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Improving the selectivity to HDS in the HDT of synthetic FCC naphtha using sodium doped amorphous aluminosilicates as support of CoMo catalysts

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ABSTRACT

CoMo catalysts supported on sodium-doped amorphous aluminosilicates (ASA) with different Si/(Si + Al) ratios were prepared. The catalytic performance of these catalysts in the HDT of synthetic FCC naphtha was compared with the one of a CoMo catalyst supported on pure alumina, as well as with another one supported on sodium-modified alumina. The catalysts results were also compared with the ones of CoMo catalyst supported on ASA without sodium. The catalysts were characterized by XRF, XRD, Raman, as well as their textural and acid properties. The sodium introduction simultaneously with the variation of the Si/(Si + Al) ratio conducts to obtain a catalyst (15% Si/(Si + Al), 3 wt.% Na) with, on the one hand, an Mo oxide species distribution with an important participation of β -CoMoO₄ crystalline species and, on the other hand, a selective formation of weak Brönsted acid sites. As a consequence of this especial balance between the acid properties and the oxidic Mo-surface-species distribution, this catalyst presented an activity similar to the one of the CoMo/Al₂O₃, but with improvements in the selectivity to HDS. Additionally, it was also encountered that when CoMo catalysts supported on materials of predominantly acidic nature are used, the linear olefins inhibit more the HDS activity than the branched ones, whereas the contrary effect was encountered when supports of a predominantly basic nature are used.

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1. Introduction

The challenge with the deep hydrotreatment (HDT) of the fluid catalytic cracking (FCC) naphtha constitues to remove the maximum of sulfur impurities avoiding olefin saturation [1]. Thus, it is imperative to search for catalysts that are more selective to the hydrodesulfurization (HDS) than the conventional CoMo/Al₂O₃ [1]. Support modification appears as one of the variables explored in literature, either by modifying the classical alumina or by using completely different materials [1–9]. Many works claim that an increment in the hydrodesulfurization/hydrogenation of olefin (HDS/HYDO) selectivity can be observed using less acidic carriers than classical γ -alumina [5,9,10]. However, improvements of the HDS/HYDO selectivity can be found using more acidic catalysts [6,9,11]. Thus, there is not a clear position about the effect of support in the HDS/HYDO selectivity and, specifically, about the involvement of its acid–base properties.

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In a previous article [12], CoMo catalysts supported on amorphous aluminosilicates with different Si/(Si+Al) ratios were essayed in the HDT of a synthetic naphtha. It was encountered that the Brönsted acidity of these catalysts increased with the Si/(Si + Al) ratio, producing acid-type reactions, such as cracking and isomerization of olefins and the alkylation of 2-methylthiophene (2-MT) with olefins [12]. These acid-type reactions competed with the HDS and the HYDO, and in the case of the catalysts with the highest Si content, even inhibiting them completely [12]. From the analysis of the product distribution of these reactions, it was concluded that a way to inhibit olefin saturation was by achieving an acid-properties balance such that the double-bond and skeletal isomerization reactions are promoted, but cracking is avoided. As a consequence, the HYDO could be inhibited by a double effect. On the one hand, olefins that are more difficult to hydrogenate are produced by double-bond isomerization [1,5,8,13]. On the other hand, there is competition for the adsorption of olefins between the acid sites and the HYDO ones [12]. However, it was concluded that the variation of the Si/(Si + Al) ratio only was not enough to finely control the acid properties [12].

Some authors have succeeded in finely controlling the acid-base properties of their catalysts by combining one modification that conducts to improve the acidity with another that conduct to reduce it [4,9]. For instance, La Parola et al. [4] showed that

improvements in the thiophene HDS can be achieve by using sodium-modified amorphous aluminosilicates (ASA) as support for CoMo catalysts. Fan et al. [9] showed that catalysts highly selective to the HDS can be obtained by doping alumina simultaneously with P and K, due to a balance of the acid properties, as well as a good compromise between the dispersion of the CoMoS phase and the stacking level of the MoS₂ slabs.

In the present work, it was intended to finely control the acid properties of the ASA supports by combining the variation of the Si/(Si + Al) ratio with the sodium introduction, aiming to use these materials as supports for CoMo catalysts. The acid properties of these materials were followed by various methods, and the dispersion and coordination of Co and Mo were also followed using Raman. These surface properties were used in an attempt to explain the catalytic behavior of the catalysts in the HDT of synthetic naphtha composed by 2-MT and different kinds of olefins.

2. Experimental

2.1. Catalyst preparation

Amorphous aluminosilicate supports with different Si/(Si+Al) molar ratios (0.15, 0.25, 0.33 and 0.5) were prepared by the sol-gel route following a procedure similar to the one described by La Parola et al. [14] using aluminum tri-sec-butoxide (Aldrich, 97%) and tetraethyl orthosilicate (Aldrich, 98%) as precursors. All operations were performed under nitrogen atmosphere. In order to check the reproducibility of the preparation method, the syntheses of supports with the same Si/(Si + Al) ratios were repeated at least twice. ASA supports were modified with sodium (3 wt.%) by incipient wetness impregnation with an aqueous solution of NaNO₃ (Merck). The impregnated solids were dried under airflow at 343 K for 2 h and, finally, air calcined at 773 K for 12 h. The unmodified and modified supports were named here ASAxx and NaASAxx respectively, where xx represent the Si/(Si + Al) ratio. CoMo catalysts supported on NaASAxx containing 10% MoO₃ and 2% CoO were prepared by successive incipient wetness impregnation. The catalysts were named as CMNaSxx. An initial impregnation step was performed with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Merck), and subsequently, the solids were impregnated with an aqueous solution of Co(NO₃)₂·6H₂O (Sigma–Aldrich). After each impregnation step, the same thermal treatment used after Na impregnation was performed. A conventional CoMo catalyst supported on a commercial Procatalyse γ -Al₂O₃ (CMA) and another catalyst supported on γ -Al₂O₃ modified with 3 wt.% Na (CMANa) were also prepared by the same method for comparison purposes. In this case, after each impregnation step, the solids were dried under airflow at 393 K for 12 h and, finally, air calcined at 773 K for 4 h. Some already published results [12] of CoMo catalysts supported on ASAxx (CMSxx) with the same %Si/(Si + Al) of the CMNaSxx catalysts were also used for comparison purposes.

2.2. Characterization of catalysts

2.2.1. Catalyst composition

The catalysts and support nominal compositions were verified by X-ray fluorescence (XRF) using a Shimadzu EDX 800 HS apparatus.

2.2.2. Textural properties

Textural properties of catalysts were determined using N₂ adsorption–desorption isotherms obtained with a Quantachrome NOVA 1200 instrument. The catalysts were previously outgassed in vacuum (1×10^{-3} mbar) all night at 343 K. The specific surface area (A_{BET}) was estimated by the BET method.

