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Tuning of activity and selectivity of Ni/(Al)SBA-15 catalysts in naphthalene hydrogenation

the larger total amount of acid sites.

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ARTICLE INFO	A B S T R A C T
Keywords: Nickel catalysts (Al)SBA-15 Hydrogenation Naphthalene Activity Selectivity	The hydrogenation of naphthalene was performed with nickel catalysts (4 wt. % of Ni) supported on SBA-15 and Al-SBA-15 in order to evaluate the effect of the support's acidity on the activity and selectivity of the catalysts. The incorporation of aluminum into the SBA-15 support was performed during the hydrothermal synthesis of the material with the aim to reach the isomorphic substitution of Si ⁴⁺ by Al ³⁺ leading to the generation of Brönsted acid sites. Two different precursors (nickel nitrate and a Ni:EDTA complex) were used for the preparation of the catalysts on each support. Catalysts were characterized by nitrogen physisorption, powder X-ray diffraction, temperature programmed reduction, temperature programmed desorption of ammonia, scanning and high-resolution transmission electron microscopy. The Al-SBA-15 support was characterized by solid state ²⁷ Al MAS-NMR. The results showed that the intrinsic activity of the catalysts' prepared using the Ni:EDTA complex were used in the catalyst's preparation. The catalysts prepared using the Ni:EDTA complex showed high selectivity to decalins and higher proportion of <i>trans</i> -decalin in the products than the catalysts prepared with nickel nitrate, which was attributed to a higher dispersion of the metallic Ni species and

1. Introduction

Nowadays, the fuel industry worldwide confronts many environmental challenges and must satisfy the demands and legislations restricting the emission limits of greenhouse gases. Conventionally, the fuels' quality is determined by the octane and cetane numbers [1]. Fuels with a high octane number are desirable for spark-ignition engines in order to avoid abnormal fuel combustion and also, to enable the use of higher compression ratios resulting in better thermal efficiency. On the other hand, fuels with good auto-ignition properties (high cetane number) are more suitable for conventional compression-ignition engines, ensuring the ignition of the heterogeneous air-fuel mixture [2]. In order to obtain a high-performance diesel fuel, the high aromatic content should be reduced by converting the aromatic compounds into cycloalkanes. With this aim, catalytic hydrogenation has been employed as a key process for upgrading aromatic-rich streams in the oil refinery [3].

Naphthalene is often used as a probe molecule, representative of Polycyclic Aromatic Hydrocarbons (PAHs), which constitute a large fraction in the diesel boiling point range products from oil refining and petrochemical plants [4]. Particularly, for the hydrogenation of naphthalene, the selectivity becomes important, since the obtained products: tetralin, *cis*- and *trans*-decalins, can be used separately as solvents [5–7], raw materials for 6,10-Nylon production [8] and jet-fuel stabilizers [9], respectively, in addition to many other possible applications. The above makes challenging the development of novel heterogeneous catalysts suitable for the production of desired products of naphthalene hydrogenation.

Supported nickel catalysts have been widely studied and applied in many industrially important catalytic processes as an alternative for the noble metal catalysts because of their attractive cost-efficiency ratio and their ability to activate hydrogen under mild conditions [10–12]. The performance of nickel catalysts may be significantly improved by the support's selection, catalyst preparation method or metal loading, according to the treating feedstock. In our previous works [13–15], the effects of the preparation method and metal loading in Ni/SBA-15 catalysts were studied in the hydrogenation (HYD) of naphthalene. It was found that the activity of nickel catalysts and selectivity to *trans*-decalin were enhanced when they were prepared from a Ni:EDTA precursor solution, which was attributed to a high nickel dispersion and

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small particle size (2.5–2.7 nm) that enabled the hydrogenation of both molecules: naphthalene and tetralin (tetrahydronaphthalene) [16-18]. In the work [19], Ni catalysts supported on SiMCM-41 and AlMCM-41 were prepared by the deposition-precipitation with urea (DPU) method. It was shown that both supports were partially destroyed during the DPU procedure, losing the long-range hexagonal pore order of the MCM-41 support. The activity of Ni/SiMCM-41 catalyst in naphthalene HYD was almost twice higher than that of Ni/AlMCM-41 prepared in the same condition that was attributed to the formation of larger Ni particles in the latter [19]. Nevertheless, the role of the support's acidity in the HYD behavior of Ni catalysts was not addressed in the above works [13–15,19]. Nowadays, it is well known that the acid sites could promote side reactions such as alkylation, ring-opening and isomerization, mainly dependent on the support's choice [20-23]. Among the studied acidic supports, many mesostructured zeolites owning the advantages of mesoporous materials (fast diffusion and accessibility for bulky molecules) and microporous zeolites (strong acidity and high hydrothermal stability) attracted attention. In both cases, the Brönsted acidity is due to the isomorphic substitution of Si^{4+} in the silica matrix by a trivalent cation such as Al³⁺. However, due to the amorphous character of the silica matrix in the mesostructured MCM-41 [24-26], SBA-15, etc. materials, their acidity is milder than that of the microporous crystalline zeolites, allowing to obtain a smaller amount of side by-products. On the other hand, the incorporation of aluminum into the silica structure of SBA-15 is challenging due to the different hydrolysis rates of aluminum and silicon alkoxides and the dissociation of the Al-O-Si bond under acid hydrothermal conditions [27]. In fact, the acidity of the amorphous silica-alumina materials strongly depends on the preparation method used and the Si/Al ratio [28]. S. Cui et al. [29] investigated the influence of the Si/Al molar ratio on the hydrogenation, isomerization and ring opening of naphthalene over silica-alumina supported Ni₂P catalysts. They correlated the hydrogenation activity to the small particle size of the active phase, whereas isomerization and ring opening activities were related mainly to the amount of acid sites depending on the Si/Al molar ratio.

In the present work, hydrogenation of naphthalene over Ni/AlSBA-15 (Si/Al molar ratio of 30) catalysts was investigated and compared over Ni/SBA-15 ones. Special emphasis was made on the effect of both, the support's acidity and the metal particle size on the activity and product selectivity of the catalysts. Two different nickel precursors (nickel nitrate and a Ni:EDTA complex) and two supports (SBA-15 silica and AlSBA-15) were used to modify the acidity and the Ni particle size in the catalysts.

