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Selective hydrogen production from formic acid decomposition over Mo carbides supported on carbon materials

D.H Carrales-Alvarado^a, A.B. Dongil^{*a}, J.M. Fernández-Morales^b, M. Fernández-García^{a,c}, A.Guerrero-Ruiz^{b,c}, I. Rodríguez-Ramos^{*a,c}

The decomposition of formic acid to obtain hydrogen has been studied using molybdenum carbides supported on an activated carbon and two high surface area graphites, H_{200} (200 m²/g) and H_{400} (400 m²/g). Particular attention is paid to the effect of Mo loading. The catalysts were prepared *in situ* using a mixture of CH₄ and H₂ up to 700°C. Under these conditions carburization was mostly complete. We observed, that the support influenced the Mo_xC phase obtained so that it seems that the ratio of defective carbon influences the phase. However, for these materials the C/Mo ratio did not influence the obtained crystal phase. The characterization by XRD showed that while β -Mo₂C phase was obtained over activated carbon and over H_{200} . In contrast MoO_xC_y was obtained over H_{400} . These catalysts reached 100% conversion on the formic acid decomposition at temperatures in the range 190-250°C and were also highly selective under these mild conditions with values for CO₂ selectivity in the range 85.0-96.5%. The best results were achieved over a 10 wt% Mo loading on activated carbon that reached 96.5% selectivity to H_2 . Also, changes in the molybdenum phases were observed on the spent catalyst. Some redox transformations during reaction were resposible of the transformation of β -Mo₂C into oxycarbide MoOXCy. In summary, the results of catalytic performance indicated that β -Mo₂C phase was more active, selective and stable than MoOXCy under the studied conditions.

1. Introduction

The need of substituting fossil sources with other more environmentally friendly alternatives that match current energy schemes, has prompted research on more sustainable energy sources. One of the possibilities is to use hydrogen as energy vector as it is well known to own a high energy density per mass, and it only produces water upon combustion. However, hydrogen actually holds a low energy per unit volume in gas phase, so it would occupy a large volume which limits its widespread application. Alternatively, hydrogen can be stored in other molecules that are more easily handled and that decompose in hydrogen when required [1]. Among them, formic acid, HCOOH, represents an interesting alternative since it offers a high content of hydrogen 4.3 wt%, it is safe and it is produced in large quantities in biorefineries as a subproduct of the Biofine process [2]. Its attractiveness is also due to the soft conditions required to decompose in hydrogen and carbon

dioxide in the presence of a catalyst. However, upon reaction conditions the catalyst may also promote the dehydration reaction of formic acid, producing carbon monoxide and water which is an undesirable reaction path, not only because of the lower hydrogen production but also because carbon monoxide is a poison of catalysts, specially those most commonly employed in fuel cells such as Pt [3].

Formic acid decomposition over heterogeneous catalysts has been studied over metals in their reduced state [4], metal oxides and more recently using immobilized noble metal complexes [5]. Despite the clear potential of these latter systems that could provide a high atom efficiency, their high cost and low stability complicates industrial application.

Moreover, an attractive catalyst should also be easy to synthetize using an environmentally safe process and cost effective. Some works using oxides such as α -Fe₂O₃, pure Al₂O₃ and MgO doped Al₂O₃ appeared, however their activity and selectivity is low even working at temperatures above 200°C [6 7].

In this context, the use of transition metal carbides emerges as an interesting alternative since they have proven to be very active and selective in several reactions. The reason for these results seems to be their structural similarity to Pt group metals. The potential of molybdenum carbide on the production of hydrogen by decomposition of several starting molecules such as methanol or formic acid has already been assessed [8,9, 10]. It was demonstrated that decomposition of formic acid over molybdenum carbide surfaces was enhanced compared to

^{a.} Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie No. 2, Cantoblanco, 28049 Madrid, Spain

^{b.} Dpto. Química Inorgánica y Técnica, Facultad de Ciencias UNED, Senda del Rey 9, 28040 Madrid Spain.

