Influence of carburization time on the activity of Mo₂C/CNF catalysts for the HDO of guaiacol

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Abstract

Carbon nanofiber (CNF) supported β -Mo₂C-based catalysts were synthesized by carbothermal hydrogen reduction at 750 °C for different times (1, 2, 4, 6 and 18 h) in order to study both the carbide phase formation and the CNF stability during this key stage. Catalysts were characterized by N₂ physisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy, inductively coupled plasma optical emission spectrometry and scanning transmission electron microscopy. Subsequently, catalysts were evaluated in the hydrodeoxygenation (HDO) of guaiacol using a batch autoclave reactor at mild conditions of temperature and pressure (300 °C and 20 bar of H₂). Liquid products were analysed after 2 h of reaction by gas chromatography. In all cases, β -Mo₂C phase was formed during the carburization, and crystal sizes increased (from 6 to 18 nm as measured by XRD) as the carburization time did. However, a deep gasification of the support was observed in catalysts carburized above 6 h, resulting in a dramatic loss of

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specific surface area. In the guaiacol HDO reaction, higher conversions (72-80 %) and HDO ratios (53-63 %) were obtained using catalysts carburized for 2 h and onwards. Considering the carbide content in the catalyst, 1 and 2 h carburized catalysts exhibited the highest values of formation of HDO products: phenol, cyclohexane + benzene and anisole. Besides this, a clear relationship between the Mo_2C surface area ($S_{\text{Mo}_2\text{C}}$) and the product formation rate could be inferred for the catalysts carburized at 1, 2 and 4 h, in which the textural properties were not affected by the carburization time. On the other hand, longer carburization times had a worse performance despite the largest values of $S_{\text{Mo}_2\text{C}}$, being this fact related to the dramatic loss of the catalyst textural properties.

Keywords: *hydrodeoxygenation of guaiacol; molybdenum carbide catalyst; carbon nanofibers; carbothermal reduction; gasification.*

1. INTRODUCTION

The hardness, thermal stability, good electrical conductivity, relative low cost preparation and high surface reactivity of molybdenum carbide have led to an increasing interest in its development [1, 2]. The contraction of the d-band due to the introduction of carbon atoms in the molybdenum lattice provides the latter similar properties than those observed in a noble metal [3, 4]. Therefore, Mo_2C based catalysts are suitable in heterogeneous reactions in which electron transfer from the catalyst to the reactant is necessary, such as hydrodeoxygenation (HDO), hydrogenation or desulphurization [5-7]. Moreover, its catalytic performance highly depends on the crystal structure presenting in the final catalyst, which is mainly determined by the synthesis route [8]. Indeed, carburization temperature, time, heating rate and the carbon source employed in

the process are of paramount importance in the correct formation of the desired Mo carbide phase [9-11]. β -Mo₂C has shown higher catalytic activity in reactions of dehydrogenation [12], hydrogenolysis [13], hydrodenitrogenation [14] and hydrodesulphurization [15] due to the disordered distribution of the carbon atoms in its lattice.

The most typical method to synthesize Mo₂C is the temperature programmed reaction where the molybdenum precursor is heated up under a carburizing gas flow [16]. In the case of carbon supported molybdenum catalysts, carbon material itself can be used as the carbon source for carburization when hydrogen is used as carburizing gas, thus avoiding the use of hydrocarbons that may promote the counterproductive formation of coke on the Mo₂C surface [17]. This variation known as carbothermal hydrogen reduction (CHR) [18, 19] is typically carried out in the temperature range of 600-800 °C [9, 11, 20-22] and it has been studied using a wide variety of carbonaceous supports. Activated carbons have been the carbon support most commonly reported [18, 20, 22-31], although other materials such as filamentous carbon as nanotubes or nanofibers [10, 17, 21, 24, 32-39], ordered mesoporous carbons (OMC) [25, 40] or carbon blacks [9, 36, 41] have also been investigated.

Despite its good performance in the synthesis of molybdenum carbides, the thermostability of the carbon support is important since gasification problems have been reported, being catalyzed by the Mo₂C formed [11, 17, 20]. Mordenti *et al.* observed a large loss of the specific surface area of a commercial activated carbon during the CHR at 700 °C [18]. He *et al.* measured a carbon loss of 47.1 wt. % after 2 h of CHR at 700 °C [22]. Liang *et al.* identified CH₄ in gas products as indication of the support gasification during the carbothermal reduction of a Mo precursor at temperatures up to 900 °C using an ultrahigh surface area carbon (> 3000 m²/g) [20]. Wang *et al.* claimed

that CH₄ generated from the carbon support during the CHR is necessary for the Mo₂C formation [11, 23].