2. Experimental

2.1. Synthesis of SBA-15

The SBA-15 support was synthesized according to the procedure described in [30]. First, 4 g of PEO_{20} - PPO_{70} - PEO_{20} copolymer ($M_w = 5800 \text{ g} \cdot \text{mol}^{-1}$, Sigma Aldrich) were dissolved in 120 mL of a 2 M HCl (J. T. Baker, 36%) solution. The temperature was set to 35 °C. Afterwards 8.5 g of tetraethyl ortosilicate (TEOS, Sigma Aldrich, 99%) was added dropwise, keeping this temperature for 20 h. Finally, temperature was raised to 80 °C and kept for 48 h without stirring in a closed Teflon-lined autoclave. The white solid product was filtered, dried at room temperature and calcined at 550 °C for 6 h for the organic template removal.

2.2. Synthesis of Al-SBA-15

The AlSBA-15 support was synthesized by the hydrothermal method following the procedure reported in [31]. First, 8.5 g of TEOS and the calculated amount of aluminum isopropoxide (Al(i-PrO)₃, Aldrich, 99%) to obtain a desired molar ratio Si/Al = 30, were added to 10 mL of aqueous HCl at pH = 1.5 upon constant magnetic stirring for 4 h.

Simultaneously, a second solution containing 4 g of PEO_{20} - PPO_{70} - PEO_{20} copolymer and 150 mL of aqueous HCl at pH = 1.5 was prepared. The latter solution was transferred in a Teflon-lined autoclave, heated to 40 °C upon constant stirring. Afterwards, the first solution containing the silicon and aluminum precursors was added dropwise to the autoclave, keeping this temperature for 20 h. The formed gel was aged at 110 °C for 24 h without stirring. The resultant yellowish white solid was filtered, washed several times with deionized water, dried at room temperature and calcined at 500 °C for 5 h in order to remove the organic template.

2.3. Preparation of catalysts

Catalysts with a nickel loading of 4 wt. % were prepared by the conventional incipient wetness impregnation method, using aqueous solutions of two different nickel precursor: a nickel nitrate (Ni (NO₃)₂·6H₂O, Sigma Aldrich) and a [Ni(EDTA)]²⁻ complex. A [Ni (EDTA)]²⁻ complex in aqueous media was prepared with a Ni:EDTA molar ratio 1:1, using nickel nitrate as a precursor and ethylenediaminetetraacetic acid as a chelating agent (C10H16N2O8, Sigma Aldrich, 99.9%). The final pH of the above solution was adjusted to 9 with an aqueous NH₃ solution. After the impregnation, the catalysts were dried at 100 °C for 12 h and calcined at 500 °C for 2 h. Hereinafter prepared catalysts will be labeled as Ni/SBA(NN), Ni/SBA(ED), Ni/AlSBA(NN) and Ni/AlSBA(ED) according to the support (SBA = SBA-15, AlSBA = AlSBA-15) and nickel precursor used (NN = nickel nitrate, ED = [Ni(EDTA)]²⁻ complex). For comparison purposes, Ni catalysts supported on commercial silica (Merck, grade 10180, 750 m²/g surface area, ~ 0.68 cm³/g pore volume and 40 Å pore size) and on γ -alumina $(222 \text{ m}^2/\text{g surface area}, 0.55 \text{ cm}^3/\text{g pore volume and 70-120} \text{ Å pore}$ size) obtained by the calcination of boehmite Catapal B (Sasol) at 700 °C for 4 h, were prepared using a nickel nitrate precursor and the procedure described above. These reference catalysts were labeled as Ni/SiO₂ and Ni/Al₂O₃, respectively.

2.4. Characterization techniques

Textural properties of supports and catalysts were determined with a Micromeritics ASAP 2020 automatic analyzer at liquid N₂ temperature (-197 °C). Prior to the experiments, the samples were degassed (P < 10^{-1} Pa) for 6 h at 270 °C. N₂ adsorption-desorption isotherms were obtained and specific surface areas were calculated by the BET method (S_{BET}). The total pore volume (V_p) was determined by nitrogen adsorption at a relative pressure of 0.98 and pore size distributions were obtained from both, adsorption and desorption isotherms by the BJH method. The reported mesopore diameters (D_{ads} and D_{des}) correspond to the maxima of the pore size distributions, whereas the micropore area (S_µ) was estimated using the correlation of t-Harkins & Jura (t-plot method).

The ²⁷Al Magic Angle Spinning nuclear magnetic resonance (²⁷Al MAS-NMR) spectra was obtained using a Varian/Agilent 600 spectrometer with rotors of ZrO_2 (diameter = 4.2 mm), at 22 °C using a source frequency of 78.2 MHz.

The XRD measurements of all samples were performed on a Siemens D5000 diffractometer, using CuK_{α} radiation ($\lambda = 1.5406$ Å) and a goniometer speed of 1°(2 θ) per minute. The diffraction patterns were recorded from 3° to 80°(2 θ).

Temperature programmed reduction (TPR) and temperature programmed desorption of ammonia (NH₃-TPD) experiments were carried out on a Micromeritics AutoChem II 2920 automatic analyzer equipped with a thermal conductivity detector. In the TPR experiments, about 50 mg of catalyst were placed in a quartz reactor in a tubular furnace, where the samples were first pretreated *in situ* at 400 °C for 2 h under air flow and then cooled in an Ar stream. Then, the reduction step was performed from room temperature to 1000 °C with a heating rate of 10 °C/min under a stream of an H₂/Ar mixture (10:90 mol:mol, 50 mL/min flow). The consumption of H₂ at different temperatures was recorded. In the TPD experiments, first 50 mg of a calcined catalyst were pretreated *in situ* at 500 °C for 30 min in a helium flow to remove water and other contaminants. Afterwards, the samples were cooled to 120 °C and exposed to a NH₃/He mixture stream (10:90 mol:mol, 20 mL/min flow) for 30 min. The desorption of ammonia was performed in a He stream (50 mL/min flow) from 120 °C to 500 °C with a heating rate of 10 °C/min, keeping the final temperature until the trace reached the baseline.

