁻⁶ mmHg. The surface areas of samples were calculated by the Brunauer–Emmett–Teller multipoint method (BET) and, total pore volume and pore size distribution were determined from the adsorption branch of the isotherm using the Barret–Joyner–Halenda (BJH) model. The total mesopore volume (V_m) and mean pore diameter (D_p) can be provided by the BJH method [44]. XRD analysis of the samples was carried out using a BRUKER D8 ADVANCE diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) and Ni filter, within the range 5° ≤ 2θ ≤ 90°, step size of 0.02° and acquisition speed of 0.08°/s. Identification of the different phases was made using the JCPDS library [45].

The surface composition of the most active sulfided catalysts were determined through of X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-Alpha spectrometer, equipped with a dual (non-monochromatic) Mg/Al anode, operated at 400 W and under a vacuum better than 10⁻⁹ torr. Calibration of the instrument was carried out employing the Au 4f₇/₂ line at 83.9 eV. A dual flood gun source of low-energy electrons and Ar + ions was used during all measurements to prevent surface charging. The internal referencing of binding energies was made using the dominating Al 2p band of the support at 74.4 eV. After ex situ sulfding for XPS analysis, samples were immersed in purified n-hexane and quickly transferred to the XPS instrument, where the solvent was slowly removed under vacuum [46]. Curve fitting of the spectra was carried out using the XPSPEAK version 4.1 and XPS GRAPH programs, employing a standard non-linear least squares curve fitting routine, mixed Gaussian/Lorentzian peak shapes of variable proportion, after baseline subtraction by the Shirley method.
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2.4 Catalytic Test

Prior to the HDN catalytic reaction, 1.0 g of NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(x) or NiMo/Al$_2$O$_3$ precursor were transferred to a fixed-bed tubular stainless-steel reactor (30 cm long, 20 mm I.D.) with an axial thermowell containing a thermocouple centered in the catalyst bed. In order to minimize internal diffusion limitations, all catalysts were thoroughly ground in a mortar to a fine powder. Subsequently, the samples were activated in situ passing through them a total flow rate of 0.33 cm$^3$ min$^{-1}$ CS$_2$ (2 vol%)/heptane and 70 cm$^3$ min$^{-1}$ of hydrogen at 623 K for 4 h to attain a reproducible and stable state at surface [43]. The HDN test conditions were as follows: The indole/hexadecane solution (80 mL, 150 ppm of N) was introduced into the autoclave (JP Inglobal) and 300 mg of catalyst was transferred to the reactor. Later, the reactor was purged for three times with N$_2$ at ambient temperature and then pressured to 3.1 MPa H$_2$. The mixture was heated from room temperature to 593 K for 6 h under constant stirring. Indole consumption and products formed during the course of reaction were followed employing a CG-2014 Shimadzu equipped with a flame ionization detector (FID) using standards of Indolee (Sigma-Aldrich 99.9%), ethylbenzene (Sigma-Aldrich 99%), ethylcyclohexane (Sigma-Aldrich 97%), o-ethylaniline (sigma Aldrich 97%) and indoleene (sigma-99% Aldrich). The effluents sampling of the reactor occurring at 0, 30, 60, 120, 180, 240, 300 and 360 min, and the catalytic activities of the catalysts were determined. Finally, the activities of indolee conversion are reported as pseudo-first-order rate constant for indolee disappearance normalized by the moles of IND per weight (m$_{cat}$, g) and surface area (S$_{BET}$, m$^2$/g) of the catalyst after 6 h of reaction time.

The alumina support and the V or Ga-modified alumina showed negligible indolee conversion. Absence of mass and heat flow transport effects was verified according to established procedures [53, 54]. All experiments reported in this work (synthesis protocols, characterizations and catalytic activity measurements) were carried out at least in triplicate. Good reproducibility was verified, better than 10% in all quantitative measurements.