2.2.3. X-ray diffraction (XRD)

XRD was performed on a Siemens D5000 diffractometer using the K α radiation of Cu (λ = 1.5418 Å). The 2 θ range was scanned between 2° and 70° at a rate of 0.02 s⁻¹. Identification of the phases was achieved by using the ICDD-JCPDS database [15].

2.2.4. Acid properties

The total acidity and the acidity strength distribution were determined by NH_3 temperature programmed desorption (TPD). The detailed procedure and equipment is described in Ref. [12]. Desorption of the adsorbed NH_3 was performed by increasing temperature until 873 K at 10 K min⁻¹. The signal corresponding to m/z of 16, assigned to NH_3 , was used for the analysis of the NH_3 TPD curves.

The Brönsted/Lewis was determined from Fourier transformed infrared (FT-IR) spectra of adsorbed pyridine. The detailed procedure and equipment is described in Ref. [12]. Samples were first dehydrated under vacuum ($<1 \times 10^{-5}$ mbar) at 773 K for 2 h. After cooling down to room temperature (r.t.), a first spectrum was taken as reference. Samples were then exposed to 10 mbar of pyridine for 30 min. FT-IR spectra were recorded after outgassing the samples ($<10^{-5}$ mbar) in four steps for 1 h: r.t., 373, 473 and 573 K.

2.2.5. Confocal laser Raman microscopy (Raman)

Raman was performed with a Labram spectrometer (Dilor) interfaced with an Olympus optical microscope. The excitation radiation was a He–Ne laser (780 nm) operated at a power of 10 mW. The 100× objective of the microscope was used, so that a spot of about 1 μ m at the surface of the sample was measured at once. Spectra were obtained by averaging 25 scans of the Raman shift range between 1400 and 100 cm⁻¹ recorded in 25 s with a spectral resolution of 1 cm⁻¹. The identity of the spectra obtained at different positions of each sample was systematically verified.

2.3. Catalytic evaluation

Catalytic tests were made in a continuous-flow stainless-steel fixed-bed reactor. The composition of the model charge was 2 wt.% 2-methylthiophene and 20 wt.% olefins dissolved in n-heptane. Dodecane (2 wt.%) was used as an internal standard for the chromatographic analysis. Two kinds of essays were performed. In the essays type A, a commercial mixture of 2,4,4-trimethyl-1-pentene (TM1P) and 2,4,4-trimethyl-2-pentene (TM2P)(3:1 approximately) was used. These are representative of terminal and internal branched olefins in FCC naphtha respectively. In the essays type B, 1-octene was used as a representative of linear olefins.

Before the reaction, 0.35 g of catalyst (0.18–0.6 mm particle size) was dried in situ under N₂ flow (100 ml min⁻¹) at 393 K for 1 h, and subsequently, activated with a H₂S/H₂ mixture (15/85, v/v) at 673 K (10 K min⁻¹) for 3 h. The following reaction conditions were fixed: 17 bar, 523 K, liquid-flow rate of 20 ml h⁻¹ and H₂/liquid feed ratio of 500. Under these conditions, the absence of any diffusion limitations was previously verified. Catalytic tests were conducted until reaching the steady state. Condensable products were analyzed offline in a HP 6890 gas chromatograph equipped with a HP-1 column (100 m × 0.25 mm × 0.5 µm) and a FID detector. Product identification was performed by GC–MS analyses and by comparing the retention times of some reagent-grade pure compounds in the FID and FPD detectors in the same column.

2.4. Expression of results

Results of the catalytic test were expressed in terms of percentage of reactants conversion (%C.2MT, C.TM1P, C.TM2P and C.1-octene) and products yield (%). The following equation was



Fig. 1. Total acidity and acidity distribution of the prepared CMNaSxx catalysts. Weak: *T* < 423 K, intermediate: 423 K < *T* < 573 K, strong *T* > 573.

used to calculate the yield of the product P (%Y.P), taking into account the conversion of reactant R:

$$%Y.P = \frac{\text{mol} PL_{\text{output}}}{\alpha_{RP} \times (\text{mol} R_{\text{input}} - \text{mol} R_{\text{output}})} \times 100$$
(1)

. ...

where α_{RP} is the ratio between the stoichiometric coefficients of product *P* and reactant *R*.

In essays type A, both kind of olefins (TM1P and TM2P) give similar product. Thus, the yield of the olefin products was calculated taking into account the addition of moles of both kind of olefins (mol R = mol TM1P + mol TM2P).

3. Results

3.1. Influence of sodium and the Si/(Si + Al) ratio on the acid-base properties of the catalysts

The total acidity and the acidity strength distribution obtained by NH₃ TPD of the CMNaSxx catalysts compared with those of the CMA and CMANa catalysts is presented in Fig. 1. The strength of the acid sites was arbitrarily classified as weak (<423 K), intermediate (423-573 K) and strong (>573) according to the temperature of NH₃ desorption [16]. The total acidity of all the CoMo catalysts supported on the sodium-modified supports is lower than the one of the CMA catalysts and it increase with the Si/(Si + Al) ratio from 0% to 50% Si/(Si+Al) ratio. In the results published previously in Ref. [12] for the CMSxx catalysts was observed that the total acidity of all the CMSxx was higher than the one of the CMA catalyst, used also as reference in that work. Therefore, sodium introduction reduce considerably the total acidity of the catalysts, however, in both CMNaSxx and CMSxx catalysts the total acidity increases with increasing the %Si/(Si+Al) up to 50%. Regarding total acid sites distribution, the CMANa catalyst exhibits the lowest total and strong acidity and the highest proportion of weak acidity. Among the CMNaSxx catalysts, the CMNaS15 present the highest proportion of weak and the lowest proportion of strong acidity. In a generalized way for the CMNaSxx catalysts, from 15% to 50% Si/(Si+Al) the tendency is to diminish weak acid sites and to decrease intermediate and strong acid sites with increasing the %Si/(Si+Al). In Ref. [12] was not observed a clear tendency for the total acid sites distribution of the CMSxx catalysts with the Si/(Si+Al) ratio and in general this distribution was rather similar to that of the CMA



Fig. 2. IR spectra of adsorbed CO₂ on the prepared CMNaSxx catalysts. Dashed lines: bidentate carbonates; continuous lines: hydrogen carbonates.

catalyst. Hence, in addition to the reduction in total acidity, sodium introduction causes a shifting in the acidity distribution to weaker sites. In another previously published work of our group [31], where CoMo catalysts supported on alumina and alkaline metal modified alumina were compared, it was found the same effect of sodium reducing total acidity and shifting the acid sites distribution to weaker sites. Mey et al. [5] also reported a reduction in the strength of the acid sites after introducing K on its CoMo/Al₂O₃ catalyst.