The chemical composition of the catalysts was determined by a SEM-EDX analysis, using a JEOL 5900 LV microscope with OXFORD ISIS equipment.

The high-resolution transmission electron microscopy (HRTEM) characterization of reduced catalysts was performed using a JEOL 2010 microscope (resolving power 1.9 Å). The solids were ultrasonically dispersed in heptane and the suspension was collected on carbon coated grids. The dispersion of Ni in reduced catalysts was determined based on the average particle size resulting from the measurements of the size of at least 300 Ni particles observed in different HRTEM images of the same sample. The dispersion of Ni (D_{Ni}) was calculated using Eqs. (1) and (2), where d_{Ni} at is the atomic diameter of nickel (2.48 Å) and d_{Ni} is the average particle size of metallic Ni in the catalyst [32,33]. Then, the number of Ni surface sites (Ni atoms accessible for interaction with reactant molecules) was calculated with Eqs. (3) and (4), where $Ni_{(T)}$ is the total number of nickel atoms on the catalyst, Ni(S) is the number of surface atoms, W_{Ni} is the mass fraction of Ni on the catalyst, and M_{Ni} is the molar mass of Ni. The number of Ni surface sites $(Ni_{(S)})$ was used to calculate the turnover frequency (TOF) of the catalysts in the hydrogenation of naphthalene.

$$D_{Ni} = \frac{5.01 \cdot d_{Ni \, al.}}{d_{Ni}}, \text{ when } d_{Ni} > 6 \, nm$$
(1)

$$D_{Ni} = \left(\frac{3.32 \cdot d_{Ni \ at.}}{d_{Ni}}\right)^{0.81}, \text{ when } 1 \text{ nm} < d_{Ni} < 6 \text{ nm}$$
(2)

$$Ni_{(S)} = D_{Ni} \bullet Ni_{(T)} \tag{3}$$

$$Ni_{(T)} = \frac{W_{Ni}}{M_{Ni}} \tag{4}$$

2.5. Catalytic activity testing

Prior to the catalytic tests, the catalysts were reduced ex-situ in a Ushaped glass flow reactor at 400 $^{\circ}$ C for 4 h, under a stream of H₂/Ar (30:70 mol:mol) at atmospheric pressure. The hydrogenation of naphthalene was performed in a 300 mL stainless steel batch reactor (Parr), with a 0.06 M solution of naphthalene (Aldrich, 99%) in hexadecane (Aldrich, 99.5%). In each activity test, 50 mL of naphthalene solution and 100 mg of reduced Ni catalyst were used. The reactions were performed at 300 $^{\circ}$ C and 7.3 MPa of total H₂ pressure for 6 h. Small aliquots of the reaction mixture were taken every 15 min for the first hour and then hourly. The course of the reaction was followed by analyzing the taken aliquots in an Agilent 6890 gas chromatograph equipped with a flame ionization detector and a non-polar methyl siloxane capillary column HP-1 (50 m x 0.32 mm inner diameter and 0.52 μm film thickness). Products' identification was performed in an Agilent 7890A GC system equipped with a 5975C MS detector. The reaction scheme of naphthalene hydrogenation is presented in Fig. 1. According to this mechanism, naphthalene is firstly hydrogenated to tetralin (intermediate product), which can suffer further hydrogenation to cis- and trans- isomers of decalin as final reaction products. Upon the reaction conditions used in the present study (large excess of hydrogen), the equilibrium between naphthalene and tetralin is shifted towards the product. Based on this, we propose a simplified reaction scheme (Eq.

(5)) for the kinetic analysis.

Naphthalene (NP) $\xrightarrow{k_1}$ Tetralin (TR) $\xrightarrow{k_2}$ Decalins(DECS) (5)

Catalytic activity was determined by measuring naphthalene concentrations at different reaction times. The conversion of naphthalene (X_{NP}) was calculated as shown in Eq. (6), where C_{NP0} is the initial naphthalene concentration $(mol \cdot L^{-1})$ in the reaction mixture and C_{NP} is the concentration $(mol \cdot L^{-1})$ of naphthalene at different reaction times (t, h). The reaction rate constants (k_1 and k_2) were determined assuming that the naphthalene (NP) and tetralin (TR) hydrogenation reactions are of the pseudo-first order (Eq. (5)) due to the excess of H₂. The rate constants k_1 and k_2 were calculated using a curve-fitting method for Eqs. (7) and (8), respectively. Finally, k_1 and k_2 were normalized (k_{1N} and k_{2N}) by the volume (V, L) of the reaction mixture per weight of the catalyst (m_{cat} , g) and amount of Ni in the catalysts (m_{Ni} , g_{Ni}/g_{cat}) as shown in Eq. (9).

$$X_{NP} = \frac{C_{NP_0} - C_{NP}}{C_{NP_0}} \times 100\%$$
(6)

$$C_{NP} = C_{NP_0} \cdot e^{-k_1 t}$$
⁽⁷⁾

$$C_{TR} = \frac{C_{NP_0} \cdot k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$
(8)

$$k_{xN} = \frac{(V)(k_x)}{(m_{cat})(m_{Ni})}, \text{ where } x = 1, 2$$
 (9)

3. Results and discussion

3.1. Supports' and catalysts' characterization

The chemical composition of the AlSBA-15 support and prepared nickel catalysts was determined by the SEM-EDX method (Table 1). The aluminum content in the AlSBA-15 support was 3.6 wt. % (Si/Al molar ratio of 31), which is consistent with the theoretically-expected Si/Al molar ratio of 30. In addition, the real Ni loadings in the catalysts were close to the theoretically-expected ones (4 wt. %).