Several authors reported the carburization temperature or heating rate study on the CHR [9-11, 17, 20, 42, 43]. Nevertheless, very few works studied specifically the influence of the carburization time and the support gasification on the morphology of the final catalyst. Pielaszek *et al.* performed an in-situ XRD study of the Mo₂C synthesis on activated carbon concluding that the Mo₂C crystallite size increased with the carburization time [31]. Wang *et al.* observed an increment of the Mo₂C phase content when the temperature was maintained 90 minutes once reached the desired temperature [23]. Very recently, Bitter *et al.* reported the effect of the temperature and carburization time using CH₄/H₂ and Ar as carburization gases [44] via in-situ XRD measurements, reporting that the β -Mo₂C reflections sharpened when the catalyst was held at 800 °C for a prolonged time (up to 6 h). However, to the best of our knowledge, the systematic study of the CHR at a given temperature using carbon supported catalyst, and particularly the effect on the Mo loading and the changes in the carbon support physico-chemical and morphological properties has not been attempted in the literature.

Following our previous work on the effect of the temperature and carburization heating ramp [10], in this study we address the effect of the carburization time on the formation of β -Mo₂C using carbon nanofibers (CNF) as both carbon source and support by carbothermal hydrogen reduction. Catalysts were evaluated in the HDO of guaiacol and the conversions as well as the distribution of products for each catalyst were determined, and the corresponding structure–activity relationship was established.

2 CATALYSTS SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1 Synthesis of Mo₂C/CNF catalysts

The production of CNF and the subsequent treatments of purification and oxidation were carried out following a procedure previously described [10]. For clarification, the purified/functionalized material is denoted as CNF hereafter. Mo₂C catalysts were synthesized by incipient wetness impregnation followed by a carburization stage with H₂ (CHR) [10]. The corresponding quantity of Mo precursor ((NH₄)₆Mo₇O₂₄·4H₂O) was deposited on the CNF to achieve a 10 Mo wt. % in the final catalyst (without considering the effect of the support gasification), and dried overnight at 60 °C. After that, the impregnated CNF were carburized at 750 °C in a fixed-bed quartz reactor using a heating ramp of 10 °C/min and a stream of H₂ of 100 mL/min. Once reached the carburization temperature, it was hold for the desired time (1, 2, 4, 6 and 18 h) and then cooled to room temperature under 100 ml/min of pure N₂ flow. To preserve the β-Mo₂C phase formed, catalysts were passivated with an O₂:N₂ flow (01:99 v/v) during 1 h at room temperature and stored until use.

2.2 Catalytic tests: HDO of guaiacol

The catalysts were tested in the HDO of guaiacol in a batch autoclave reactor of 100 mL at 300 °C and 2 h. In each test, 0.2 g of catalyst, 40 mL of n-decane and 1.2 mL of guaiacol were placed in the reactor, which was purged and loaded with 20 bar of pure H₂ at room temperature. The reactor was heated up to 300 °C (10 °C/min) reaching a pressure of 32 bar. After reaction, the liquid phase was separated from the catalyst by filtration and chemically analyzed by GC. The gas chromatograph used for the detection of compounds formed after the HDO of guaiacol was a CLARUS 580 (Perkin Elmer) equipped with a FID detector (330 °C) and a 30 m long and 250 μm diameter Elite-5 column (crossbond: 5 % diphenyl-95 % dimethylpolysiloxane). The liquid was

vaporized at 275 °C and introduced to the column with a split ratio of 19/1. The oven program started at 40 °C during 2 min, ramped to 275 °C (5 °C/min), further ramped to 300 °C (15 °C/min) and held it for 5 min to ensure the complete elution of all products. The products were identified as described in a previous work [10], allowing the determination of guaiacol conversion (X_{Gua}), yield to a product i (Y_i), yield to a product i normalized per mol of Mo (specific product yield = SPY_i), HDO ratio (which consider both partial and full deoxygenation compounds according to the numbers of oxygen atoms removed: 2 = 2-oxy, 1 = 1-oxy) and carbon balance (C; molar %). These formulas can be found in the supplementary information.