3 Results and Discussion

3.1 Chemical Analysis

The Table 1 shows the chemical analysis of Al$_2$O$_3$-Ga$_2$O$_3$(SG), Al$_2$O$_3$-Ga$_2$O$_3$(I), NiMo/Al$_2$O$_3$, NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG) and NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I) by XRF. The results for all catalysts were in agreement, within experimental accuracy, with the nominal metal contents and the Mo/ Ni and (V + Ni)/(V + Ni + Mo) atomic ratios proposed in this
work of 6 and 0.35, respectively [43]. The relative deviations between experimental and theoretical values showed in Table 1 could be related to the synthesis procedures of the supports and precursors.

### 3.2 Textural Properties

All the N₂ physisorption isotherms shown in Fig. 1 are type IV in the IUPAC classification [55]. Likewise, hysteresis loops can observe both at intermediate and high relative pressures (P/P₀ > 0.5) for each isotherm. In this sense, Al₂O₃ and Al₂O₃-Ga₂O₃(SG) are type H1 due to uniform mesopores, Al₂O₃-Ga₂O₃(I) and NiMoV/Al₂O₃-Ga₂O₃(SG) are type H2 related to the ink-bottle type of mesopores, and NiMoV/Al₂O₃-Ga₂O₃(I) displayed a combination of H2 and H3 due to ink-bottle and laminar type mesopores, suggesting the influence of the synthesis method of Al₂O₃-Ga₂O₃(x) on the surface area, pore volume and pore diameter of the catalysts [55].

The textural characteristics of the supports and catalysts are summarized in Table 2. The overall surface area: NiMoV/Al₂O₃-Ga₂O₃(I) < NiMoV/Al₂O₃-Ga₂O₃(SG) < Al₂O₃-Ga₂O₃(I) < NiMo/Al₂O₃ < Al₂O₃-Ga₂O₃(SG) < Al₂O₃; whereas the pore volume showed a similar increased except for Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(SG). This behavior can be related with the migration of the metallic phase (Ni, Mo, Ga and V) into the support pores probably by the generation of microporosity induced during the impregnation process of

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**Table 1** Experimental Composition of supports NiMoV/Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(x) catalysts

| Solid                  | Experimental composition (wt%) | CHONS elemental analysis |
|------------------------|--------------------------------|--------------------------|
|                        | Mo   | Ni   | Ga₂O₃ | V₂O₅ | V+Ni/Mo+V+Ni | Mo/NI | % wt S | % wt C |
| Al₂O₃                  |      |      |       |      |             |       |        |        |
| Al₂O₃-Ga₂O₃(SG)        |      |      |       |      |             |       |        |        |
| Al₂O₃-Ga₂O₃(I)         | 21.7 | 2.3  | 5.4   | 0.39 | 5.8         | 13.2  | 0.6    |        |
| NiMoV/Al₂O₃            | 20.2 | 2.1  | 2.9   | 5.1  | 0.38        | 6.2   | 13.7   | 0.4    |
| NiMo/Al₂O₃             |      |      |       |      |             |       |        |        |
| NiMoV/Al₂O₃-Ga₂O₃(SG)  | 21.2 | 2.1  | 2.9   | 5.1  | 0.38        | 6.2   | 13.7   | 0.4    |
| NiMoV/Al₂O₃-Ga₂O₃(I)   | 20.7 | 2.2  | 3.2   | 5.2  | 0.39        | 5.8   | 11.8   | 0.9    |

wt% percentage by weight, SG sol–gel synthesis, I impregnation synthesis. Composition Nominal: (V+Ni)/(Mo+V+Ni)=0.35, Ni/Mo=6; S ~ 14 wt%
the material that decreases their pore volume and therefore the surface area [56].

The Al₂O₃-Ga₂O₃(SG) support increased the surface area and the pore diameter is unchanged, which means that the Ga³⁺ ions are incorporated into the Al₂O₃ structure, where the radius of the Ga³⁺ ion (0.062 nm) is larger than that of Al³⁺ ion (0.051 nm) due to the sol–gel method forms Al-O-Ga bonding in the process of gelation [57]; whereas in Al₂O₃-Ga₂O₃(I) support the Ga³⁺ ions are unlikely to substitute Al³⁺ ions into the alumina matrix, leading to a decrease in the surface area by blocking of alumina pores, going from 7.7 to 6.3 nm [56]. The pore volume does not have an appreciable variation when Ga is added to Al₂O₃ through the SG method (around 3.5%), while becomes more pronounced in materials obtained through a process of impregnation which reduces the pore volume in Al₂O₃ by 28%. In this respect, it is expected that the addition of V will cause a decrease of pore volume. However, when impregnating V and NiMo on supports obtained by the SG method, the variations in porosity are small, which shows that there may be a better dispersion of V and NiMo on these catalysts.