The ²⁷Al MAS-NMR spectrum of the AlSBA-15 support presented two signals (Fig. 2). The first higher-intensity signal located at 55 ppm was assigned to the tetrahedrally-coordinated Al^{3+} species (AlO₄ structural units, Al(Td)). These aluminum species were incorporated into the silica structure isomorphically substituting Si⁴⁺ cations and they were responsible for the generation of the Brönsted acid sites [34]. The second, lower intensity signal at 0 ppm was attributed to the octahedrally-coordinated Al^{3+} species (AlO₆ structural units, Al(Oh)) corresponding to extra-framework aluminum oxide that is not a part of the SBA-15 structure [34–36]. The integration of the areas of the Al(Td) and Al(Oh) peaks resulted in the Al(Td):Al(Oh) ratio = 1.6:1, indicating that the majority of the added aluminum (~60%) was incorporated into the SBA-15 framework structure.

The SBA-15 and AlSBA-15 supports exhibited a type IV nitrogen adsorption-desorption isotherm (Fig. 3A and A', respectively) corresponding to mesoporous solid materials. The H1 hysteresis loop of the SBA-15 material is associated to the presence of uniform cylindrical pore channels. On the other hand, the AlSBA-15 support presented the H2 hysteresis loop due to either pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. This kind of hysteresis has also been observed for silica gel or mesostructured materials such as SBA-16 or KIT-5 [37]. The difference in the shape of the hysteresis loop between SBA-15 and AlSBA-15 materials can be due to the different conditions of the synthesis of these supports (see experimental part) and to the incorporation of aluminum into the SBA-15 structure leading to its distortion. All Ni catalysts preserved the characteristic isotherm features of the corresponding supports (Fig. 3). Nevertheless, a decrease in the specific textural characteristics (S_{BET}, S_u



Fig. 1. Scheme of the naphthalene hydrogenation.

Table 1				
Chemical composition ^a and textural	characteristics ^b	of the	prepared	supports
and catalysts.				

Sample	Ni loading (wt. %)	S _{BET} (m ² /g)	S _μ (m ² / g)	V _p (cm ³ / g)	D _{ads} (nm)	D _{des} (nm)
SBA-15 Ni/SBA(NN) Ni/SBA(ED) AlSBA-15	- 4.1 ± 0.7 4.2 ± 0.7	861 737 523 570	129 121 51 17	1.12 0.94 0.85 0.92	7.8 7.6 7.4 9.3	6.1 5.6 6.3 7.0
Ni/AlSBA(NN) Ni/AlSBA(ED)	3.9 ± 0.6 4.0 ± 0.8	534 433	14 40	0.86 0.80	9.3 9.3	6.8 6.8

^a Determined by SEM-EDX. The theoretical Ni loading in the catalysts was 4 wt. %.

 $^b~S_{BET}$, BET surface area; S_{μ} , micropore area; V_p , total pore volume; D_{ads} and D_{des} , pore diameters determined from adsorption and desorption branches of N_2 adsorption-desorption isotherm, respectively.



Fig. 2. $^{27}\mathrm{Al}$ MAS-NMR spectrum of the AlSBA-15 support (Si/Al molar ratio = 30).

and V_P) was observed after the incorporation of nickel to the supports (Table 1) associated to the increase of the materials' density. The BET surface area of the AlSBA-15 support was ~34% lower than of the SBA-15. Also, the amount of micropores was significantly smaller in the AlSBA-15 than in the SBA-15 analog. This can be attributed again to the difference in the preparation conditions used for the synthesis of these materials and to the presence of extra-framework alumina species in the

Al-containing support. Fig. 3B and B' show the pore diameter distributions of SBA-15 and AlSBA-15 supports and their respective catalysts. A monomodal and uniform distribution of pore sizes was observed for the SBA-15 materials and Ni/SBA catalysts, while for the AlSBA-15 material and Ni catalysts, broader pore size distributions were obtained, with the pore size maxima located at 9.3 nm (adsorption) and 7 nm (desorption). This pore broadening is consistent with the higher temperature used for the synthesis of AlSBA-15 material [38,39] and moreover, to the increasing amount of isopropanol present in the reaction mixture, which is formed by the hydrolysis of the aluminum precursor that is inserted into the Pluronic P123 micelles, increasing their size [38,40]. Additionally, pore size distributions obtained from the desorption branches of the isotherms for the AlSBA-15 support and catalysts (Fig. 3C') were also broader than those of the corresponding materials of the SBA-15 series. In spite of the above-described differences in the textural properties, all prepared Ni catalysts had attractive textural characteristics, being smaller the BET surface areas and total pore volumes in the catalysts prepared using a $[Ni(EDTA)]^{2-}$ complex. In this case, the impregnation solutions used in the catalysts' preparation had a basic pH value (9) that could have provoked the partial dissolution of SBA-15 and AlSBA-15 materials in the basic media leading to a decrease in the textural properties.

The diffraction patterns of the SBA-15 and AlSBA-15 supports and prepared Ni catalysts in their oxide form are shown in Fig. 4A. All of the XRD patterns exhibited a broad signal between 15 and 30° (20) characteristic of the amorphous silica. In addition to the above signal, four reflections were observed at 37.2, 43.3, 62.9 and 75.4°(20) in the diffraction patterns of the Ni/SBA(NN) and Ni/AlSBA(NN) catalysts evidencing the presence of the crystalline NiO phase (JCPDS-ICDD card 01-071-1179). For the Ni/SBA(ED) and Ni/AlSBA(ED) catalysts, no reflections of any crystalline phase were detected. These results show that the nickel precursor used in the catalyst's preparation has an important effect on the dispersion of the supported NiO species. The use of a [Ni(EDTA)]^{2–} complex resulted in a better dispersion of the deposited Ni species on both SBA-15 and AlSBA-15 supports. It seems that the effect of the precursor on the dispersion of NiO is much stronger than the effect of the incorporation of aluminum to the SBA-15 material.

TPR profiles of the calcined Ni catalysts are shown in Fig. 5. The reduction of NiO takes place in a single step (NiO + $H_2 \rightarrow Ni + H_2O$). The reduction profile of the Ni/SBA(NN) catalyst showed a broad interval of hydrogen consumption (between 300 and 500 °C) with a maximum at 382 °C (Fig. 5A). It can be seen that this broad peak is formed by multiple overlapped signals that indicates the presence of nickel species of different characteristics. Therefore, it can be concluded that the Ni/SBA(NN) catalyst should have some nickel oxide species located on the external surface of the SBA-15 support (detected by



Fig. 3. (A) N₂ adsorption-desorption isotherms of the SBA-15 support and SBA-15-supported Ni catalysts. (B and C) Pore size distributions from the adsorption and desorption isotherm branches, respectively. (A', B', C') The same for the AlSBA-15 support and the AlSBA-15-supported Ni catalysts.