In Fig. 2 is presented the IR spectra of adsorbed CO₂ on the prepared catalysts, which could be used to estimate the possible modification of the catalyst basicity by sodium introduction [5,17]. It is observed that compared with CMA the only catalyst showing an important increase in the adsorption of CO₂ is the CMANa. Additionally, the shift of the peaks of CO₂ adsorption for the CMANa catalyst compared with the ones of CMA suggest a change in the preferred adsorbed species from hydrogen carbonates (1359 and 1585 cm^{-1}) to bidentate carbonates (1449 and 1653 cm⁻¹) [5], whereas the CMNaSxx catalysts present an adsorption similar to the one of CMA with similar adsorbed carbonate species. de Miguel et al. [18] have shown that Na is selectively adsorbed on the Al⁺³ tetrahedrically coordinated-Lewis sites of alumina, which gives rise to the formation of a [=Al–OH]⁻Na⁺ complex. This fact has been demonstrated by ²⁷Al-RMN studies where the disappearance of the band attributed to Al⁺³ was observed [18]. Thus, a double effect on the alumina surface is produced; the stronger acid sites are poisoned and at the same time the [=Al-OH]-Na⁺ complex formation increased the basicity of the site. On the other hand, on CMNaSxx catalysts, sodium only blocked the acid sites diminishing a lot the total acidity in comparison with the respective withoutsodium catalysts [12], as described in the previous paragraph, but no important creation of basic sites is observed.

The kind of acid sites existing in the catalysts was quantified using IR spectra of adsorbed pyridine after desorption at r.t., 373, 473 and 573 K. Peaks at 1453 and 1545 cm⁻¹ in the IR spectra of adsorbed pyridine (not shown), attributed in literature to pyridine bonded to Lewis and Brönsted sites respectively [14,19], were mathematically decomposed using Gauss-type curves. The values resulting from their integration were used to calculate the Brönsted/Lewis ratio, which was plotted as a function of the %Si/(Si + Al) in Fig. 3 for both CMNaSxx and CMSxx catalysts. Zero points in curves for CMSxx (gray curves) and for CMNaSxx (black curves) catalysts represent the CMA and CMANa catalysts respectively. For the CMA and CMANa catalysts, the Brönsted/Lewis ratio is zero because



Fig. 3. Brönsted/Lewis ratio of sodium-modified-ASA supported CoMo catalysts at 373, 473 and 573 K. CMSxx catalysts: gray lines; CMNaSxx catalysts: black lines. *xx* represents the %Si/ (Si + Al).

no Brönsted sites were detected using pyridine as model molecule. For both CMNaSxx and CMSxx catalysts the Brönsted/Lewis ratio increases continuously with the increase of the Si/(Si+Al) ratio at 373 K. Similar trends are observed at 473 and 573 K; however, at 473 K for CMNaSxx catalysts Brönsted sites are only detected for catalysts with $Si/(Si+Al) \ge 25$ and at 573 K for catalysts with a $Si/(Si + Al) \ge 50$. Desorption of pyridine at different temperatures was performed in order to obtain information about the strength of the Brönsted and Lewis sites. The higher the temperature of desorption the higher the strength of the Brönsted or Lewis site [14,19]. Thus, with increasing the %Si/(Si + Al) of the support the acid sites present in the CMNaSxx get stronger: CMNaS15 contains only weak Brönsted sites desorbing at 373 K, CMNaS25 and CMNaS33 contain weak and intermediate strength sites desorbing at 373 and 473 K respectively; and CMNaS50 contains strong sites desorbing at 573 K in addition to weak and intermediate strength sites.

By observing Fig. 3 Brönsted/Lewis ratio results of CMNaSxx catalysts can be compared with those of CMSxx [12] in order to elucidate the sodium effect. It could be observed in Fig. 3 that for weak sites desorbing at 373 K the Brönsted/Lewis ratio of CMNaSxx catalysts is higher than the one of the CMSxx catalysts with the same %Si/(Si+Al). Whereas, in the case of the intermediate and strong sites desorbing at 473 and 573 K the opposite behavior was observed. Hence, it could be inferred that sodium introduction shifts the strength distribution of the Brönsted acid sites to weaker acid sites. This shifting effect was more evident in the catalysts with lower Si/(Si+Al) ratio where sodium introduction brings about the disappearing of the intermediate and stronger Brönsted sites.

It has already been demonstrated, by analyzing the OH groups present on the ASA supports surface using FT-IR and by using other techniques [12,20-22], that ASA supports are composed by two different phases; a mixed Si-Al and a segregated alumina phase which dilutes the other one. It has also been demonstrated that the increase of the Brönsted/Lewis ratio with the %Si/(Si+Al) can be ascribed to an increase in the concentration of the mixed Si-Al oxide phase and a decrease of the concentration of a segregated alumina phase techniques [12,20-22]. The increasing in the substitution of Al in the Si framework or vice versa gives rise to new superficial defects, which create new Lewis and, specially, new Brönsted acid sites [4]. Sodium introduction also affects the acid-base properties: it brings about the reduction of the total acidity as well as the reduction of the strength of total acid sites. Sodium introduction also caused a shifting of the Brönsted sites to weaker strength ones. As already mentioned above in alumina supports

Table 1

Comparison of specific surface area (A_{BET}) for ASAxx supports and CMSxx and CMNaSxx catalyst. xx represents the %Si/ (Si + Al).

| Si/(Si+Al) ratio | $A_{\rm BET}({ m m}^2{ m g}^{-1})$ | | |
|------------------|------------------------------------|-------|-----------------|
| | ASAxx | CMSxx | CMNaS <i>xx</i> |
| 0 | 210 | 194 | 183 |
| 15 | 397 | 269 | 88 |
| 25 | 550 | 259 | 253 |
| 33 | 378 | 146 | 110 |
| 50 | 508 | 264 | 165 |

Zero (0) %Si/(Si + Al) represents alumina, CMA and CMANa.

have been demonstrated [18,31] that alkaline metals are deposited on the strongest acid sites causing two effects a decrease of the total acid sites and a shifting of the acid sites distribution to weaker acid sites. A similar effect could be happening with ASAxx supports with sodium introduction, having into account the existence of a alumina segregated phase in the ASAxx supports. In previous paragraphs was annotated also that the acid properties of supports with lower %Si/(Si + Al) were more affected by sodium introduction. This fact coincides with results in Ref. [12], where a higher concentration of the alumina segregated phase was found on the aforementioned supports.

3.2. Influence of sodium and the Si/(Si + Al) ratio on the structure of the catalysts

Table 1 presents the A_{BET} of the CMNaSxx catalysts compared with those of CMSxx catalysts and ASAxx supports. The ABET results for y-Al₂O₃, CMA and CMANa were also included. From the analysis of the adsorption-desorption curves hysteresis (not shown), it can be inferred that all materials are mainly mesoporous with only a small proportion of micropores as expected due to the basic hydrolysis used in the sol-gel synthesis of these materials [14,23]. There is not a defined trend of the A_{BFT} with the Si/(Si + Al) ratio; however, it is notable that the CMNaS15 catalyst, which is the one with the lowest A_{BFT}. In a previous article [12], we have shown that there was a great reduction of the A_{BFT} when comparing the unmodified ASAxx supports with the respective CoMo catalysts supported on them (CMSxx). The deterioration of the ASAxx textural properties after active metal incorporation, especially the A_{BET}, has also been reported by other authors [4,14,24]. This reduction was explained by the blocking of both the micropores and the smallest mesopores as a consequence of the Mo and Co deposition. Comparing the results in Table 1 for ASAxx, CMSxx and CMNaSxx, it is noted that the reduction in the A_{BET} was accentuated by the sodium introduction. For instance, the A_{BET} was reduced from 397 cm² g⁻¹ for the ASA15 support to $269 \text{ cm}^2 \text{ g}^{-1}$ for the CMS15 catalyst and $88 \text{ cm}^2 \text{ g}^{-1}$ for the CMNaS15. On the next paragraph a possible explanation for this effect is given.