2.3 Characterization techniques

The specific surface area (S_{BET}) and the total pore volume (V_t) of the support and the catalysts were determined by 77 K N₂-physisorption (Micrometrics ASAP2020). The S_{BET} was calculated by applying the BET method to the adsorption isotherm and V_t at a relative pressure of $p/p_0 > 0.989$.

X-ray diffraction (XRD) was employed for the determination of the crystal sizes and phase identification of the catalysts using DIFRAC PLUS EVA 8.0 and TOPAS software. The catalysts were scanned at $2\theta = 20-80^\circ$ each 0.05° every 3 s by a Bruker D8 Advance Series 2 diffractometer using Ni-filtered CuK α radiation and a secondary graphite monochromator.

X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were recorder in an ESCAPlus (OMICROM) spectrometer under vacuum ($< 5 \times 10^{-9}$ Torr). The apparatus was equipped with a hemispherical electron energy analyzer and the X-ray were used at 225 W (15 mA and 15 KV) with a non-monochromatized MgAl α ($h\nu = 1486.7$ eV) radiation. The spectra analysis was obtained using CASA XPS software applying Shirley type background.

Inductively coupled plasma optical emission spectrometry (ICP-OES) were performed to the catalysts to determine the final metal composition in a Spectroblue (AMETEK), the catalysts were treated by sodium peroxide fusion procedure.

Scanning transmission electron microscope (STEM) was used to mapping the catalyst in a Tecnai F30 (FEI) using 300 KeV. The catalysts were deposited on amorphous carbon coated copper grids.

3 RESULTS AND DISCUSSION

3.1 Effect of the carburization time on the catalyst properties

The XRD patterns of the CNF and the catalysts obtained at 750 °C and different CHR times are shown in Figure 1. Four different crystal phases were identified: graphitic carbon, β -Mo₂C (orthorhombic structure system identified by the plane (101) at 39.4 [17, 45]), MoO₂ and metallic Mo. The characteristic reflections of the graphite phase from the CNF support correspond to the planes: (002), (100), (101), (004) and (110) [46]. These reflections showed a decrement of their intensities, whereas the opposite is observed for the β -Mo₂C signals, resulting in an increase in the β -Mo₂C crystal sizes (Table 1). The disappearance of the graphitic signals can be tentatively explained due to the carbon consumption during the carbide phase formation and/or the catalytic gasification of the support by the Mo₂C nanoparticles formed [11, 17, 20], which in the case of the Mo₂C/CNF supported catalyst started at ca 525 °C [10]. However, other authors have attributed the decrease on the intensity of the graphite diffraction peaks to the absorption of the X-rays by the large molybdenum carbide particles formed during the synthesis. XRD diffraction pattern of the catalyst carburized during 18 hours also showed the appearance of Mo⁰ (bcc system [47]), which is only detected in this catalyst.

Additionally, small reflections of MoO₂ were identified in some catalysts due to the passivation step.

Figure 1. XRD patterns of the CNF and the catalysts carburized at 750 °C during different times (1, 2, 4, 6 and 18 h).

Table 1. Characterization results of CNF and catalysts after carburization.

Carburization time (h)	β -Mo ₂ C ^a (nm)	Mo ^b (wt. %)	Weight loss (wt. %)	S_{BET} ^c (m ² /g)	V_t ^c (cm ³ /g)	$S_{Mo_2C} \cdot 10^4$ ^d (cm ² /g)
CNF	-	-	-	98.7	0.392	-
1	6.5	11.5	20.1	68.4	0.427	9.6
2	10.3	14.0	30.2	69.5	0.441	12.1
4	12.4	17.0	47.4	73.5	0.404	8.8
6	18.6	27.0	63.1	60.6	0.316	10.7
18	24.1	72.0	88.2	19.4	0.071	25.6

^a = XRD; ^b = ICP-OES; ^c = N₂ physisorption; ^d = Specific Mo₂C surface area calculated according to [48] taking into account the Mo content in the catalyst (see Supporting Information).