All the pore size distribution was unimodal (see Table 2 and box Fig. 1) with pore diameters of the catalysts and supports principally located in the range of mesoporous (2–50 nm) [55], with values of BJH mesopores mean size between 6.13 and 7.68 nm in the order: NiMoV/Al₂O₃-Ga₂O₃(SG) < NiMoV/Al₂O₃-Ga₂O₃(I) < Al₂O₃-Ga₂O₃(I) < Al₂O₃-Ga₂O₃(SG) < NiMo/Al₂O₃ < Al₂O₃[56].

### 3.3 XRD Analysis

The XRD patterns of oxidic precursor varying the synthesis method of the support are shown in Fig. 2. In this figure, regardless of the synthesis method of the support, all the precursors showed diffraction peaks corresponding to (NH₄)₄[NiMo₆O₂₄H₆]·5H₂O (JCPDS 22-0506) at 2θ = 17.374, 15.291, 11.037, 29.455, 23.772, 28.494, 12.300, 33.027, 16.372, 32.054, 34.062 and γ-Al₂O₃ (JCPDS 10-0425) at 2θ = 67.034, 60.899, 45.863, 39.492, 37.604. The diffraction peaks corresponding to (NH₄)₄[NiMo₆O₂₄H₆]·5H₂O are narrow, intense and defined suggesting high crystallinity. Also, the Fig. 2, revealed no diffraction lines due to Ga₂O₃ and V₂O₅ probably because their concentrations were low and/or the crystallites are too small or the particles of were well dispersed on the support [58].

### 3.4 XPS Analysis

The XPS spectra of the Mo 3d₃/₂–₅/₂ region shown in the Fig. 3 confirms the presence on the surface of Mo⁴⁺ (229 eV) attributable to MoS₂ and Mo⁶⁺ (232.5 eV) which can be identified as MoO₃[59]–[61]. It can observe that the presence or not of gallium and vanadium are reflected in a higher amount of Mo⁴⁺ species (sulfided). Likewise, in the Mo 3d₃/₂–₅/₂ region is found a shoulder at 226.5 eV, corresponding to the 2 s signal of sulphur, which can be confirmed by the presence of three bands in the S 2p₃/₂ region [60]: a signal at 161.7 eV due to terminal disulfide and/or sulfide (S²−) ligands in MoS₂, NiS or NiMoS phases, another signal at 163.1 eV corresponding to bridging disulfide (S₂²−) ligands and the signal at 168.9 eV, which can be assigned to SO₄²⁻. The signals due to sulfide and disulfide species are much more important for samples that do not contain Ga, which showed no presence of sulfates (see Table 3 and Fig. 4).

The Ni 2p region spectra of the Fig. 3 shows four Ni 2p₃/₂–₁/₂ peaks at 852.5–853.0, 853.5–854.0, 856.1–856.7 and 862 eV [62, 63]. These signals are attributed to the presence of Ni₅S₇ sulfide phases (Ni₅S₇, Ni₉S₈ or NiS), NiMoS phase, NiMoO₄ species and the strong shake-up lines characteristic of Ni²⁺ species in a Ni-Mo-O matrix, respectively. Note that the signal assigned to NiMoS is more prominent