The XRD spectra of the CMA, CMNaS15, CMNaS25 and CMNaS50 catalysts compared with the respective catalysts supported on the unmodified supports: CMS15, CMS25 and CMS50 are shown in Fig. 4. No peaks corresponding to Mo or Co compounds are observed, which indicate a good dispersion of these on the different supports. In the CMA catalysts, broad bands typical of γ -Al₂O₃ with poor cristallinity are only observed [15]. A similar XRD spectrum was obtained for the CMANa catalyst (not shown). Whereas, in the catalysts supported on the unmodified ASA supports no peaks are observed as a consequence of the amorphous nature of ASA. However, when comparing the XRD spectra of CMNaS25 with CMS25, it is observed that the bands corresponding to γ -Al₂O₃ begin to appear. The same was observed in the CMNaS33 XRD spectrum compared with the one of CMS33 (not shown). This fact is even more evident when CMNaS15 and CMS15 are compared; the



Fig. 4. XRD of some selected CMSxx and CMNaSxx catalysts. xx represents the %Si/ (Si+Al).

 γ -Al₂O₃ bands are now observed clearly along with peaks corresponding to Na₂Al₂O₄ [15]. On the contrary, peaks are observed neither in the XRD spectrum of CMNaS50 nor in the one of CMS50. Thus, it could be inferred that sodium introduction increased the crystallinity of the segregated alumina phase present in the supports with less than 50% Si/(Si+Al), even forming a crystalline compound with sodium itself in the CMNaS15 catalyst. It has been already reported in Ref. [12] the presence of alumina type IB and IIA OH groups of Knözinger classification [25] in the ASAxx unmodified supports with a Si/(Si + Al) ratio less than 50%. This fact confirms the presence of a segregated alumina phase, which dilutes the Si-Al mixed oxide phase, in the ASAxx supports belonging that range of Si/(Si + Al) as have been suggested by other authors before [20-22]. This increase in the segregated alumina phase cristallinity could explain, at least in part, the great reduction in the A_{BFT} observed when comparing catalysts supported on the unmodified ASA support with those supported on the sodium-modified one.

The Raman spectra of the CMNaSxx catalysts compared with that of CMA and CMANa are shown in Fig. 5. First of all, it can be noticed that both Co and Mo are well dispersed on the different supports, because of the lack of peaks characteristic of Co compounds (681, 477 and 199 cm^{-1}) and free MoO₃ aggregates (990–1000 cm⁻¹) [3,26,27]. Additionally, the presence of Al₂(MoO₄)₃ (1000–1010 cm⁻¹) can be ruled out [27]. Beginning

the analysis by the CMA catalyst spectrum, it is observed a broad band at ca. 920-950 cm⁻¹, with shoulders at both sides ca. 900 and 960 cm⁻¹. There are also other broad bands at ca. 320–360 and 225 cm^{-1} . The region 750–1000 cm⁻¹ is where the bands for stretching of Mo-O bonds are typically observed [3,27]. Inside the broad band at ca. 920-950 a variety of Mo species could be placed; the more likely according to literature [3,26–29] are Mo₇O₂₄⁶⁻ octahedral species (946–951, 360 and 220 cm⁻¹, continuous lines) and MoO₄²⁻ with distorted tetrahedral symmetry (916 and 320 cm⁻¹, dotted lines). Some contributions from Mo–O–Co stretching vibrations in CoMoO₄ species (939, 873, 820, 370 and 340 cm⁻¹, dashed lines) cannot be ruled out [30]. The shoulder at ca. 900 cm⁻¹ can be attributed to monomeric undistorted MoO_4^{2-} species (at ca. 892 and 807 cm^{-1}) and the other shoulder at ca. 960 cm⁻¹ to larger polymeric species such as $Mo_8O_{26}^{4-}$ $(958-960 \,\mathrm{cm}^{-1}).$

Comparing the spectra of the CMANa catalysts with the CMA one, it is observed that bands belonging to octahedral Mo₇O₂₄⁶⁻ and CoMoO₄ practically disappear. Some contribution of MoO_4^{2-} distorted tetrahedral species is still observed as well as a sharp peak close to 897 cm⁻¹, which is attributed to undistorted tetrahedral species such as those present in the Na₂MoO₄ compound [26,27]. Even though the presence of Na₂MoO₄ was not detected in the XRD spectrum of the CMANa catalyst, it is presumed that it exists but the size of its crystals is not high enough to be detected by this technique. However, it is high enough to be detected by Raman. In fact, its presence in a CoMo catalyst supported on alumina with 5 wt.% Na was clearly demonstrated by XRD analyzes in a previous work of our group [31], as well as in another works of the literature [26,32]. The formation of the Na₂MoO₄ implicate a very strong linkage of the Mo with the support, even stronger than the one present in the catalysts supported on unmodified alumina [4,32,33]. This fact is detrimental to the HDS and HYDO activities of the catalysts because the strong linkage Mo-support gives origin to Mo species very hard to reduce/sulfide [4,32-35].

Regarding the CMNaSxx catalysts Raman spectra, it is observed that the one of the CMNaS15 catalyst is clearly different to the others. It is the only one that exhibits markedly defined peaks; a clear sign of crystallinity, whereas in the other catalysts there are predominantly amorphous species. These well-defined peaks match well with β -CoMoO₄ species [30,32]. The detection of crystalline Mo species in the CMNaS15 catalyst using Raman is in agreement with the detection of more crystalline support species by XRD. Thus, this fact supports the idea, already expressed above, that the ASA15 was the support most sensitive to sodium regarding the increase in crystallinity, not only of the phases which compose the support itself, but also of the supported Co and Mo. However, the β -CoMoO₄



Fig. 5. Raman spectra of the prepared CMNaSxx catalysts. xx represents the %Si/ (Si + Al).