It is worth mentioning that the samples suffer a progressive mass loss during the carburization step (see Table 1), with values ranging from 20.1 to 88.2 wt. % for carburization times between 1 and 18 h, respectively. This seems to corroborate that the disappearance of the graphite signals from the XRD diffractograms can be related to the carbon gasification at prolonged carburization times. For this reason, a clear deviation from the targeted final Mo content (10 wt. %) was observed comparing the ICP-OES results: catalysts carburized during 1 h showed a Mo content close to the nominal value (11.5 wt. %), while times of 6 and 18 h presented larger Mo contents from 27 to 72 wt. %, respectively.

The specific surface area (S_{BET}) and total pore volume (V_t) are listed in Table 1. Those catalysts carburized at 1, 2 and 4 h did not show large differences in the textural properties of the catalysts, although S_{BET} values were reduced by ca. 30% as compared to the CNF support. As the carburization time increased to 6 h., S_{BET} and V_t values diminished, being this reduction much more obvious at the longest carburization time tested. Thus, the catalyst carburized for 18 h had a S_{BET} of 19.4 m²/g, value close to those reported for unsupported Mo₂C, evidencing the consumption of the carbon support.

In order to gain better insights about the structure-activity relationship and to consider the effect of the Mo content and the Mo₂C particle size, the Mo₂C specific surface area (S_{Mo_2C}) was calculated according to [48], taking into account the nanoparticles diameter determined by STEM and the Mo₂C content determined by ICP (formulas used for the calculus can be found in the supporting information). The Mo₂C specific surface area first increased between 1 and 2 h to reach a maximum and then it decreased for the catalysts carburized for 4 h. The Mo₂C surface area increased again for longest

carburization times, being this increase dramatic for the catalyst carburized for 18 h, as expected due to the very high Mo content.

In order to assess the surface chemistry and the Mo oxidation state in the catalysts, XPS analyses were performed. The deconvolution of the XPS Mo3d region, XPS spectra and the atomic composition of catalysts carburized at different times are shown in Figure 2, Figure S1 and Table 2, respectively. The Mo/C surface ratio was ca. 0.02-0.04 in the catalysts carburized during 1, 2 and 4 h, much lower than the values obtained for those carburized at 6 or 18 h (0.15 and 0.50, respectively), where the gasification of the support was much higher, indicating a significant increase in the surface Mo as the carburization time increased. This fact also resulted in the increase of the NiCo nanoparticles used to grow the CNF due to a concentration effect. Regarding the Mo oxidation state in the catalysts, four components were identified in the deconvolution of the Mo3d region (Figure 2): Mo^{2+} (228.1-228.3 eV), $\text{Mo}^{\delta+}$ (228.7-229.0 eV), Mo^{4+} (229.9-230.3 eV) and Mo^{6+} (232.3-232.6 eV). The existence of an intermediate between MoO_2 and Mo_2C , $\text{Mo}^{\delta+}$ ($2^+ < \delta^+ < 4^+$) was attributed to an oxycarbide phase [11, 49]. The catalysts prepared at carburization times lower than 18 h showed a similar distribution of Mo states. In the case of the 18 h-carburized catalyst, Mo^0 (226.9 eV) was also found in this region. Oxidation of Mo_2C (mainly Mo^{6+} and Mo^{4+} signals) can be ascribed to the passivation step [10]. The oxygen content also increased at longer carburization times. This fact is attributed the increase in the Mo content as the carburization time did, implying larger oxygen requirement to passivate the catalyst. Regarding the contribution of carbide phases (Table 2), Mo^{2+} relative content in the catalysts increased as the carburization time did (10.7 to 27.0 at. %), while on the contrary, the oxycarbide phase ($\text{Mo}^{\delta+}$) decreased (27.8 to 10.1 at. %). CH_4 produced as consequence of gasification might react with the oxycarbides to produce more Mo_2C .

However, the atomic composition of those species (considered as catalytically active towards HDO reactions) increased as the carburization time did. The catalyst carburized at 18 h also showed the appearance of a new peak located around 227.0 eV related to Mo^0 , which could have been formed due to carbon deficiency during the carburization at prolonged times.

Figure 2. Deconvolution of the XPS Mo3d region of the catalysts obtained at different times of carburization: 1, 2, 4, 6 and 18 h.

Table 2. Molybdenum oxidation state and atomic composition determined by XPS for catalysts obtained at different times of carburization: 1, 2, 4, 6 and 18 h.