^c UA UNED-ICP(CSIC), Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, Madrid, Spain.

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metallic molybdenum even at low temperatures [9]. Indeed, the selectivity obtained over C-Mo (110) was 15 times higher than over Mo (110).

Other authors studied the effect of carbon source on unsupported molybdenum carbide structure and its relation to formic acid decomposition [11]. One of the challenges of molybdenum carbide to be used in heterogeneous catalysis is obtaining a high surface area material to maximize the activity. In this respect, some alternative synthetic procedures such as using other carbon precursors have been studied, but still surface areas below 40 m²/g were obtained [12]. Another possibility is to support the carbide onto a high surface area material. In this sense, the use of carbon supports can be beneficial for several reasons. The carbon support may favour the formation of the carbide by providing additional carbon source for the synthesis. Also, since water might be produced during the reaction, a hydrophobic and stable support under such conditions is preferred.

The effect of the nature of carbon support and its influence on the catalytic performance on reactions like steam reforming of methanol or dry reforming of methane has been reported [13]. Still, the catalytic behaviour of carbon-supported molybdenum carbide on formic acid decomposition has been scarcely investigated and assessing the effect of its structure is highly challenging and not fully understood.

Hence, we have studied the synthesis of molybdenum carbide using a mixture of CH_4 and H_2 over two commercial high surface area graphites and we have compared their performance with the activated carbon supported counterpart to evaluate the effect of the graphitic structure.

2. Results and discussion

External surface area of the catalysts was measured for each sample and results are summarized on Table 1. The SBET of the parent supports is 950, 400 and 200 m^2/g for AC, H_{400} and H_{200} respectively. It can be observed that \boldsymbol{S}_{BET} decreases as the amount of carbide increases. The reduction of S_{BET} for the high surface area graphite-based catalysts is higher than the expected value due to the weight percentage of carbide on the surface. The loss of surface area in carbon supports upon carburization has been well reported and ascribed to the poreblocking due to the carbon growth during the carburization and/or the metal nanoparticles or to partial gasification of the support [14]. However, considering the structure of high surface area graphites, the observed decrease on surface area is likely due to the agglomeration of the graphite particles upon thermal treatment. The higher loss of surface area on active carbon could be ascribed either to the easier gasification of carbon on that material and particularly, to its large proportion of porous in the microporous range which are easily blocked. The external surface area of the activated carbon without microporous is 400 m²/g.

Table 1. Textural, physical-chemical properties of the catalysts and intrinsic activity.

			_	
Catalyst	S _{BET} (m²/g)	d _{тем} (nm)	Mo/C XPS	Activity (mol $CO_2/mol Mo h^{-1}$)
5MoxC/H ₄₀₀	217	2.0	0,0049	85
10Mo _x C/H ₄₀₀	213	2.2	0,0103	112
20Mo _x C/H ₄₀₀	204	3.8	0,0105	73
10Mo _x C/H ₂₀₀	107	na	-	61
20Mo _x C/H ₂₀₀	72	8.1	-	10
10Mo _x C/AC	377	2.1	-	240

Diffractograms of molybdenum carbides samples, in Fig.1, differ depending mainly on the type of support.

The XRD patterns of $10Mo_xC/AC$ and $20Mo_xC/H_{200}$ show quite sharp diffractions at 20 of 34.4°, 37.7°, 39.4° and 61.5°. On the other hand, the catalysts prepared over H₄₀₀, 5-20 wt% Mo and $10Mo_xC/H_{200}$, display similar XRD profiles showing wide diffractions with maxima shifted to lower angles, ca. 20 of 36.7°-36.9°, compared to $20Mo_xC/H_{200}$ and $10Mo_xC/AC$, a fact suggesting that the contribution of several phases and/or the amorphous structure of the resulting supported nanoparticles. Moreover, none of the XRD of the fresh catalysts prepared over H₄₀₀ and AC display diffractions of the oxide phases. This confirming that the carburization treatment was mostly effective. Nonetheless, the XRD pattern of the catalyst $20Mo_xC/H_{200}$ shows two small diffraction peaks at 20 of 23.7° and 49.1° corresponding to MoO₃ (JCPDS-PDF 05-0508 and 76-1003).