is not the only Mo specie present in the catalyst. Even if all the Co exists in the form of CoMoO₄, due to the Co/(Co+Mo) ratio used in this work, only one third of the Mo will be consumed. In fact, the CMNaS15 Raman spectrum shown in Fig. 5 is multiplied by 0.5 for a better observation of the other spectra, but observing it in detail, shoulders at ca. 950 and 920 cm⁻¹ are also observed. Thus, there are also Mo₇O₂₄⁶⁻ and distorted tetrahedral MoO₄²⁻ species on the catalyst. In this case, the higher intensity of bands corresponding to β -CoMoO₄ species is only sign of a higher crystallinity, and it cannot be affirmed that it is in a higher proportion [27]. The relative intensity of the shoulder at ca. 920 cm⁻¹ is higher than the one of the shoulder at ca. 950 cm⁻¹. Thus, the CMNaS15 catalyst could fit in the tendency shown by the other CMNaSxx catalysts, but with an important additional presence of β -CoMoO₄ species. In the other CMNaSxx catalysts, Raman spectra at low Si/(Si+Al) ratios is observed a prevalence of distorted tetrahedral monomeric MoO₄²⁻ species with some presence of Na₂MoO₄. However, different to the catalyst supported on the sodium-modified alumina where the Na₂MoO₄ was the majority tetrahedral Mo specie, the distorted MoO_4^{2-} one was the majority on the CMNaSxx catalysts. With increasing the Si/(Si+Al) ratio, it is observed an increase of the octahedral species at expense of the tetrahedral ones.

Comparing CMNaSxx catalysts with CMSxx ones, in both kinds of catalysts was observed the same tendency of increasing the population of octahedral species at expense of the tetrahedral ones with increasing the Si/(Si+Al) ratio. However, the prevalence of tetrahedral species is higher in sodium-doped catalysts than in the undopped ones. Undistorted tetrahedral species are present in the CMNaSxx ones but not in the CMSxx catalysts. Therefore, it is inferred that sodium introduction increase the Mo-support bond strength. The increment of octahedral Mo species with increasing the Si/(Si+Al) is related with the heterogeneity of phases encountered in the ASAxx supports. It has been already shown in the literature that the maximum of the mixed Si-Al oxide phase is encountered at 50-75% Si/(Si+Al) and that below that content, the mixed Si-Al oxide phase is diluted by a segregated alumina phase [12,20-22]. Taking into account that this mixed Si-Al phase is related with the increase of the acidity and acidity strength of the ASA supports as it was described in Section 3.1 [12,20-22], it will be expected that the point of zero charge (PZC) of the support decrease with increasing the Si/(Si + Al) ratio. It is also known that during the impregnation process, the Mo species which will be deposited on the support surface seem to be governed by the surface pH, more precisely by its PZC [27,29] according to Eqs. (2) and (3). Thus, at pH values higher than 6.5 the MoO₄²⁻ anion is stable and a decrease in pH to 4.5 leads to complete formation of Mo₇O₂₄^{6–} [27]. A further decrease in pH to 1.5 leads to polymerization of Mo₈O₂₆⁴⁻ [27]. This fact could also explain the increase of the prevalence of tetrahedral species with the sodium introduction because sodium introduction cause a decrement in acidity and consequently increase the PZC.

$$Mo_7O_{24}^{6-} + 4H_2O \leftrightarrow 7MoO_4^{2-} + 8H^+$$
 (2)

$$Mo_7O_{24}^{6-} + 7MoO_4^{2-} + 2H^+ \leftrightarrow [H_2Mo_8O_{26}]^{6-}$$
 (3)

3.3. Influence of sodium and the Si/(Si + Al) ratio on the catalytic performance

In previous articles [12,31], we have already proposed reaction schemes for 2-MT, branched (TM1P and TM2P) and linear (1-octene) olefins based on the product identification along with the comparison with other reaction schemes proposed in the literature [1,5–8,33,36–38]. Regarding branched olefins, both kinds of branched olefins (TM1P and TM2P) were present in the feedstock; thus, there was an equilibrium between them related to the doublebond isomerization [5,8]. Thus, it is considered that products come



Fig. 6. Reactant conversions and their product yields in essays type A: feed compose by 2-MT and branched olefins (TM1P and TM2P).

from both olefins. The HYDO product was isooctane (iC8), the cracking products were isobutene and isobutane (iC4s); and the skeletal isomerization products (iC8-ske) were other trimethylpentenes (TMP) different from 2,4,4-TMPs and dimethylhexenes in a lower proportion. Regarding linear olefins, their main reactions were the double-bond isomerization of 1-octene to internal olefins such as 2-, 3- and 4-octenes (nC8s=) and the HYDO of both internal and terminal olefins to octane. On the other hand the oligomerization products yield was too low (<1%) and thiols were not observed at least in guantifiable concentrations, neither in essays with branched olefins nor in essays with linear ones [12,31,38]. Regarding 2-MT, it was observed 2-methyltetrahydrothiophene (2-MTHT) as the main intermediate product and C5 hydrocarbons (C5s) as the final HDS products [1,5,33,38]. On the other hand, alkylmethylthiophenes (AMT), product of the alkylation of 2-MT with the olefins present in the reaction environment, were also observed [5,12,37].

The reactant conversions as well as their product yields in essays type A and B are presented in Figs. 6 and 7, respectively for the CMNaSxx catalysts compared to the CMA and the CMANa ones. Reactants conversions are plotted as dashed lines, and the yield of products are plotted as continuous lines. When the performance of the CMNaSxx catalysts in the HDT of FCC naphtha are going to be compared to the one of the conventional catalyst used in the industry (CMA), two separated effects should be considered: the sodium introduction and the variation of the Si/(Si + Al) ratio. The



Fig. 7. Reactant conversions and their product yields in essays type B: feed compose by 2-MT and linear olefins (1-octene).

effect of the variation of the Si/(Si+Al) ratio will be described first by comparing the catalytic performance of the CMNaSxx catalysts to the one of CMANa. In Fig. 6a is observed that the essay type A with the CMANa catalyst produced only HDS products: intermediate and final (2-MTHT and C5s, respectively) (Fig. 6a). With increasing the Si/(Si + Al) ratio alkylation products appeared and consequently the yield of the addition of intermediate and final HDS products diminished. Increments in the Si/(Si+Al) ratio up to 25% conducted only to very small increments in the alkylation yield, conversely, higher increments in the Si/(Si+Al) ratio conducted to important increments in the alkylation yield. Even, in the CMNaS50 catalysts a yield of the AMT of 85% is observed. A similar trend is observed for the yield of the olefin products (Fig. 6b). In this case for the CMANa catalyst, a yield of 95% is observed for the HYDO product accompanied by lower yields to skeletal and double-bond isomerization reactions. It is interesting to highlight the detection of the double-bond isomerization from terminal to internal olefins by the detection of a production of the internal olefin (TM2P) instead of being consumed. With increasing the Si/(Si + Al) ratio, the yield of HYDO diminishes meanwhile the yield to skeletal isomerization and cracking products increase. However, the yield of cracking products increases faster than that of the skeletal isomerization. Again, the higher variations of the product yields are observed when the Si/(Si + Al) ratio is increased to 33% and 50%.