Carburization Time (h)	XPS (atm. %)									
	Mo^0	Mo^{2+}	$\text{Mo}^{\delta+}$	Mo^{4+}	Mo^{6+}	Mo	O	C	Ni+Co	Mo/C
1	0.0	10.7	27.8	4.0	57.5	2.0	3.8	94.2	0.0	0.02
2	0.0	14.9	22.6	13.7	48.8	2.8	6.5	90.7	0.1	0.03

4	0.0	14.4	23.7	12.1	49.8	3.3	8.9	87.8	0.1	0.04
6	0.0	20.0	13.9	12.0	54.1	10.0	23.0	66.9	0.4	0.15
18	14.3	27.0	10.1	13.1	35.4	18.6	45.1	35.1	1.01	0.53

The morphology of the catalysts can be found in the STEM images shown in Figure 3. Samples showed rounded molybdenum nanoparticles (bright spots) decorating the CNF as confirmed by EDX (see Figure S2 in the supplementary information). The average size of the Mo nanoparticles (see particle size distributions in Figure S3 in the supplementary information) increased as the carburization times did due to sintering effect: 1 and 2 h carburized catalysts showed 5.7 ± 2.7 nm and 4.2 ± 1.7 nm nanoparticles; catalysts carburized at 4 and 6 h had larger nanoparticles of 7.1 ± 8.3 nm and 9.3 ± 7.3 nm; and catalyst carburized at 18 h showed large like-filamentous nanoparticles (16.9 ± 10.6 nm) along the size of the CNF. In addition, small nanoparticles smaller than 2 nm (figure 3. c, f, i and l) were detected covering the CNF surface in catalysts carburized at 6 h and below. On the other hand, in catalysts carburized above 4 h the gasification effect was noticed. These catalysts showed longitudinal indentation in the surface of the nanofibers (Figure 3. h, i and k, circles in yellow) and a length shortening thereof. The catalyst carburized 18 h (Figure 3. m, n and o) showed that Mo_2C was located covering the entire support surface. For that reason, the images were so bright that they did not allow differentiating the nanoparticles from the CNF. However, in Figure 3 (m and o, yellow arrows), a shortening of the CNF due to the extreme gasification suffered during the CHR can be observed.

Figure 3. STEM images of catalysts carburized at different times: a, b, c) 1 h; d, e, f) 2 h; g, h, i) 4 h; j, k, l) 6 h; and m, n, o) 18 h.

3.2 Activity of the Mo₂C/CNF catalysts in the HDO of guaiacol

The catalysts activity was tested in the HDO of guaiacol during 2 h at 300 °C and 20 bar of H₂. The products obtained in the liquid phase resulted from the different reaction pathways [10]: HDO reactions (cyclohexane + benzene, phenol, anisole and methylcyclohexanol) and reactions of demethylation/methyl substitution (cresol, xlenol and catechol). In order to give a better insight about the catalyst performance, these products were grouped according to the number of oxygen atoms removed from guaiacol: non-deoxygenated (0-oxy), including catechol; mono-deoxygenated (1-oxy),

including phenol, anisole, methylcyclohexanol, cresol and xlenol; and fully deoxygenated (2-oxy) compounds such as cyclohexane and benzene. In Table 3 can be found the results obtained for the catalysts carburized at different times: guaiacol conversion (X_{Gua}), HDO ratio (which consider partial deoxygenation, 1-oxy; and full deoxygenated compounds, 2-oxy) and the carbon balance (C mol. %) whereas Table S1 in supporting information shows the yield to each product. Establishing structure-activity relationship in this case is not straightforward since as previously commented, the carburization time exerted marked differences in the physicochemical properties of the catalysts, namely Mo and support content, the Mo₂C crystal size, the textural properties and the surface Mo species composition. A first inspection of Table 3 revealed that a clear trend between the guaiacol conversion and the carburization time cannot be established, although as expected due to the increasing Mo content, this parameter showed relatively higher values at prolonged carburization times.

Table 3. Conversion, HDO ratio and carbon balance for the catalysts carburized at different times.