Fig. 1 XRD patterns of the catalysts. Dotted lines represent $\beta\text{-Mo}_2\text{C}$ (red) graphite

There are several reports with different assignations for the XRD and no clear consensus exists. In order to assess for the carburisation mechanism taking place and the obtained structures, we followed the synthesis of $10Mo_xC/H_{400}$ using in situ Mo K-edge X-ray absorption near-edge spectroscopy (XANES). The Mo K-edge spectra, in Fig. SI 1, show the evolution of molybdenum species under the CH₄/H₂/He atmosphere during the temperature treatment. Application of principal component analysis (PCA) [15] to this set of spectra evaluates the number of Mo chemical species involved during the synthesis process and their concentration evolution. This information is summarized in Fig. 2. The absorption edges This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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(obtained using the derivatives of the spectra) were used to estimate the oxidation state of each species by using the linear correlation obtained with the reference Mo compounds (see Figures SI2 and SI3). In figure 2B the two Mo⁶⁺ species spectra exhibit similar characteristics to those of the AHM reference with a pre-edge feature in the spectra that does not appear in the other Mo species. So, the sample initially contains the supported ammonium heptamolybdate (AHM), in which Mo⁺⁶ is in six-fold coordinated sites (see reference spectra in Figure SI3). It is possible to observe three characteristics XANES resonances whose relative intensity is influenced by the local order around Mo atoms in octahedral symmetry [16]. Upon heating, the supported AHM is transformed into another Mo⁶⁺ species also in octahedral coordination, molybdenum oxide type structure, whose XANES spectrum shows higher intensity of the second XANES resonance relative to the first and third. This indicates changes in the specific surrounding environment of Mo atoms, likely an increase in the cluster size of the molybdenum oxide [16]. This process takes up to 350°C when the first Mo⁶⁺ is mostly absent. Meanwhile, a Mo⁺² species ascribed to molybdenum oxycarbide [16], MoO_xC_y, starts to appear at 300°C while the second Mo⁶⁺ species decreases. In the temperature range of ca. 400-600°C, the fraction of MoO_xC_y is mostly constant indicating that simultaneous formation and consumption of MoO_xC_v takes place with parallel formation of a Mo1+ species with XANES spectrum similar to that corresponding to the molybdenum carbide phase $\beta\text{-Mo}_2\text{C}$ (Figure SI2). Upon heating up to 700°C, it resulted in further carburisation with a final proportion of ca. 90% of β -Mo₂C and 10% of MoO_xC_y.



Figure 2. Concentration profiles (A) and Mo K-edge XANES spectra (B) of the different pure Mo species observed during the synthesis of $10 Mo_x C/H_{\rm 400}$

Based on XANES experiments we can now assign the XRD peaks as follows. The diffraction peaks observed for the catalyst 10Mo_xC/AC correspond to the (100), (002), (101) and (110) planes of the β -Mo₂C hcp phase (JCPDS-PDF 77-0720). The higher angle at which the maximum is observed for the other catalysts, would be in agreement with the presence of MoO_xC_y phase that holds a face-centered-cubic (fcc) structure with diffraction peaks at 37.1°, 44.1° and 62.9° [17, 18]. It must be noted, however, that XANES showed a higher proportion of β - ARTICLE

Mo₂C on the selected 10Mo_xC/H₄₀₀ sample than a what live observed by XRD. This can be attributed to the smalls ନିର୍ଦ୍ଧ ଭାଦନାର supported carbide particles which would be below the detection limit of XRD, i.e. < 5 nm, as also the TEM images, in Fig. 3 and Fig. SI4, confirmed. On the contrary for 10Mo_xC/AC, both large and small particles are carburised as the XRD and HRTEM images showed. For this sample, the well-resolved lattice fringes of 0.23 nm that correspond to the β -Mo₂C (101) planes are observed in particles as small as 2 nm. Similar findings are observed for $10Mo_xC/H_{400}$ for which also β -Mo₂C (101) is observed in small particles.