Thus, in essays type A the HDS and the HYDO reactions are replaced progressively for acid-type reactions such as alkylation in the case of 2-MT products and, skeletal isomerization and cracking in the case of olefin products. This fact seems to agree with the increase in the Brönsted sites density and strength described in Section 3.1. This Brönsted sites would compete with the HDS and the HYDO sites for the adsorption of the reactants. Consequently, when the density and the strength of the Brönsted sites increase sufficiently, the reactants are adsorbed predominantly on these sites instead of on the HDS and HYD ones. This competitive effect has been already observed in previous works [12,31] using diverse sets of CoMo catalysts supported on acidic materials, such as, borated aluminas [12] with different contents of B and ASA with different Si/(Si + Al) ratios [31].

On the other hand, the effect of sodium introduction could be observed by comparing the performance of the catalysts supported on the sodium modified materials (ASA or alumina) with the one of the catalysts supported on the respective bare material with the same Si/(Si+Al) ratio. In the case of the catalysts supported on alumina, it is observed that the low cracking yield of the CMA catalysts disappeared as a consequence of the huge reduction in the total acidity and acidity strength when the CMA and the CMANa catalysts are compared (Section 3.1). A similar effect of sodium is observed when the performance of the CMNaSxx catalysts in Fig. 6 is compared with that of the CMSxx catalysts presented in Ref. [12]. In the case of the CMNaSxx catalysts the important increments in the yield of the acid-type reaction are observed only for the CMNaS33 and CMNaS50 catalysts with 27% and 87% yield to alkylation products, respectively; and 45% and 76% yield to cracking products, respectively. Only the catalysts with 50% Si/(Si+Al) ratio presented a majority of the yield of acid-type products of both 2-MT and olefins (Fig. 6). In the case of CMSxx catalysts, even the CMS15 catalyst present a 8% and 30% yield to alkylation and cracking products respectively. The main increments in the yield of the acid-type reactions for CMSxx, with a majority of these, are observed for the catalysts with a Si/(Si + Al) ratio $\geq 25\%$ [12] with yields to alkylation products higher than 80% and yields to cracking products higher than 70%. As in the case of alumina-supported catalyst, a great reduction in the acid sites density and strength, specially the Brönsted ones, was observed for the CMNaSxx compared with the CMSxx ones [12] (Section 3.1).

In the case of essays type B (Fig. 7), reactions using CMNaSxx catalysts with less than 50% Si/(Si + Al) only produced intermediate and final HDS products; i.e., 2-MTHT and C5s. On the other hand using the CMNaS50 catalyst a 30% yield of AMT was also observed. In the case of the CMSxx catalysts a 6% yield was observed for the CMS15 catalysts and yields higher to 50% were observed for catalyst with Si/(Si + Al) ratio \geq 25% [12]. This fact confirms the same effect of sodium introduction encountered in essays type A. Regarding the olefin products, other acid-type reactions different from double-bond isomerization were not detected when using linear olefins, even with the CMSxx catalysts [12]. In these essays, even for the CMA catalyst, the yield of double-bond isomerization (53%) is higher than the one of hydrogenation (47%). Compared to the CMA catalysts the yield of double-bond isomerization is higher for all the other catalysts: approximately 70% for the CMANa, CMNaS15 and CMNaS25 catalysts and approximately 80% for the CMNaS33 and CMNaS50 catalysts. As in the case of the essays type A, it is observed that the catalysts with 33% and 50% are the ones with the highest yields of the acid-type reaction; however, the difference with the other catalysts is not so marked in the case of essays type B.

Thus, in the case of essays type B, the product distribution is less affected by the support modification. This fact could be explained because linear olefins interact less easily with the acid sites because their corresponding carbocations (secondary) are less stable than the ones formed for the branched olefins (tertiary) [13,19,39,40]. As a consequence, those reactions which need stronger acid sites to be undergone like cracking, skeletal isomerization and alkylation [19,39,40] were more affected. The acid sites density and strength of the catalysts used in this work are not high enough to produce other reaction different from the double-bond isomerization of the linear olefins and only the catalyst which presented strong Brönsted sites (CMNaS50) produce the alkylation of 2-MT with linear octenes. However, when branched olefins are used, even CMA catalyst wich contains no Brönsted sites (but it contains strong Lewis sites) and the CMNaS15 which only contains weak strength Brönsted sites could produce skeletal isomerization in addition to the doublebond isomerization. The catalysts with intermediate Brönsted sites (CMNaS25 and CMNaS33) produce in addition cracking and alkylation reactions in moderate yields, and finally, the catalyst with strong Brönsted sites (CMNaS50) produce alkylation and cracking in very high yields. In the essays type B, there were less differences in the products distribution among the different catalysts because the only reaction performed by olefins was the double-bond isomerization, which needs less strong acid sites to be preformed than cracking and skeletal isomerization, and these sites exist even in pure alumina [19,40].

It is also interesting to highlight that the CMANa catalysts present a yield of the double-bond isomerization reaction similar to the one of the more acidic CMNaSxx catalysts. In Section 3.1 was shown that the acid sites density and strength of the CMANa catalysts is much lower than the ones of the other catalysts, but at the same time an important increment in basic sites was observed. This increment in the basic sites could explain the high yield of the double-bond isomerization exhibit by this catalysts. Solid basic catalysts have been recognized early as efficient catalysts for the double-bond migration of alkenes with one advantage over solid acid ones, which is its lack of C—C bond cleavage ability [17]. This fact explains also why the increment of the yield of the acid-type reactions for the CMANa catalyst was only observed in reactions type B but not in reactions type A.

The variations in product distribution along with other factors that will be analyzed below produces variations in the total conversion of the reactants. In Fig. 6a is observed that in essays type A the total conversion of 2-MT for the CMANa catalyst is extremely low compared with the CMA catalyst (around 70% reduction), whereas for the CMNaS15 and CMNaS25 the reduction is within error limits. However, for the CMNaS33 a significant reduction (60%) is observed again and for the catalyst CMNaS50 the contrary trend was observed (around 50% increment). In Fig. 6b is observed that the conversions of TM1P and TM2P have a similar trend to the one described for 2-MT. However, more drastic variations are observed for the olefin conversions than for 2-MT, especially in the case of TM2P. For this olefin, the most drastic variation is observed in the case of the CMANa catalyst, which presents a zero conversion of TM2P and instead of being consumed it is produced by the doublebond isomerization of the TM1P [5,41]. This fact, make us think that the double-bond isomerization from external to internal positions is also present in the other catalysts. Thus, the double bond isomerization along with the steric effects of the more substituted double bond of TM2P explains the differences in the conversion of TM2P and TM1P [7,8].