| Table 2 Textural properties, density of acidic sites and ²⁷Al NMR Al₆/Al₈ ratio of supports and NiMoV/Al₂O₃-Ga₂O₃(x) catalysts varying the synthesis method (x = SG and I) | Solid | Specific Surface Area and Porous Characteristics | Potentiometric titration with n-butylamine | Al₆/Al₈ (²⁷Al NMR) |
|---|---|---|---|---|
| | SBET (m²/g) | Vp (cm³/g) | Dp (nm) | Ei (mV) | density of sites (μmol m⁻²) |
| Al₂O₃ | 265 | 0.57 | 7.7 | –151.0 | 7.6 | 0.29 |
| Al₂O₃-Ga₂O₃(SG) | 272 | 0.55 | 7.1 | –106.0 | 9.9 | 0.24 |
| Al₂O₃-Ga₂O₃(I) | 232 | 0.41 | 6.3 | –151.0 | 7.8 | 0.31 |
| NiMo/Al₂O₃ | 233 | 0.26 | 7.2 | –72.2 | 10.3 | 0.29 |
| NiMoV/Al₂O₃-Ga₂O₃(SG) | 188 | 0.29 | 6.1 | –24.2 | 9.9 | 0.25 |
| NiMoV/Al₂O₃-Ga₂O₃(I) | 124 | 0.21 | 6.2 | –6.1 | 4.3 | 0.33 |

w% percentage by weight, SG sol–gel synthesis, I impregnation synthesis, Al₆/Al₈ Al octahedral/tetrahedral ratio, SBET BET surface area, Vp volume of pores, Dp mean pore diameter, Ei initial electrode potential. NiMoV/Al₂O₃ (SBET = 193 m²/g; Ei = 13.2 mV; 14.5 μmol m⁻²)
for the gallium-free catalyst. However, these have a lower proportion of Ni$_x$S$_y$, suggesting that most of the Ni is as NiMoS.

Figure 4 shows the XPS spectra in the Ga 3d and V 2p$_{3/2}$ regions, where the Ga$^{3+}$ (20.5 eV) and V$^{5+}$ (517.1 eV) signals can be assigned to Ga$_2$O$_3$ and V$_2$O$_5$, respectively [64, 65]. Increasing the Ga and V content from 0.4/0.2 to 0.6/0.6 atomic % in the NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG) catalysts, which is agreement with textural analysis results. The atomic percentages present in Table 3 suggest that the synthesis method of Al$_2$O$_3$-Ga$_2$O$_3$(I) generated a larger proportion of vanadium on the surface, which could influence less reducibility of the species of Mo and Ni, probably due to the presence of V$_2$O$_5$ polymeric chains whose effect is similar in NiMoV/Al$_2$O$_3$ [66]. The relative quantities of low oxidation state Mo, Ni and S species in the catalysts followed the order NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I) < NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG) < NiMoV/Al$_2$O$_3$, suggesting a relation with the synthesis method of the support. A higher proportion of NiMoS is obtained on NiMo/Al$_2$O$_3$, in which 48% of the nickel atoms are engaged, while this value is about

![Fig. 2](image_url)
36% for NiMoV/Al₂O₃-Ga₂O₃(SG) and 38% for NiMoV/Al₂O₃-Ga₂O₃(I).

Recent studies have reported that amounts greater than 3 wt% in V allows the presence of different V⁵⁺ species on surface [66]; in this regard, when the support is modified with Ga, V₂O₅ rich-aggregates on the surface could predominate depending on their dispersion associated to the solubility of the precursors during synthesis, i.e. small V₂O₅ nanoclusters could predominate on the surface when the V is supported on the unmodified Al₂O₃ which decrease

Fig. 3 X-ray photoelectron spectra Mo 3d and Ni 2p regions of sulfided NiMoV/Al₂O₃-Ga₂O₃(x) catalysts varying the synthesis method (x = SG and I): a Mo 3d and b Ni 2p. (I) NiMo/Al₂O₃; (II) NiMoV/Al₂O₃; (III) NiMoV/Al₂O₃-Ga₂O₃(SG); (VI) NiMoV/Al₂O₃-Ga₂O₃(I).
the relative quantities of reduced species. Likewise, the 
$\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3(3\%-\text{SG})$ support presents a large number of 
$\text{Ga}^{3+}$ sites that will be available after impregnating the $\text{V}$ compared to $\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3(3\%-\text{I})$. In these supports the 
$\text{vanadium could be presented as isolated tetrahedral or poly-
meric chains of V}^{5+}\text{ oxides, affecting the reducing properties of Ga that are reflected in the low sulfiding of the catalyst}$ [67, 68].