Carburization time (h)	X_{Gua} (%)	HDO (%)	C (molar %)
1	34.5	21.0	89.1
2	72.0	52.8	71.5
4	56.7	44.5	72.3
6	72.3	57.0	62.3
18	79.7	62.7	68.9

HDO ratio, which is an indication of the efficiency for O removing, showed a similar trend as guaiacol conversion. Thus, catalyst carburized during 1 h showed a relative low conversion (34.5 %) and HDO ratio (21.0 %), whereas catalyst obtained at carburization times above 1 h achieved conversions and HDO values in the range 56.7-79.7 and 44.5-62.7 %, respectively. The 2 h-carburized catalyst showed similar conversion and HDO

values that the catalyst carburized during 6 h, despite the marked differences in Mo content (both bulk measured by ICP and at the surface measured by XPS, see Table 1 and Table 2). This is tentatively related to the differences in Mo₂C crystal sizes: 10.3 vs 18.6 nm measured by XRD (Table 1), and 4.2 ± 1.7 vs 9.3 ± 7.3 nm determined by TEM (Figure S3), which resulted in a better Mo₂C dispersion, i.e. larger specific Mo₂C surface area, for the 2 h carburized catalyst (Table 1). Carbon balance closed typically in the range 62.3-89.1 %. Again, even though a clear relationship cannot be inferred, shorter carburization times resulted in better carbon balance, implying that the formation of soluble higher molecular weight products that could not be detected by GC (and grouped as “Others”, see Figure 4) calculated by the difference in mass balance is less pronounced at lower Mo loading and smaller β -Mo₂C crystal sizes.

Figure 4. a showed the distribution of products identified by GC of the liquid phase grouped according to the number of oxygen atoms removed from guaiacol, as previously commented. Two catalytic behaviors were observed depending on the carburization time. For carburization below 6 h, a maximum in the production of full deoxygenated (2-oxy) products was obtained for the 2 h carburized catalyst (21.1 wt. %). This could be explained by the relatively good dispersion of the Mo₂C phase in this catalyst, resulting in the largest high Mo₂C surface area (12.1 cm²/g) among the catalyst carburized between 1 and 6 h. In contrast, the 1-oxy products, having the largest proportion among the different products families (0-,1- and 2 oxygen atoms removed), decreased as the carburization time increased.

Catechol (0-oxy product) formation was attributed to the support acidity [42]; in this case, longer carburization times resulted into higher support loss by gasification (Table 1), which might affect the catalyst acidity due to the progressively removal of the surface oxygen groups of acidic character. For this reason, the catalyst carburized for 1

h showed the highest 0-oxy concentration (8.8 wt. %) and the catalyst carburized at 6 h only showed a 0.6 wt. %. The production of soluble heavy compounds (labelled as “others”) showed the opposite trend as that observed for the 1-oxy compounds, obtaining the largest concentration for the catalyst carburized at 6 h. Again, the differences in the surface chemistry of the catalyst at different carburization time may be the reason of the differences observed in the formation of this high molecular weight compounds, although the differences in the Mo_2C crystal size can not be excluded, being this mechanism yet to be elucidated.

The results obtained for the catalyst carburized the longest time (18 h) were aside of the observed behaviour for the 1, 2, 4 and 6 h. The highest concentration observed in the liquid was 2-oxy compounds (30.7 wt. %), as a probably consequence of high $S_{\text{Mo}_2\text{C}}$ and Mo loading. The severe CNF gasification may result in a very limited acid character of the final material, thus yielding a high concentration of *Others* and relative low 0-oxy content.

Figure 4. Products of the HDO of guaiacol for the catalysts carburized at different times expressed as: a) oxygen removal from guaiacol and b) specific product yield.

Figure 5. Relationship between the specific product yield, carburization time and Mo₂C surface area.

The specific product yield (SPY), i.e., the yield to each product normalized per Mo (expressed as moles of a product *i* formed after 2 h reaction time per moles of Mo determined from ICP data) for the catalysts carburized at different reaction times is shown in Figure 4. b. All the catalysts showed higher SPY to HDO products (phenol, anisole and cyclohexane + benzene) than products that resulted from demethylation/methyl substitution of guaiacol and products (catechol, xylene and cresols) (Figure 4.b). Regarding the normalized product distribution, the maximum production of cyclohexane + benzene was obtained for the catalyst carburized during 2 h, as observed in the product composition (Figure 4. a). On the other hand, the production of phenol decreased using longer carburization time catalysts. Xylene was only identified in the liquid product obtained using the catalyst carburized at 1 h.