In order to try to explain the complicated trend of the total conversion of both reactants along the prepared catalysts, let us separate the catalysts into two groups according their product distribution: those where the HDS and HYDO prevailed (CMA, CMANa, CMNaS15 and CMNaS25) and those where the acid-type reactions do (CMNaS33 and CMNaS50). Starting by the first group, the great reduction of the total conversion of 2-MT observed for the CMANa catalyst in comparison with CMA could be interpreted like a reduction of the HDS activity, because only HDS products were detected

for this catalyst. In Section 3.2, it was observed that for the CMANa catalyst the main Mo oxide specie detected by Raman was the Na_2MoO_4 . The presence of Na_2MoO_4 in the catalysts has been associated with a very low HDS activity, because these species implicate a very strong linkage of the Mo with the support and, consequently, they are very hard to reduce/sulfide [4,32–35]. As the HYDO reaction is also associated with the state of reduction suphuration of the Mo phase [36], the great reductions in the olefin total conversions observed for the CMANa catalysts compared with the CMA one could also be explained by the majority of Na_2MoO_4 .

As in the case of CMA and CMANa catalysts, the catalytic performance of the CMNaS15 one is governed by the reactions promoted by the Mo and Co phases: HDS and HYDO. As stated before, the HDS activity of this catalyst was close to that of CMA, the one with the highest HDS activity. However, great differences were observed in its Mo species distribution in comparison with CMA. The predominant species encountered in the CMNaS15 catalyst Raman spectra were MoO_4^{2-} distorted and β -CoMoO₄ species. The β -CoMoO₄ species have been also reported before by other authors in CoMo catalysts supported in sodium modified ASA [4,32]. The presence of these species has been associated with HDS highly active catalysts, contrary to that observed when the alpha species are present [4,32,42]. This difference in the catalytic performance of the α and β -CoMoO₄ species was assigned to the coordination of Mo in the oxidic precursors. β-Species exhibit a tetrahedral coordination, meanwhile α -ones exhibit an octahedral one [42]. Unlike other tetrahedral Mo species such as the Na₂MoO₄, where the formation of it implicate a strong linkage of the Mo species with the support, which difficult the reduction/sulfidation process, the formation of β -CoMoO₄ species implicate less interaction with the support and also the prevention of forming less active CoAl₂O₄ and Co_3O_4 species, and the Na_2MoO_4 itself.

The CMNaS25 is the other catalysts presenting a similar value of the HDS activity to that of the CMA and CMNaS15 ones. In this catalyst, although some presence of Na₂MoO₄ and octahedral Mo₇O₂₄^{6–} species exist, the predominant Mo species are the distorted tetrahedral MoO₄²⁻ ones. These distorted tetrahedral MoO₄²⁻ species were also reported to be predominant in other previous work of our group using CoMo catalyst supported on ASA without sodium with low Si/(Si + Al) ratios [12], as well as in works of other laboratories [43] using similar catalysts. It is consider that the undistorted tetrahedral monomeric Mo, although they are easier to reduce that the undistorted ones, they are more difficult to reduce/sulfidate than octahedral polymeric ones, and consequently less active [33,43]. However, it should also be considered that the presence of the undistorted tetrahedral Mo species could improve the Mo dispersion [26,33]; thus, compensating somehow its lack of reduction/sulfidation easiness. This fact could explain why the HDS activity of the CMNaS25 is quite similar to the CMA despite of its different distribution of Mo oxide species.

On the other hand, in the CMNaS33 and CMNaS50 catalysts acidtype reactions prevailed; thus, the inhibition of the HDS and the HYDO activities is not related to the structure of the CoMo phase. In this case, the inhibition is more related with a competition of the HDS and HYDO sites with the acid ones for the adsorption of the reactants. For instance, the CMNaS33 Raman spectrum is similar to that of the CMA catalysts; however, the total conversion of both reactants for the CMNaS33 catalyst diminishes with respect to CMA one. This could be explained because in the CMNaS33 catalyst, its Brönsted acid sites density and strength is not as high as in the CMNaS50 one. As a consequence, the acid sites compete with the HDS and the HYDO sites preventing their adsorption, but the density and strength of the acid sites is not high enough to produce the quantity of acid-type products to replace the HDS and HYDO products and equal the CMA catalyst total conversions. Conversely, the acid sites density and strength present in the CMNaS50 catalysts are high enough to assure that the acid-type reactions prevailed over the HDS and the HYDO ones. Thus, the increment in the total conversions of both reactants observed in the essays type A is due to the high increment in the acid-type reactions activity. On the other hand, the decrease in the 2-MT total conversion in essays type B is because of the less stability of the carbocations of linear olefins that we already state above.

Let us highlight the fact that the 2-MT conversions in essays type B were lower than the ones observed in essays type A for all catalysts, except for the CMANa catalyst (13% C.2MT in essay A vs 17% C.2MT in essay B) where the contrary was observed. The same phenomenon was observed for other catalysts supported on sodium-doped alumina with different sodium concentrations (1, 3 and 5 wt.%) in Ref. [31]. It has been already shown by other authors that the presence of olefins in the feed could inhibit the HDS of sulfur compounds [2,36,38,44]. In this sense, it could be said that in the catalysts different from CMANa the linear olefins inhibit more the HDS than the branched ones; meanwhile, the contrary occurs in for the CMANa catalysts. This fact could be explained taking into account the different acid-base properties of these groups of catalysts. The inhibitory effect that olefins have on the HDS arises from the fact of a competitive adsorption of both reactants on the coordinative unsaturated sites (CUS) promoted by Co, the HDS ones [2,36,38,44]. On one hand, it is known that, because of steric effects, the more the double-bond carbons are alkyl-substituted the more difficult to hydrogenate is the olefin [1,5,8,13,38,44]. On the other hand, branched olefins interact easier than linear ones with the Brönsted acid sites because their carbocations are more stable [13,19,40]; on the contrary, linear olefins interact easier than branched ones with the basic sites because their carbanions are more stable [13,17]. Thus, in the catalysts supported on predominantly acidic materials (all catalysts used in this work except for CMANa: see Section 3.1) two factors favor the higher inhibition of the HDS by linear olefins. First, the branched olefins interact easily with the acid sites; as a consequence, linear olefins are freer to interact with the HDS site. Second, the linear olefins interact easier with the HDS sites because of the steric effect affecting branched ones. Whereas, in the case of catalysts supported on predominantly basic materials such as the CMANa (see Section 3.1) the two factors are in contradiction. The linear olefins can interact easier with the basic sites than the branched ones, so, branched olefins are freer to interact with the HDS sites and inhibit the HDS reaction more. This last effect overcompensates the steric effect, which would avoid the adsorption of branched olefins on the HDS site. Taking into account that in the FCC naphtha the majority olefins are the branched ones, thus it would be better using acidic catalysts because the HDS activity of these is less inhibit by this kind of olefins.