![Figure 4 X-ray photoelectron spectra S 2p, Ga 3d and V 2p regions of sulfided NiMoV/Al$_2$O$_3$-Ga$_2$O$_3(x)$ catalysts varying the synthesis method (x = SG and I): a) S 2p, b) Ga 3d and c) V 2p. (I) NiMo/Al$_2$O$_3$; (II) NiMoV/Al$_2$O$_3$; (III) NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG); (VI) NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I)]

Table 3 Atomic chemical composition of Mo, Ni and S oxidation states in NiMoV/Al$_2$O$_3$-Ga$_2$O$_3(x)$ catalysts varying the synthesis method (x = SG and I)

| Catalysts                              | Mo 3d$_{3/2}$–3d$_{5/2}$ | Ni 2p$_{3/2}$–2p$_{1/2}$ | S 2p$_{3/2}$–2p$_{1/2}$ |
|----------------------------------------|--------------------------|--------------------------|--------------------------|
|                                        | Mo$^{6+}$ 229 eV (at.%)  | Ni$_x$S$_y$ 852.9 eV (at.%) | S$^{2-}$ 161.7 eV (at.%) |
| NiMo/Al$_2$O$_3$                        | 3.30                     | 0.26                     | 6.50                     |
| NiMoV/Al$_2$O$_3$                      | 2.99                     | 0.29                     | 4.40                     |
| NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG)      | 4.99                     | 0.087                    | 3.05                     |
| NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I)       | 2.31                     | 0.072                    | 2.43                     |

Fig. 4 X-ray photoelectron spectra S 2p, Ga 3d and V 2p regions of sulfided NiMoV/Al$_2$O$_3$-Ga$_2$O$_3(x)$ catalysts varying the synthesis method (x = SG and I): a S 2p, b Ga 3d and c V 2p. (I) NiMo/Al$_2$O$_3$; (II) NiMoV/Al$_2$O$_3$; (III) NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG); (VI) NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I)
3.5 Raman Spectroscopy

The Raman spectra (see Fig. 5) collected after sulfidation at 623 K for NiMoV/Al₂O₃-Ga₂O₃(x) and NiMo/Al₂O₃ catalysts display two main Raman active modes characteristic of the bulk or multilayered MoS₂, the E₂g¹ and A₁g[69, 70]. The E₂g¹ mode represents an in-plane vibration, and the A₁g one corresponds to an out-of-plane of S–Mo–S bonds. In the spectra of the catalysts an increase in the frequency of the two mentioned vibration modes, displaying an influence by the presence of Ga and V as follow: NiMoV/Al₂O₃-Ga₂O₃(SG) < NiMo/Al₂O₃ < NiMoV/Al₂O₃-Ga₂O₃(I), which partially suppress the vibration of the atoms in MoS₂, suggesting an interaction of the sulfide with the support. It has been shown that the frequency difference between E₂g¹ and A₁g modes can be used as a robust and preliminary diagnostic method of the layers number of MoS₂ samples [69]. In this regard, the frequency differences of catalysts are 24.2 cm⁻¹, which suggest around 2 or 3 layers [70]. The spectrum of each catalyst shows a difference between the intensities of the E₂g¹ and A₁g vibration modes, which is related to the growth of MoS₂ crystal size [70], following the order: NiMoV/Al₂O₃-Ga₂O₃(I) < NiMo/Al₂O₃ < NiMoV/Al₂O₃-Ga₂O₃(SG). These results can be related with the sulfur analysis by CHONS (Table 1), which is larger in NiMo/Al₂O₃, NiMoV/Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(SG) than NiMoV/Al₂O₃-Ga₂O₃(I), suggesting the increase in the active phase-support interactions.