XRD), which can be easily reduced, and other NiO species, more difficult to be reduced, that are in stronger interaction with the silica support or are located inside the mesopores of the SBA-15 support [41,42]. The TPR profile of the Ni/SBA(ED) catalyst was symmetric, with the maximum at increased temperature (456 °C), indicating a stronger metal-support interaction than in the Ni/SBA(NN) catalyst. On the other hand, the reduction temperatures of the main reduction signal of the AlSBA-15-supported nickel catalysts (Fig. 5B) were similar to those of the SBA-15-supported ones. A similar increase in the reduction temperature (from 385 to 450 °C) was observed when the nickel precursor was changed from nickel nitrate to a [Ni(EDTA)]²⁻ complex. In addition, the reduction of nickel species in the AlSBA-15-supported catalysts was also prolonged at a higher temperature interval (500-700 °C) that can be associated to NiO species in a stronger interaction with the framework and extra-framework aluminum species of the AlSBA-15 support. Table 2 shows the degrees of reduction of the catalysts (α), determined taking as a reference the theoretical hydrogen consumption of each catalyst based on its real Ni content estimated by

SEM-EDX. It was observed for the SBA-15-supported catalysts, the Ni/ SBA(ED) had a lower degree of reduction than the Ni/SBA(NN) sample. In line with the positions of the reduction peaks described above, this can be attributed to a stronger metal-support interaction in the first catalyst that makes more difficult the complete reduction of the supported NiO species to the metallic Ni. Similar trends were also observed for the AlSBA-15-supported catalysts, where the Ni/AlSBA(ED) catalyst showed a lower reducibility than its Ni/AlSBA(NN) counterpart. Nevertheless, the difference in the values of α was much smaller for the AlSBA-15 series of the catalysts than for the SBA-15-supported samples. This points out that on the Al-containing support, the nature of the nickel precursor used has a small effect on the degree of reduction of the deposited Ni species, probably, because of a strong metal-support interaction. By the same reason, the proportions of the reduced Ni species in the Ni/AlSBA catalysts (α , Table 2) were smaller than in the corresponding Ni/SBA ones.

The ammonia TPD profiles of the supports and calcined catalysts are displayed in Fig. 6 and the results of the quantification of the amount of

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Fig. 4. Powder X-ray diffraction patterns of (A) supports and nickel catalysts in their oxide state and (B) reduced catalysts. ▲ NiO (JCPDS card 01-071-1179), ★ Ni (JCPDS card 01-071-4655).

acid sites are presented in Table 3. In this table, it can be observed that the incorporation of aluminum to the SBA-15 material resulted in a more than five times increase in the total amount of acid sites compared to the SBA-15 silica support. For the Ni catalysts, also the samples supported on the AlSBA-15 exhibited significantly higher total acidity than the corresponding Ni/SBA catalysts. Regarding the nickel precursor used, the catalysts prepared from a [Ni(EDTA)]2- complex showed higher surface acidity than their analogs prepared from nickel nitrate, which can be correlated with the dispersion of the deposited NiO species in the catalysts (XRD results, Fig. 4). It is worth mentioning that the Ni/AlSBA(ED) catalyst showed the highest amount of total acid sites among all catalysts prepared in the present work. In order to separate the contributions of the support and the supported Ni oxide species to the acidity of the catalysts, specific acidity was calculated. This acidity represents an increase in the amount of acid sites normalized per m² of the catalyst surface due to the incorporation of nickel oxide species in the catalysts. This specific acidity was larger on the Alcontaining SBA-15 support, as well as when a $[Ni(EDTA)]^{2-}$ complex was used in the preparation.

3.2. Characterization of the active phase in reduced catalysts

After the catalysts' reduction at 400 °C for 4 h under a H₂/Ar stream, the active phase was characterized by XRD and HRTEM. The XRD patterns of the reduced catalysts are shown in Fig. 4B. Three catalysts, Ni/SBA(NN), Ni/AlSBA(NN) and Ni/AlSBA(ED), presented three reflections at 44.6, 52.0 and 76.3° (20), attributed to metallic Ni (JCPDS-ICDD card 01-071-4655). In addition, the catalysts prepared using a nickel nitrate solution, Ni/SBA(NN) and Ni/AlSBA(NN), also had three low-intensity reflections of the remaining NiO phase. The size of Ni crystallites in the reduced catalysts, estimated using the Scherrer equation, increased from Ni/AlSBA(ED) (7.2 nm) to Ni/SBA(NN) (11.0 nm) and Ni/AlSBA(NN) (12.1 nm) (Table 4). It is worth mentioning that, according to the XRD results for the catalysts in oxide state (Fig. 4A), the size of the NiO crystallites in the calcined catalysts also increased in the same order; namely, no NiO crystals were detected in the Ni/AlSBA(ED) sample (size below 5 nm), while for the Ni/SBA(NN) and the Ni/AlSBA(NN) catalysts, the size of the NiO crystallites was 13.0 nm and 16.8 nm, respectively (Table 4). Larger NiO and Ni crystallites were formed on the AlSBA-15 support compared to those on the



Fig. 5. Reduction profiles of the calcined Ni catalysts supported on (A) SBA-15 and (B) AlSBA-15.

Table 2

Hydrogen consumptions and degree of reduction (α) of the prepared nickel catalysts.

Catalyst	H_2 consumption (m	mol/g)	α^{a}
	Experimental	Theoretical	
Ni/SBA(NN)	0.581	0.699	0.84
Ni/SBA(ED)	0.494	0.716	0.69
Ni/AlSBA(NN)	0.484	0.664	0.73
Ni/AlSBA(ED)	0.479	0.682	0.70

^a α , degree of reduction was determined as a ratio of hydrogen consumed by each catalyst to the theoretical hydrogen consumption calculated based on the experimentally determined Ni loading.