Up until now, we have discussed about the effects of sodium and the Si/(Si+Al) ratio on the catalysts product distribution and reactants total conversion of the prepared catalyst. In the FCC naphtha HDT process like in all industrial process is important the activity but what really matters in this process is not losing the octane number of the FCC naphtha [1–9]. Thus, at the end what we want to obtain is a catalyst with an HDS activity similar or higher to the one of the conventional CoMo catalysts supported on alumina but with an improved selectivity HDS/HYDO. In essays type A, two kinds of branched olefins were used: terminal (TM1P) and internal (TM2P). Thus, in order to take into account individually the reactivity of each olefin, two selectivities HDS/HYDO were defined according to the olefin used to calculate it. (i) The selectivity defined as the ratio between the HDS activity and the conversion of terminal branched olefins, named here as $S^{(HDS/HYDO-Bt)}$ (Eq. (4)) and (ii) the one defined as the ratio between the HDS activity and the conversion of internal branched olefins S^(HDS/HYDO – Bi) (Eq. (5)). With these definitions, cracking products are also taking into account as detrimental ones in the process. In essays type B, only 1-octene was used



Fig. 8. Selectivity to the HDS according to the olefin used in essays type A and B.

as representative of linear olefins, thus the selectivity was defined as the ratio between the HDS products and the HYDO products and named here as $S^{(HDS/HYDO-L)}$ (Eq. (6)).

$$S^{(\text{HDS/HYDO}-Bt)} = \frac{\text{Y.C5s} \times \text{C.2MT}}{\text{C TM1P}}$$
(4)

$$S^{(\text{HDS/HYDO}-\text{Bi})} = \frac{\text{Y.C5s} \times \text{C.2MT}}{\text{C.TM2P}}$$
(5)

$$S^{(\text{HDS/HYDO}-L)} = \frac{\text{Y.C5s} \times \text{C.2MT}}{\text{Y.C8} \times \text{C.1 1-octene}}$$
(6)

These three selectivities are presented in Fig. 8 for the CMNaSxx catalysts compared with the one of the CMA and the CMANa ones. It is observed that the CMANa presented the highest value of the selectivity S^(HDS/HYDO - Bi). As we said before, the conversion of TM2P for this catalyst was zero; thus, according to our definition of the $S^{(\text{HDS/HYDO}-B\tilde{i})}$ in Eq. (5), the value of it for this catalyst is indefinite (α). However, the inexistent HYDO of the internal branched olefins is overcompensated by a high HYDO activity of the terminal ones; consequently a diminution of 50% is observed for the $S^{(HDS/HYDO-Bt)}$ in comparison with the CMA catalyst. A similar diminution is observed for the $S^{(HDS/HYDO - L)}$ of these catalysts. On the other hand, a value of twice the selectivity $S^{(HDS/HYDO - Bi)}$, a slight improvement in the $S^{(HDS/HYDO-Bt)}$ and a base value of S^(HDS/HYDO – L) were observed for the CMNaS15 catalyst in comparison with the CMA. A similar behavior to the CMNaS15 catalyst is observed for the CMNaS25; however, lower values of the selectivities $S^{(HDS/HYDO-Bi)}$ and $S^{(HDS/HYDO-Bt)}$ were observed. For the CMNaS33 catalysts, a high value of the S^(HDS/HYDO – Bi) was observed again, but very low values of the $S^{(HDS/HYDO-Bt)}$ and $S^{(HDS/HYDO-L)}$. Finally, for CMNaS50 catalyst very low values were observed for all selectivities.

Thus, the CMNaS15 catalyst was the one with the best integral performance because it was the only one presenting an important improvement of the $S^{(HDS/HYDO-Bi)}$ (twice that of the conventional CMA catalysts) without deterioration of the other selectivites or, even, the HDS activity. To explain this behavior, two important factors have to be considered. On the one hand, the Mo oxide species distribution, with the presence of β -CoMoO₄ species, it conducts to a relatively high HDS activity rather similar to that of the CMA catalyst [4,32,42]. On the other hand, the singular acid-base properties of this catalyst, which only has weak Brönsted acid sites, makes that practically the only acid-type reaction promoted was the double-bond isomerization from terminal to internal positions

[13,19,39,40]. Consequently, there are not acid-type reactions competing with the HDS reaction, and the double-bond isomerization promotes the formation of internal olefins, which are more difficult to hydrogenate [1,5,8,13,38,44].

The same factors could be used to explain the values of the selectivities observed in the other catalysts. For instance, for the CMANa catalysts, although its basic sites also could promote selectively the double-bond isomerization over the other acid-type reaction [17], the Na₂MoO₄ present on its surface favored the formation of less active HDS and HYDO species [4,32–35]. The Na₂MoO₄ produce less active species because it is very difficult to reduce/sulfide so forming less quantity and less active CUS sites [4,32–35]. In this sense, some authors have stated that the CUS sites responsible of the HDS reaction are more reduced that the ones responsible for the HYD reaction [45,46]. Thus, it would be logical that hard to reduce/sulfide species such as the Na₂MoO₄ produce a higher quantity of CUS sites capable of perform the HYD than those capable of perform the HDS.

On the other hand, the CMNaS25 catalyst was a catalyst very similar to the CMNaS15 in product distribution and catalyst activity, but its selectivity value were lower to that of the CMNaS15. The explanation of this fact is that the CMNaS25 catalysts has also a low percentage of intermediate strength Brönsted sites (desorbing at 473 K) which cause a significant production of cracking products, thus increasing the olefins total conversion and the values of the denominators in Eqs. (4) and (5). In the case of the CMNaS33 and CMNaS50 catalysts the existence of a higher density and strength of Brönsted sites could also explain their selectivity values.

As a general remark it could be said that by combining the variation of the Si/(Si + Al) ratio of the ASA supports with the introduction of sodium it was possible to obtain a support with the ideal characteristics to prepare CoMo catalysts with a high selectivity to the HDS reaction as well as a good HDS activity. This support permits from one hand obtain Mo and Co oxidic precursors with a good compromise between its capability of dispersion of the active phase and that of reduction/sulfidation. Furthermore, this support has specific acid–base properties; consequently, it could promote selectively the double-bond isomerization; a reaction which helps avoid the HYDO.

4. Conclusions

Combining the variation of the Si/(Si+Al) ratio along with sodium introduction, it was possible to finely tune the acid-base properties of amorphous aluminosilicates and obtain a material (15% Si/(Si+Al) ratio, 3 wt.% Na) with a selective formation of weak Brönsted sites. Because of these singular acid-base properties, the only acid-type reaction promoted by this catalyst was the double-bond isomerization from terminal to internal positions. Consequently, there were not acid-type reactions competing with the HDS reaction, and the double-bond isomerization promotes the formation of internal olefins, which are more difficult to hydrogenate. In addition, using this material as support of CoMo catalysts, a Mo oxide species distribution with an important participation of β -CoMoO₄ crystalline species was obtained. As a consequence of this especial balance of the acid properties and of the oxidic Mo-surface-species distribution, this catalyst presented an activity similar to that of the CoMo/Al₂O₃, but with improvements in the selectivity to HDS.

Additionally, it was also encountered that when CoMo catalysts supported on materials of predominantly acidic nature are used the linear olefins inhibit the HDS activity more than the branched ones, whereas the contrary effect was encountered when supports of a predominantly basic nature are used.

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