3.6 ²⁷Al NMR Analysis

Regardless of the synthesis method the typical ²⁷Al NMR spectra (see Fig. 6) displayed characteristics chemical shift ranges of the γ-Al₂O₃ phase in octahedral coordination (AlO₆) at 10.8–12.6 ppm (narrow peaks) and 70.1–76.5 ppm for γ-Al₂O₃ phase in tetrahedral coordination (AlO₄, broad peaks) [71, 72, 73]. By integrating the peak areas, the Al octahedral/tetrahedral ratio was in the order: NiMoV/Al₂O₃-Ga₂O₃(I) > Al₂O₃-Ga₂O₃(I) > Al₂O₃ ~ NiMo/Al₂O₃ > NiMoV/Al₂O₃-Ga₂O₃(SG) > Al₂O₃-Ga₂O₃(SG), as seen in Table 2. The AlO₄ content in the materials shows that it has a dependence on the type of synthesis method of the support; suggesting that the method of impregnation, the gallium is interacting with the alumina tetrahedral sites as GaAlO₄[42].

3.7 SEM Analysis with Energy Dispersive X-Ray Spectroscopy and Elemental Mapping

The SEM microscopy of the NiMoV/Al₂O₃-Ga₂O₃(SG) and NiMoV/Al₂O₃-Ga₂O₃(I) catalysts revealed that the morphologies consist of particle conglomerates with irregular geometries, being smaller particles for NiMoV/Al₂O₃-Ga₂O₃(SG) as displayed the Fig. 7a, b. The EDX elemental mapping confirmed the presence in the catalysts of the constituent elements (Ni, Mo, Al, Ga, V and S) and it shows that the atoms constituting the catalysts are well-distributed on support (Fig. 7a, b). However, the Mo, Ni, V and S atoms in NiMoV/Al₂O₃-Ga₂O₃(I) could not disperse in the whole selected area due to that the elements could be embedded in pores of the support and/or distributed on few support surface zones forming aggregates [73].

3.8 High-resolution Transmission Electron Microscopy

The HRTEM analysis of representative micrographs for NiMoV/Al₂O₃-Ga₂O₃(SG) and NiMoV/Al₂O₃-Ga₂O₃(I) are shown in Fig. 8a, b and Table 4. These HRTEM micrographs display the presence of homogeneously dispersed MoS₂ crystallites with multi-layers (black thread-like fringes with separation of 0.65 nm characteristic of the basal planes (002)), whose values of D showed that the dispersion of...
NiMo species improved in the catalyst obtained via sol–gel was (D = 0.19 vs 0.20). The Fig. 7a/b show that the length and stacking distribution of MoS2 crystallites changes with the support synthesis method (SG vs I), which varied from 5.67 to 6.01 nm and 2.46 to 2.74, respectively. Thus, HRTEM image show for NiMoV/Al2O3-Ga2O3(I) the formation of crystallites that led to the agglomeration of Ni, Mo and V, which was confirmed with the increase average length and stacking number of the NiMoS phase corroborated with the shifting in the frequencies of the two vibration modes of its Raman spectrum and EDS elemental mapping. Meanwhile, the edge-to-corner ratio a MoS2 slab (fe/fc)Mo increased as the average slab length increased (7.4–7.9).

3.9 Catalytic Test

The indole hydrodenitrogenation activities in function of the product selectivity of the NiMo/Al2O3, NiMoV/Al2O3-Ga2O3(SG) and NiMoV/Al2O3-Ga2O3(I) catalysts are presented in Fig. 9. In this figure can be seen that the products identified by gas chromatography were indoleine (HIND), o-ethylaniline (OEA), ethylbenzene (EB) and ethylcyclohexane (ECH); these accounted for more than 98% of the total products, suggesting a modified indole HDN reaction network as proposed by Ledesma et al. [2]. The Table 4 show a large effect of the support synthesis method on intrinsic HDN activities, since the overall activities were found to increase as follows: NiMoV/Al2O3 < NiMoV/Al2O3-Ga2O3(I) < NiMo/Al2O3 < NiMoV/Al2O3-Ga2O3(SG), i.e., overall pseudo-first-order rate constants’ values (k) of 0.29, 1.57, 1.83 and 2.78 mol/(m2·h), respectively.