SBA-15 silica, which can be attributed to the smaller surface area of the AlSBA-15 support $(570 \text{ m}^2/\text{g})$ than that of the SBA-15 $(861 \text{ m}^2/\text{g}, \text{Table 1})$. According to the above results, the incorporation of aluminum to the SBA-15 support did not improve the dispersion of the NiO and Ni phases. Finally, it should be mentioned that the Ni/SBA(ED) catalyst was the only one in which the presence of any crystalline phase of nickel (NiO or Ni) was not clearly detected by XRD (Fig. 4A and B) evidencing the best dispersion of the deposited nickel species in both, oxide and reduced states.

HRTEM images of the reduced Ni catalysts are presented in Fig. 7. Large Ni particles with a size varying from 5 to 25 nm were observed on the images of the Ni/SBA(NN) catalyst. In contrast, for the Ni/SBA(ED) catalyst, only the presence of very small Ni particles (from 1 to 6 nm) was detected, that is in line with the results obtained for this catalyst by XRD, as described above. Regarding the catalysts supported on the Alcontaining support, Ni/AlSBA(NN) showed Ni particles with a size between 5 and 25 nm, while the Ni/AlSBA(ED) had smaller particles (from 3 to 12 nm size). More detailed information on the dispersion of metallic Ni in the catalysts was obtained from the particle size distributions also shown in Fig. 7. These distributions were calculated by measuring the size of at least 300 Ni particles on different images of the same catalyst. The average particle size of metallic Ni in the reduced catalysts was also estimated from these distributions giving the results shown in Table 4. According to these results, the average particle size of reduced Ni particles increased in the following order: Ni/SBA(ED) < Ni/AlSBA(ED) < Ni/SBA(NN) < Ni/AlSBA(NN). This result is in a good agreement with the particle sizes calculated from the XRD patterns of the reduced catalysts (Table 4). In both cases, the Ni/SBA(ED) catalyst showed the lowest Ni particle size among all the catalysts.

The average particle size of metallic Ni determined based on the HRTEM results was also used for the calculation of Ni dispersion (D_{Ni} , Table 4) in the reduced catalysts. It was observed that the highest dispersion of Ni was obtained in the Ni/SBA(ED) catalyst (38.2%) followed by the Ni/AlSBA(ED) catalyst (20.0%). On the other hand, the catalysts prepared using a nickel nitrate solution, Ni/AlSBA(NN) and Ni/SBA(NN), presented similar and relatively low Ni dispersions (10.1% and 10.5%, respectively). The above results point out to the clear effect of the nickel precursor used on the dispersion of metallic Ni on the SBA-15 and AlSBA-15 supports, namely, the use of a [Ni (EDTA)]^{2–} complex led to a high dispersion, while a nickel nitrate to a low one.

3.3. Catalytic performance in the hydrogenation of naphthalene

Catalytic performance of the prepared Ni catalysts was evaluated in the hydrogenation (HYD) of naphthalene (NP). Table 5 shows the kinetic parameters $(k_1, k_2, k_{1N} \text{ and } k_{2N})$ obtained based on the simplified reaction scheme (Eq. (5)) and assuming that both hydrogenation reactions (HYD of naphthalene and HYD of tetraline) are of the pseudofirst order, since hydrogen was taken in a large excess. According to this, k_1 and k_{1N} constants correspond to naphthalene hydrogenation, whereas k_2 and k_{2N} represent hydrogenation of tetralin. It can be observed in Table 5 that the catalytic activity of the Ni/SBA(NN) and Ni/ AlSBA(NN) catalysts prepared in the present work was higher than that of the reference Ni/SiO₂ and especially the Ni/Al₂O₃ samples prepared using nickel nitrate as a precursor. It is interesting to note that the k_1 and k_{1N} values obtained for the Ni/SiO₂ reference were only slightly lower than those of the Ni/SBA(NN), which can be attributed to the high surface area of the commercial silica $(750 \text{ m}^2/\text{g})$ used as a support for the reference catalyst. The catalysts prepared using a [Ni(EDTA)]²⁻ complex, Ni/SBA(ED) and Ni/AlSBA(ED), resulted to be more active in the hydrogenation of both, naphthalene and tetralin (k_1 and k_2 values, respectively) than the catalysts prepared from a nickel nitrate precursor, Ni/SBA(NN) and Ni/AlSBA(NN). A similar trend was also observed for the specific activity of the catalysts represented by the k_{1N} and k_{2N} constants normalized per gram of Ni and per volume of the reaction mixture (Table 5). Comparison of k_{1N} values points out that the rate of hydrogenation of naphthalene increased in the following order Ni/Al₂O₃ < Ni/SiO₂ < Ni/SBA(NN) < Ni/AlSBA(NN) < Ni/ SBA(ED) < Ni/AlSBA(ED), whereas the order of activity of the catalysts



Fig. 6. Ammonia TPD profiles of the supports and the calcined Ni catalysts supported on (A) SBA-15 and (B) AlSBA-15.

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Table 3

Acidic properties of the supported nickel catalysts.

Sample	Amount of acid sites (µmo	Specific acidity ^a (μ mol NH ₃ /m ²)			
	Weak (120–200 °C)	Medium (200-400 °C)	Strong (400–500 °C)	Total	
SBA-15	5.0	41.4	12.1	58.5	_
Ni/SBA(NN)	10.4	56.7	33.1	100.2	0.06
Ni/SBA(ED)	60.8	157.6	36.9	255.3	0.38
AlSBA-15	107.8	208.2	29.7	345.7	-
Ni/AlSBA(NN)	140.1	293.5	46.7	480.3	0.25
Ni/AlSBA(ED)	146.0	379.9	59.0	584.9	0.55

^a Calculated as the difference between the total acidity of the catalyst and the total acidity of the corresponding support, normalized per S_{BET} of the catalyst.

Table 4

Average particle size and dispersion of nickel in the prepared catalysts.