Besides this, the overall SPY (as sum of the SPY for each product) increased from 1 to 2 h carburization time, reaching a maximum and then it decreased progressively as the carburization time increased. This result can be again tentatively related to the specific surface area of Mo_2C ($S_{\text{Mo}_2\text{C}}$, Table 1): thus, if we only consider the catalyst carburized at 1, 2 and 4, where it was assessed that the textural properties of the support were unaltered, then the maximum in SPY coincides with a maximum in the $S_{\text{Mo}_2\text{C}}$, as it is illustrated in Figure 5. However, if we take into account the $S_{\text{Mo}_2\text{C}}$ calculated for those catalysts carburized at longer reaction times (6 and 18 h), it is obvious that the correlation between the SPY and the $S_{\text{Mo}_2\text{C}}$ is not maintained. As an example, catalysts carburized at 2 and 6 hours showed $S_{\text{Mo}_2\text{C}}$ values of $12.1 \cdot 10^4$ and $10.7 \cdot 10^4 \text{ cm}^2/\text{g}_{\text{cat}}$, respectively, although the SPY value of 2 h-carburized catalyst doubled the one obtained with the catalyst carburized for 6 h. This clearly indicates that the consumption of the CNF, either by reaction with Mo to form the carbide phase or to gasification, affected negatively the catalyst performance. The extreme case can be found for the catalyst carburized for 18 h: it showed the largest $S_{\text{Mo}_2\text{C}}$ ($25.6 \cdot 10^4 \text{ cm}^2/\text{g}_{\text{cat}}$) and the largest contribution of carbide/oxycarbide species at the surface, although it displayed the worst performance in the HDO of guaiacol. As mentioned in previous section, this catalyst showed the largest weight loss and therefore had the lowest values of both S_{BET} and V_t (Table 1) due to a severe gasification, probably catalyzed by the Mo_2C nanoparticles thus formed. These facts highlights the importance of avoiding gasification in CHR to preserve the support. In this case, CNF was not active in the HDO of guaiacol (10.1 % of conversion with a liquid composition based in phenol (5.9 wt. %), catechol (7.2 wt. %), methylcyclohexanol (1.5 wt. %) and toluene product (38.1 wt. %) with a high production of *Others* (47.3 wt. %)) but it has been evidenced how its

presence affect the Mo_2C dispersion, the textural properties and the catalyst acidity, thus affecting the catalytic performance.

4 CONCLUSIONS

Carbon nanofiber (CNF) supported $\beta\text{-Mo}_2\text{C}$ -based catalysts were synthesized by carbothermal hydrogen reduction at 750 °C for different times: 1, 2, 4, 6 and 18 h, and evaluated in the HDO of guaiacol at 300 °C, 20 bar of H_2 during 2 h. The carburization time had a crucial influence in the $\beta\text{-Mo}_2\text{C}$ crystal formation, size and concentration in the final catalyst. Carburization times below 6 h showed a surface Mo concentration in the range of 2.0-3.3 at. % and $\beta\text{-Mo}_2\text{C}$ sizes around 6.5-12.4 nm (seen by XRD). After 6 h, the gasification of the support is excessive, with noticeable weight losses in the catalysts (63.1-88.2 wt. %) and their texture, resulting in a substantial increase in both the surface Mo content (10-18.6 at. %) and the size of the carbide crystals formed (18.6-24.1 nm) as a result of sintering. Additionally, the catalyst carburized at 18 h presented the appearance of Mo^0 , which could have been formed by carbon deficiency (from the CNF) to form the carbide phase during the carburization step. Regarding the catalytic activity of these catalysts, a higher guaiacol conversion (72-80 %) and HDO ratios (53-63 %) were obtained using catalysts carburized for 2 h and onwards. Considering the oxygen removal efficiency and the HDO products, 1 and 2 h carburized catalyst exhibited the larger proportions to 1-oxy and 2-oxy compounds. Besides this, a clear relationship between the specific Mo_2C surface area and the SPY could be inferred from the catalysts carburized at 1, 2 and 4 h, in which the CNF textural properties were not affected by the carburization time. On the other hand, despite the CNF did not showed an important catalytic activity, catalysts carburized at longer reaction times had a worse

performance despite the largest values of S_{Mo_2C} , being this fact related to the dramatic loss of the catalyst textural properties. This clearly indicating that the carbon support affects the Mo_2C dispersion, the textural properties and the catalyst acidity, thus affecting the catalytic performance.

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