Hence, it can as well be inferred that larger particles are more difficult to carburise. This is agreement with the diffraction peaks ascribed to MoO₃ observed on 20Mo_xC/H₂₀₀ which is the sample with the largest particle size, ca. 8.1 nm as estimated by TEM in Table 1.



Fig. 3 Typical HRTEM images of a)10MoxC/H $_{400}$; b) 10MoxC/AC and c) 20MoxC/H $_{200}$ and the corresponding Fast-Fourier transform (FFT) pattern.

The XRD patterns of the samples with different Mo loading also seem to indicate that under the studied conditions the Mo/C loading did not influence the obtained carbide phase.

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It has been reported that the synthesis of molybdenum carbides through the TPR method may follow one of these paths: a) firstly, the decomposition of the molybdate precursor into MoO_3 takes places, which is then reduced to MoO_2 to finally result in the β -Mo₂C. b) Alternatively, after MoO_3 formation, this oxide may suffer a partial carburization to an oxycarbide MoO_xC_y , which is eventually transformed into β -Mo₂C [19]. This latter path proposed in literature, agrees quite well with the XANES results obtained in the present work, where both oxycarbide and β phases are observed.

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With the aim of gaining more information on the synthesis mechanism and the effect of the support, additional XANES experiments were performed with 20MoxC/H400 sample but using a H₂/He atmosphere. The analysis of the in situ Mo k-edge XANES spectra (Figure SI5) showed that the same MoO₃, MoOxCy and β -Mo₂C species are obtained as when CH₄/H₂/He is employed over the $10Mo_xC/H_{400}$ sample (see Figures 2 and 4). These results suggest that under the studied conditions, the carbon source to obtain the carbide is the support itself independently of the reaction atmosphere. Similar results were reported previously for temperatures below 600°C [19]. The slight differences between samples, i.e. the 20Mo_xC/H₄₀₀ is somewhat more resistant to reduction in agreement with XRD experiments, may be attributed to effects of the different particle size in the samples (Table 1). The 20Mo_xC/H₄₀₀ sample with larger particles is more difficult to carburize.



Figure 4. Concentration profiles (A) and Mo K-edge XANES spectra (B) of the different pure Mo species observed during the treatment of Mo20/H400 H2/He atmosphere.

Also, considering these stages it is reasonable to presume that the availability of more reactive carbon atoms from the support would aid on the formation of β -Mo₂C. In this sense, the carbon supports are characterized by their different proportion of edges to basal planes, i.e. the size of the graphitic layers, so that, a higher proportion of edges means more reactive carbon. This feature is given by the Raman spectra that allows comparison by using the intensity of the so-called D and G bands [20]. The Raman spectra of the supports, in Fig. SI6, used in the present work show that I_D/I_G ratio follows the trend AC >H₄₀₀ >H₂₀₀. Since external CH₄ does not seem to be involved on the carburisation mechanism, we performed H₂-TPR experiments coupled to mass spectrometry of the impregnated samples 10Mo_xC/H₂₀₀. 10Mo_xC/H₄₀₀ and 10Mo_xC/AC to assess for differences, among the supports. The masses corresponding to the main magnetic of H₂O (m/z 18), CO (m/z 28), CO₂ (m/z 44) and NH₃ (m/z 17) and the secondary of CH₄ (m/z 14) were followed along with other secondary fragments of H₂O and NH₃ (m/z 16, 15) and shown in Fig. 5



The three samples, displayed evolution of m/z 18-16 and 17 with maxima at 200-210°C and 290°C in a proportion that indicates they correspond to NH_3 and H_2O . These gases would be generated from the decomposition of the precursor, AHM, and the temperature range agrees with that observed in XANES for this transformation.