Furthermore, NiMo/Al2O3 and NiMoV/Al2O3-Ga2O3(SG) had the highest production of ECH and EB (EB < ECH), and NiMoV/Al2O3-Ga2O3(I) showed the highest production of OEA. The NiMoV/Al2O3-Ga2O3(SG) and NiMoV/Al2O3-Ga2O3(I) catalysts produce ECH with a progressive increase of OEA, suggesting that ECH derive from HIND, except NiMoV/Al2O3 which produces EB; whereas NiMo/Al2O3 shows that OEA concentration is very low at short times, indicating that ECH derives in the high proportion of OEA. Hence, according to the reaction pathways for indole HDN suggested by Zhang and Ozkan, NiMoV/Al2O3-Ga2O3(SG) and NiMoV/Al2O3-Ga2O3(I) catalysts prefer the hydrogenation of HIND to octahydroindole (OHIND) and this subsequent may be hydrogenated to o-ethycyclohexylamine (OECHA) and ethylcyclohexene (ECH) until form ECH. Meanwhile, NiMo/Al2O3 and NiMoV/Al2O3 followed the hydrogenolysis of HIND to OEA. This behavior is not clearly associated to its textural properties, however, the dispersion and structural properties of those vanadium species depended of the support nature, which in turn leads to a greater dispersion of the sulfided Ni-Mo species.

Thus, the introduction of Ga and V to NiMoV/Al2O3-Ga2O3(SG) resulted in almost a 1.5-fold increase of the rate constant than their unpromoted analog probably due to the increase of the number of Lewis acid sites as revealed Haneda [41], while NiMoV/Al2O3-Ga2O3(I) was almost the
Fig. 7  a EDX elemental mapping of Mo, Ni, S, Ga, V, Al and O in sulfided NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(SG).  b EDX elemental mapping of Mo, Ni, S, Ga, V, Al and O in sulfided NiMoV/Al$_2$O$_3$-Ga$_2$O$_3$(I)
same activity as NiMo/Al₂O₃. This result suggests that the way to incorporate Ga into Al₂O₃-framework influences the dispersion of the V⁵⁺ species by increased number and strength of acid sites (see Tables 2 and 3) [66, 74]. It is possible that, in the NiMo/Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(SG) catalysts, an adequate number of active sites have been

**Table 4** HDN apparent rate constants at 5 h and morphology of the MoS₂ active phase determined by HRTEM of NiMoV/Al₂O₃-Ga₂O₃(x) catalysts varying the synthesis method (x = SG and I)

| Catalysts                  | HDN rate constants, mol/ (m²·h) × 10⁻⁶ | Product selectivity (%) at 10% conversion | MoS₂ characteristics |
|----------------------------|------------------------------------------|-------------------------------------------|----------------------|
|                            |                                          | HIND  | OEA  | EB  | ECH | L (nm) | N  | (fe/fc)Mo |
| NiMo/Al₂O₃                 | 1.83                                     | 46    | 3    | 13  | 39  |        |    |            |
| NiMoV/Al₂O₃               | 0.29                                     | 49    | 25   | 19  | 8   |        |    |            |
| NiMoV/Al₂O₃-Ga₂O₃(SG)     | 2.78                                     | 32    | 30   | 10  | 29  | 5.67   | 2.46 | 7.36       |
| NiMoV/Al₂O₃-Ga₂O₃(I)      | 1.57                                     | 25    | 36   | 11  | 28  | 6.01   | 2.74 | 7.90       |

L (average length) and N (average stacking degree) of MoS₂ crystallites; (fe/fc)Mo estimated fraction of Mo atoms on the edge surface of MoS₂ particles.
generated to disperse efficiently sulfided NiMo; whereas NiMoV/Al₂O₃-Ga₂O₃(I) and NiMoV/Al₂O₃ exhibited the lowest catalytic activity despite of the high proportion of V₂O₅ and/or Ga₂O₃ on the surface; this suggests that the low presence of sites can be related to their high carbon content and the available sites bind more strongly to organonitrogen compounds, suggesting that they are of the type NiMoS M-edge [75], which could be affecting its catalytic activity. In the regard, the adsorption strength of the nitrogen compound on the catalyst surface influences its HDN performance [8, 76], suggesting that HIND and OEA may show higher adsorption on acid surface and compete with indole for adsorption sites on the catalyst, so the force of acid sites and/or density of sites influence the HDN activity as found for our catalysts where it can be seen similar trends with corresponding (fe/fc)Mo fraction (NiMo/Al₂O₃: 10.3 μmol m⁻², NiMoV/Al₂O₃: 14.5 μmol m⁻², NiMoV/Al₂O₃-Ga₂O₃(SG): 9.87 μmol m⁻² and NiMoV/Al₂O₃-Ga₂O₃(I): 4.29 μmol m⁻²). Thus, we consider that Ga and V act as structural promoters in the NiMo catalysts supported on Al₂O₃ that allows the largest generation of NiMoS M-edge and BRIM sites for HYD and coordinative unsaturated sites (CUS) for HDN [77, 78].