Catalyst	NiO particle	Ni particle size (nm)		D_{Ni}^{c} (%)	$Ni_{(S)}^{d}$	
	size (iiiii)	XRD ^a HRTEM ^b			(IIIIIOI _{Ni} / g _{cat})	
Ni/SBA(NN) Ni/SBA(ED) Ni/AlSBA(NN) Ni/AlSBA(ED)	13.0 n. d. ^e 16.8 n. d.	11.0 n. d. 12.1 7.2	11.8 2.7 12.3 6.2	10.5 38.2 10.1 20.0	0.073 0.273 0.067 0.137	

^a Determined by the Scherrer equation from the main reflection peaks of NiO and metallic Ni in each catalyst.

^b Determined from the measurement of the size of at least 300 Ni particles observed on different HRTEM images of the same sample.

 $^{\rm c}$ D_{Nis} nickel dispersion calculated based on the average size of Ni particles determined from HRTEM.

 $^d~Ni_{(S)},$ nickel atoms located on the surface of Ni particles (Ni atoms accessible for interaction with reactant molecules).

^e n. d., crystalline phases were not detected by XRD.

in the hydrogenation of tetralin was different: $Ni/Al_2O_3 = Ni/SiO_2 < Ni/AlSBA(NN) < Ni/SBA(NN) < Ni/AlSBA(ED) < Ni/SBA(ED).$ For the hydrogenation of both molecules, the catalysts pre-

pared using a $[Ni(EDTA)]^{2-}$ complex were more active than those prepared from a nickel nitrate solution.

The turnover frequency (TOF) values were also calculated for HYD of naphthalene with the tested catalysts based on the nickel dispersion determined from the HRTEM characterization of the reduced catalysts. The TOF values represent the intrinsic activity of the prepared catalysts normalized per one Ni atom located on the catalyst's surface and accessible for the interaction with naphthalene molecules. It was observed that the TOF values increased in the following order: Ni/SBA(ED) < Ni/ SBA(NN) < Ni/AlSBA(NN) < Ni/AlSBA(ED), which differs from the trends observed for the rate constants. The Ni/SBA(ED) catalyst had the lowest TOF value of 150 h^{-1} , while the Ni/AlSBA(ED) catalyst showed the highest TOF value $(320 h^{-1})$. This result points out that in general, the dispersion of metallic Ni species (depending on the nickel precursor used, Table 4) and the acidity of the catalysts (Table 3) contribute to the TOF values. It can be mentioned that the catalysts prepared in the present work have two types of acidity: Brönsted acidity that can be attributed to the support used and Lewis acidity generated by the deposition of the nickel species during the catalyst's preparation. An increase in the support's acidity and the presence of Brönsted acid sites due to the incorporation of Al atoms into the SBA-15 support resulted in higher TOF values of the Ni catalysts in hydrogenation of naphthalene. On the other hand, the effect of employing a [Ni(EDTA)]²⁻ precursor instead of nickel nitrate was not as clear: a slight decrease of the TOF value was observed for the Ni/SBA(ED) catalyst compared to the Ni/ SBA(NN), while the Ni/AlSBA(ED) catalyst showed a notorious increase in the TOF value in comparison with Ni/AlSBA(NN).

In the case of the catalytic activity represented by the reaction rate constants, it seems that the hydrogenation of naphthalene, as well as of tetralin, is related mostly to nickel particle size. Thus, higher kinetic parameter values (both k_1 and k_2) were obtained for the catalysts with smaller metallic Ni particles, Ni/SBA(ED) and Ni/AlSBA(ED). Particularly, this effect was stronger for the hydrogenation of tetralin (k_{2N} , Table 5), which is structure-sensitive from the adsorption point of view [43]. However, the intrinsic activity of nickel catalysts (TOF values, Table 5) was improved by increasing the support's acidity by aluminum incorporation. The above results are reasonable from the point of view of the literature reports, where it was noted that the electron-deficient surface of metallic Ni enhances the adsorption of H₂ (beneficial for the intrinsic hydrogenation activity), which is favored with acidic supports [44,45].

Table 6 shows the composition of reaction products obtained with each catalyst at 50 and 95% of naphthalene (NP) conversion. It can be observed that the catalysts prepared using a nickel nitrate solution, Ni/ SBA(NN) and Ni/AlSBA(NN), showed a high proportion of tetralin in the products (above 90%) even at a high naphthalene conversion (95%). The Ni/AlSBA(NN) catalyst was 100% selective to tetralin at 50% of NP conversion and 99.3% selective at 95% of NP conversion. This can be attributed to a large average size of the reduced Ni particles in these catalysts (11.8 nm in Ni/SBA(NN) and 12.3 nm in Ni/AlS-BA(NN), Table 4). On the other side, the catalysts prepared using a [Ni (EDTA)]²⁻ complex, having smaller Ni particles (2.7–6.2 nm, Table 4) and higher acidity, resulted in the formation of considerable amounts of cis- and trans-decalins at both naphthalene conversions (50 and 95%). The Ni/SBA(ED) catalyst showed the highest selectivity to decalins among all prepared samples. This result is in line with previous report [43], where it was shown that tetralin hydrogenation is structure-sensitive to very fine nickel particles [43]. In addition, the Ni/SBA(ED) catalyst showed an increase in the ratio of trans-decalin to cis-decalin with the increase of naphthalene conversion (from 1.24 at 50% of NP conversion to 2.27 at 95% conversion) that indicates the ability of this catalyst to cis-/trans- isomerization of decalins. The isomerization of decalins on this catalyst became more notorious at high NP conversions (above 80%), when concentrations of both naphthalene and tetralin were small (Fig. 8). Other catalyst, Ni/AlSBA(ED), also selective to decalins, showed only a small increase in the trans-decalin/cis-decalin ratio (from 1.37 to 1.43) with increasing NP conversion from 50 to 95%. In this case, the cis-/trans- isomerization of decalins was not accelerated even at high NP conversion (Fig. 8). It can be observed that the isomerization of decalins does not follow the trends of the changes in the acidity of the catalysts, since the Ni/SBA(ED) catalyst with the highest isomerization activity was less acidic than the Ni/AlSBA(ED) and Ni/AlSBA(NN) counterparts (Table 3). This points out to the bifunctional character of the cis-/trans- isomerization of decalin, which is a saturated bicyclic molecule. This molecule cannot be activated directly on the Brönsted acidic site of the catalyst because of very low basicity, similar to that of the other saturated hydrocarbons (paraffins). Therefore, the most probable mechanism is through the participation of two types of active sites: the metal and the acid ones. At the first step, dehydrogenation of cis-decalin occurs at a metal active site leading to the formation of a double bond, which can be easily protonated at a Brönsted acid site with the subsequent cis-/trans-isomerization of the



Fig. 7. HRTEM micrographs and particle size distributions of the reduced nickel catalysts.

able 5	
ctivity of the prepared Ni catalysts in the hydrogenation of naphthalene and tetrali	n.