At higher temperatures, the profile is different for $10Mo_xC/AC$. This sample, shows a maximum at $400^{\circ}C$ in which contributions

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of m/z 18-16 are observed in a proportion that suggest that they correspond to H₂O. The same masses are observed at ca. 600°C but the intensity of these latter peaks is lower. Small intense signals for m/z 28 and 44 at ca. 290°C and 415°C are also observed. The samples $10Mo_xC/H_{200}$ and $10Mo_xC/H_{400}$ also display contributions of m/z 18-16 which can be ascribed to H₂O. However, the maxima appeared at 400°C and 660°C, this latter being the most intense peak. Also, simultaneous evolution of m/z 28 due to CO is also observed, although its intensity is very low.

The XANES results suggested that the source of carbon is the support itself and that carburisation already starts at 300°C, with the formation of the oxycarbide which is then transformed into β -Mo₂C (reaction 1).

$MoO_3+C^*+H_2 \rightarrow MoO_xC_Y+H_2O \rightarrow \beta-Mo_2C+CO$ (1)

In this range of temperatures, carburisation must be preceded by the formation of gaseous carbon species, most likely CH₄ coming from the reaction with hydrogen and releasing H₂O. However, the intensity of m/z 16-14 in the profiles up to 700°°C does not suggest the evolution of CH₄ and only above that temperature, an intense peak started to appear. We believe this is due to the consumption of the evolved CH₄ on the carburisation process.

Also, the different intensity of the MS-TPD peaks at 400°C and 600°C for AC and the two H samples seem to indicate that the extent in which the first step occurs in AC is greater than on H_{200} and H_{400} samples. This is reasonable since in this first step the incorporation of carbon takes place and, as already pointed out, activated carbon holds a larger proportion of reactive carbon atoms. In turn, it also suggests that carburisation took place in a larger extent, as also the XRD showed.

Regarding previous literature results, it has been reported that the synthesis of molybdenum carbide over carbon nanofibers and carbon nanotubes using the TPR method (CH₄/H₂) also led to the formation of the β -Mo₂C and that above 700°C no molybdenum oxide was observed [21, 22]. Other authors also analysed the effect of surface chemistry and structural properties of the support using an oxidized graphite and oxidized activated carbon [23]. Although a clear correlation of surface chemistry and structural properties with the formed molybdenum phase was difficult to obtain, the authors suggested that the defective carbon was somehow responsible for the formation of the β -Mo₂C and that the controlled reduction of the molybdenum precursor was a critical factor to determine the formed crystal phase.

Some authors proposed that Mo/C ratio on an ordered mesoporous carbon support controls the Mo_xC phase [24]. We observed that samples with different loading, mainly $10Mo_xC/H_{200}$ and $20Mo_xC/H_{200}$ displayed different XRD profile. However, this seems to be more related to the contribution of larger particles to the XRD profile, which are present in a higher ratio on samples with greater loading.

Our results are in agreement with some literature, that reported oxycarbide and β -Mo₂C as the only detected phases. We can add that even in a CH₄/H₂ atmosphere the source of

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3.2 Reaction results

The conversion of formic acid decomposition measured at each temperature is given in Fig 6A for all the tested catalysts. As the Figure shows, all the catalysts were active, however the temperature at which 100% conversion was reached varied greatly in the range 190°C to 250°C. Among the catalysts, the conversion curve was very similar for the samples $10Mo_xC/H_{400}$, $20Mo_xC/H_{400}$ and $10Mo_xC/AC$, while those of $5Mo_xC/H_{400}$, $10Mo_xC/H_{200}$ and $20Mo_xC/H_{200}$ shifted to higher temperatures.