4 Conclusions

The effect of changes in the support’s composition with gallium and vanadium as promoter on indole HDN have been presented. The chemical analyses by FRX for all NiMoV/Al₂O₃-Ga₂O₃(x) catalysts were within experimental accuracy, obtaining stoichiometric ratios of Mo/Ni ~ 6 and (V + Ni)/(V + Ni + Mo) = 0.31–0.34. EDS spectra and elemental mapping confirmed the presence of Ni, Mo, V,

Fig. 9 Indolee HDN conversion vs product yield (%) of NiMoV/Al₂O₃-Ga₂O₃(x) catalysts varying the synthesis method (x = SG and I). (●) HIND, (▲) OEA, (■) ECH and (♦) EB
Al₂O₃ and NiMo/Al₂O₃ produce EB by hydrogenolysis of suggest that ECH derive from HIND, while NiMoV/ catalysts produce ECH with a progressive increase of OEA, previous observations allow us to conclude Furthermore, Al₂O₃ > NiMoV/Al₂O₃-Ga₂O₃(SG) > Al₂O₃-Ga₂O₃(SG), are mesoporous with surface area, pore volume and average pore radius related to the method of modification with Ga and V; hence NiMoV/Al₂O₃-Ga₂O₃(I) catalyst shown by interaction of the catalyst with the support (NiMoV/ Al₂O₃ < NiMo/Al₂O₃ < NiMoV/Al₂O₃-Ga₂O₃(I) < NiMoV/ Al₂O₃-Ga₂O₃(SG)). XPS showed that the reduced Mo, Ni and S species on surface depend on the presence of Ga and V, predominating the presence of NiMoS phase in NiMo/ Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(SG). The ²⁷Al-NMR tetrahedral/octahedral ratio was related with the type of precursor, whose relations vary between 0.25 and 0.33: NiMoV/Al₂O₃-Ga₂O₃(I) > Al₂O₃-Ga₂O₃(I) > Al₂O₃ ~ NiMo/ Al₂O₃ > NiMoV/Al₂O₃-Ga₂O₃(SG) > Al₂O₃-Ga₂O₃(SG), which. The HRTEM analysis shown that the length and stacking distribution of MoS₂ crystallites changes with the gallium addition method varied from 5.67 to 6.01 nm and 2.46 to 2.74, respectively. The activities as indolee HDN pseudo-first-order rate constants’ values (k_HDN) from 0.29 to 2.78 mol/(m²·h): NiMoV/Al₂O₃ < NiMo/Al₂O₃ < NiMoV/Al₂O₃-Ga₂O₃(I) < NiMoV/Al₂O₃-Ga₂O₃(SG). The previous observations allow us to conclude Furthermore, NiMo/Al₂O₃ and NiMoV/Al₂O₃-Ga₂O₃(I) had the highest production of ECH and EB (EB < ECH), and NiMoV/Al₂O₃-Ga₂O₃(I) showed the highest production of OEA (see Fig. 9). The NiMoV/Al₂O₃-Ga₂O₃(SG) and NiMoV/Al₂O₃-Ga₂O₃(I) catalysts produce ECH with a progressive increase of OEA, suggesting that ECH derive from HIND, while NiMoV/ Al₂O₃ and NiMo/Al₂O₃ produce EB by hydrogenolysis of HIND to OEA. In the regard, the Ga and V act as structural promoters in the NiMo catalysts, which contribute in the generation of NiMoS M-edge-like and BRIM sites for HDN.

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