Catalyst	Pseudo-first orde	er rate constants		$\text{TOF}^{a} (\text{mmol}_{\text{NP}} \text{ mmol}_{\text{Ni}(S)}^{-1} \cdot h^{-1})$	
	k_1 (h ⁻¹)	k_2 (h ⁻¹)	k_{IN} (L· g_{Ni}^{-1} · h^{-1})	k_{2N} (L·g _{Ni} ⁻¹ ·h ⁻¹)	
Ni/SBA(NN)	0.41	0.20	5.0	2.4	168
Ni/SBA(ED)	1.36	22.02	16.2	262.1	150
Ni/AlSBA(NN)	0.48	0.06	6.2	0.8	215
Ni/AlSBA(ED)	1.46	3.31	18.3	41.4	320
Ni/SiO ₂	0.38	0.0	4.7	0.0	n. d. ^b
Ni/Al ₂ O ₃	0.19	0.0	2.4	0.0	n. d.

^a TOF (turnover frequency) was calculated for naphthalene (NP) hydrogenation by multiplying the initial reaction rate by the volume of the reaction mixture and then dividing among the amount of accessible surface Ni sites ($N_{i(S)}$) in the catalyst used.

^b n. d., not determined.

obtained carbocation and deprotonation. Finally, hydrogenation of the obtained isomer takes place again at the metal site. This supposition considering participation of the metal active sites at the beginning of the reaction can be confirmed by the fact that the *cis-/trans*-isomerization of decalins is related to the size of the metallic Ni particles in the catalysts. Thus, the isomerization occurs quickly at the Ni/SBA(ED)

catalyst with very small Ni particles (average size 2.7 nm, 38.2% of Ni dispersion, Table 4), it becomes much slower at the Ni/AlSBA(ED) sample (average size of Ni particles 6.2 nm, 20.0% of Ni dispersion) and no isomerization was detected on the Ni/SBA(NN) and Ni/AlSBA(NN) catalysts (Fig. 8) with large Ni particles (11.8–12.3 nm, about 10% Ni dispersion). In addition, the above results are in line with the previous

Table 6

Product yields and selectivity to decalins obtained with the prepared Ni catalyst at different naphthalene (NP) conversions.

Catalyst	Yields of the products ^a (%)			Selectivity to decalins	
	TR trans-DEC		cis-DEC	S _{DECS} ^b (%)	trans-DEC/cis- DEC ratio
	At 50 %	% of NP convers	ion		
Ni/SBA(NN)	90.4	4.0	5.6	9.6	0.71
Ni/SBA(ED)	19.2	44.8	36.0	80.8	1.24
Ni/AlSBA(NN)	100.0	0.0	0.0	0.0	-
Ni/AlSBA(ED)	44.2	32.2	23.5	55.8	1.37
	At 95 %	6 of NP convers	ion		
Ni/SBA(NN) ^c	-	-	-	-	-
Ni/SBA(ED)	0.9	68.8	30.3	99.1	2.27
Ni/AlSBA(NN)	99.3	0.3	0.4	0.7	0.75
Ni/AlSBA(ED)	8.5	53.8	37.7	91.5	1.43

^a TR, tetralin; cis-DEC, cis-decalin; trans-DEC, trans-decalin.

 $^{\rm b}~S_{\rm DECS},$ selectivity to decalins calculated as a sum of cis- and trans-decalins in the products.

 $^{\rm c}$ Maximum naphthalene conversion reached with this catalyst at 6 h reaction time was 56%.

study [46], where the isomerization of the C₆ naphthenic rings of decalins was studied with the bifunctional Pt/USY catalyst. It was observed that the isomerization rate and the formation of ring opening products increased in the presence of Pt in the Pt/USY catalyst, as compared to the monofunctional USY sample, and with increasing the proximity between the Pt and acid sites. According to this report and our results, it can be concluded that the efficient catalyst for the *cis*-/ *trans*-isomerization of decalins should be bifunctional with very small Ni particles and Brönsted acid sites.

4. Conclusions

In the present work, two series of nickel catalysts supported on SBA-15 and AlSBA-15 were prepared using two different precursors (nickel nitrate and a $[Ni(EDTA)]^{2-}$ complex). The changes in the support's composition and the nickel(II) compound used resulted in catalysts with different acidity and dispersion of the metallic Ni particles. The evaluation of the prepared catalysts in the hydrogenation of naphthalene showed that the catalysts presented significant differences in the activity and selectivity of the products. It was found that the use of nickel nitrate as a precursor resulted in catalysts with relatively large reduced Ni particles (11.8–12.3 nm average size), which were highly selective towards the formation of tetralin. On the other hand, the catalysts prepared using a [Ni(EDTA)]²⁻ complex were more active than those prepared from a nickel nitrate and showed high selectivity to the formation of cis- and trans-decalins. In addition, the Ni/SBA(ED) catalyst resulted to be the only one among all prepared samples with high activity for the cis-/trans-isomerization of decalins, which was attributed to the acidic characteristics of this catalyst and the presence of very small (2.7 nm average size) metallic Ni particles. Therefore, the principal contribution of the present study is that it was shown that the correct selection of the Ni(II) precursor and the SBA-15 support, with or without Al, opens a wide field of possibilities for the preparation of supported Ni catalysts with improved activity and tunable selectivity to the desired products.

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Fig. 8. Reaction product compositions obtained in the hydrogenation of naphthalene.

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