Fig 6. A) Conversion of FA vs T and b) CO_2 selectivity vs T. Reaction conditions: 1 bar, GHSV= 20000 $\rm h^{-1}.$

In order to minimize the effect of Mo loading, the activities at 150 °C were estimated and the results are displayed in Table 1. The activity follows the trend $10Mo_xC/AC > 10Mo_xC/H_{400} > 5Mo_xC/H_{400} > 20Mo_xC/H_{400} > 10Mo_xC/H_{200} > 20Mo_xC/H_{200}$. The activity values and the similar particle size of the carbide on $10Mo_xC/H_{400}$ and $10Mo_xC/AC$, seem to indicate that the catalyst presenting exclusively β -Mo₂C phase is more active than those in which MoO_xC_y appeared as well. Regarding the effect of metal carbide loading, the activities for the sample with 10 wt% Mo supported on H₄₀₀ was significantly higher than those of 5

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wt% and 20 wt%. According to the microscopy, carbide nanoparticles are larger on the sample with higher loading, $20Mo_xC/H_{400}$, in agreement with the similar Mo/C surface ratio obtained by XPS for $10Mo_xC/H_{400}$ and $20Mo_xC/H_{400}$, shown in Table 1. This can explain straight forward the lower activity of $20Mo_xC/H_{400}$ and suggest that, in the studied system, above 10% wt. Mo there is an optimum loading before particles tend to form large agglomerates that diminished the active area, as observed in other carbon supported systems [25]. Similar and even more clear effect is observed for the catalysts supported on H_{200} .

The selectivity to CO_2 at each temperature, Fig 6B, was estimated considering the total concentration of CO_2 and CO as the only detected products and revealed significant differences. The catalysts displayed maximum selectivity in the range 85.0-96.5%, the catalyst $10Mo_xC/AC$ offering the best selectivity among the tested systems. This also points to a beneficial effect of β -Mo₂C phase compared to MoO_xCy.

Indeed, if we compare the selectivity achieved with the catalysts $10Mo_xC/AC$ and $10Mo_xC/H_{400}$, it is clear that the different phase influences the concentration of H₂ in the products. While with $10Mo_xC/AC$ selectivity to CO₂ reached 96.5% at conversions above 50%, with $10Mo_xC/H_{400}$ the selectivity for conversions over 50% was 91%.

Regarding molybdenum-based catalysts, previous literature reported that 100% formic acid conversion was achieved at temperatures above 250°C for unsupported molybdenum carbide systems [11] and over 200°C for supported systems over activated carbon with selectivity around 98% [26]. However, the catalysts employed in Ref. 11 and 26, were prepared using liquid phase mixture with organic compounds that is less attractive from an industrial point of view and may leave impurities on the catalysts.

Nevertheless, the reported catalytic performance using molybdenum carbide and our own results are better than other reported for non-noble metal systems like metal oxides, α -Fe₂O₃ for which maximum conversion was around 24% at temperatures of 200°C with low selectivity to H₂ [27,7] and other systems where Ag and Mg were used as dopants for Mo_xC that reached 90% selectivity [28].

Interestingly, the selectivity profiles with temperature shown in Fig 6B are similar. All the catalysts prepared over high surface area graphite, showed an initial selectivity decrease up to 140-180°C which corresponds to formic acid conversions in the range 10-12 % followed by a selectivity increase, up to temperatures above 200-260°C, i.e. when conversion reached 90%. These results are in agreement with previously reported selectivity profiles where other authors observed that CO_2 selectivity decreased with temperature in the temperature range 100-150°C [6]. However, the evaluation of the catalysts at higher temperatures performed in the present work shows that selectivity increased from conversions above 15%, and at 95% conversion the selectivity decreased again.

As long as the stability is concerned, additional experiments in time on stream at temperatures of 180-190°C for all the catalysts and at 220°C for the $20Mo_xC/H_{200}$ were performed during 12 hours. Both conversion and selectivity profiles, in Fig.

7, remain stable with time for all the catalysts, except for the conversion achieved with 20Mo_xC/H₂O¹ that 39/Showed ⁸⁸ a continuous decrease with time, while selectivity was constant. It is known that the decomposition of formic acid may take place through two paths: dehydrogenation (HCOOH \rightarrow H₂ + CO₂) and dehydration (HCOOH \rightarrow CO + H₂O). Also, water gas shift and/or the reverse reaction may take place producing CO₂+H₂ or CO and H₂O respectively [1].



Fig 7. Time on stream A) Conversion of FA and B) CO₂ Selectivity, Reaction conditions: 1 bar, T: 180-190 $^{\circ}$ C (220 $^{\circ}$ C for 20MoxC/H₂₀₀) GHSV= 20000 h⁻¹.

According to DFT studies described in literature, the surface of molybdenum carbide leads exclusively to the formation of CO₂ and H₂ since both Mo and C sites can chemisorb oxygen and eliminate it as CO₂ [8]. Also, the simulations performed in that investigation suggested that molybdenum carbide decreased the rate of dehydration (undesired reaction to form $CO+H_2O$). Regarding WGS reaction, theoretical studies reported that neither Mo⁰ or Mo-terminated Mo₂C are active on the WGS reaction [29]. However, oxygen covering C-terminated surfaces, O-C-Mo₂C, were active on WGS apparently due to the formation of oxycarbide species as a consequence of the presence of H_2O . Moreover, we performed additional reaction tests using molybdenum oxide supported on H₄₀₀ and tested in the FA decomposition. The results indicated that molybdenum oxide is active above 190°C when conversion reached 16% but selectivity to CO₂ was 22% (see Fig SI7).

Thus, considering the potential reactions and the selectivity profiles we could explain the results as follows. β -Mo₂C would be selective to the dehydrogenation of FA producing mainly CO₂+H₂. The presence of small amounts of a different phase other than β -Mo₂C produced during the reaction on 10Mo_xC/AC, i.e. MoOxCy and/or molybdenum oxide, could explain the 96.5% selectivity to CO₂ obtained with that catalyst.

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On the other hand, for the catalysts presenting also MoO_xC_y , it is plausible that both FA dehydrogenation and dehydration occur at the beginning of the experiment and when conversion reaches 10% the formed CO and H₂O through dehydration, react to produce CO₂ and H₂ via the water gas shift reaction, this increasing the selectivity. If this happens it is plausible that only limited oxidation of molybdenum carbide occurs since water would be consumed by WGS. Hence, we performed the XRD of the spent catalysts to assess for potential changes and are shown in Fig 8 labelled as "catalyst-PR".



Fig. 8 XRD patterns of the spent catalysts.

However, different results were observed. On the one hand, 10Mo_xC/H₄₀₀-PR displayed diffractions at 20 of 34.4°, 37.7°, 39.6° and 61.5° and sharper than those of the fresh catalyst that correspond to sintered particles of the β -Mo₂C phase. On the other hand, 20Mo_xC/H₄₀₀-PR shows diffractions at 20 of 35.2°, 36.7° and at 20 of 53.5° which can be ascribed to MoO₂ [30, 31]. For 5Mo_xC/H₄₀₀-PR, no diffractions other than those of the support were observed. This is probably due to the small particle size and/or the low concentration of species, below the detection limit.

In any case, the detected changes on the catalysts phase, either conversion to β -Mo₂C or to oxycarbide agree with the selectivity profiles observed for $10Mo_xC/H_{400}$ -PR and $20Mo_xC/H_{400}$ -PR since both new phases may promote the CO₂ selectivity either by direct transformation of FA to CO₂ or through WGS.

A different case is that of the catalyst $20Mo_xC/H_{200}$. This catalyst initially presented both carbide and oxide phases and the selectivity to CO_2 is below the other tested catalysts but it also showed the selectivity increase at around 10% conversion. The XRD of the spent catalyst, shows diffractions at 20 of 34.4°, 37.8°, and 39.8° from the β -Mo₂C along with peaks at 35.7°, 38.2° and 60.1°. The position of these latter peaks seems to indicate that they correspond to oxycarbide. Again, it seems that oxycarbide is formed during the reaction and, although β -Mo₂C phase is still detected, the intense and sharp diffraction ascribed to oxycarbide seems to indicate that large particles of these species have been formed on the surface. Despite these new nanoparticles appeared, the selectivity remained stable with time probably due to the positive effect of the new oxycarbides species which are active in WGS. However, the larger particle size inferred from the sharp **NRD** peaks would be responsible of the conversion decrease with time.

In contrast, the XRD pattern of the $10Mo_xC/AC$ sample after reaction also corresponds to the β -Mo₂C and no other diffraction is envisaged, in agreement with the higher selectivity to CO₂ and better stability. Nonetheless, the selectivity below 100% could also suggest that small undetected amounts of another phase are present. So, even in the presence of oxidants, H₂O or CO₂, this catalyst resulted to be highly stable under the reaction conditions.

The change of molybdenum phase under reaction conditions have already been reported. For example, during dry reforming of methane reaction, deactivation of β -Mo₂C catalysts due to oxidation to MoO₂ has been reported [32]. Ledoux et al. also found that β -Mo₂C changed to MoO₂, while α -Mo_xC was transformed into MoO₂ and eventually to β -Mo₂C [19]. Similarly, phase changes were also observed in the spent catalysts after steam reforming of methanol reaction [33].

Some authors, have reported that other phase such as α -MoC is more active on formic acid decomposition than β -Mo₂C [5]. However, chloro and nitrogen containing compounds were used as carbon source to prepare the catalysts and the effect of those elements should have been considered. Indeed, in the same report it is also shown that a conventional β -Mo₂C prepared from a CH₄/H₂ mixture was the most active and selective catalyst. In line with our results, molybdenum carbide prepared over activated carbon was more active and selective than when carbon nanotubes were used as support [6]. Even though the crystallographic phase of the molybdenum carbides were not shown, it is likely that the $\beta\text{-Mo}_2\text{C}$ phase was formed over activated carbon as already shown in several literature and in the present work [23,26]. As demonstrated by XRD, in the present work the main phase on the catalysts was β -Mo₂C, although MoO_xC_y could be found on H_{400} and H_{200} based catalysts, so our results are in quite good agreement with

literature, showing that β -Mo₂C is more active and selective. Very recently, the reaction mechanisms of both dehydration and dehydrogenation reaction of formic acid on molybdenum carbide have been studied [34]. The authors proposed that the target reaction leading to CO₂ and H₂ takes place through bridged formate species that evolve into monodentate formate, and transformed to CO₂ and H* following a Langmuir-Hinshelwood mechanism. On the other hand, the dehydration reaction follows an Eley-Rideal path in which gaseous HCOOH reacts with adsorbed H* to form H₂O and CO. Considering these paths, the rate in which dehydrogenation occurs might depend on the easiness of the bridge type adsorption of the formate. The carbon/molybdenum ratio influences the physico-chemical properties of the carbides and so the catalytic properties. In this sense, it has already been reported that a higher C/Mo ratio has a negative impact on the reactivity. In this respect, the MoOxCy surface would be more saturated and less metallic than the unsaturated Mo₂C surface [35]. Following this argument, it is plausible that the cleavage of the O-H bond and adsorption of the formate on the less saturated surface of β -Mo₂C would be energetically favoured than over MoO_xC_v.

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3.1 Synthesis of materials

3. Experimental

Metal carbides were prepared by wetness impregnation followed by carburization treatment. Activated carbon (Type CO-850 from Petrochil S.A) was used as support and was first grounded and sieved to < 150 μ m particle size, and then dried at 110°C for 2 h before impregnation. Commercial high surface area graphite (H400 and H200, from Timcal Graphite).

An aqueous solution of the precursor (NH4)6Mo7O24 (99% from Aldrich) was impregnated on the support using the corresponding amount to obtain the metal loading, left for maturation for 6 h, and dried overnight at 80°C. The carburization was carried out in situ prior to the reaction, under the mixture composition at 80/20 of H2/CH4 (%vol) at 700 °C, (5°C.min-1) for 2 h. Resulting catalysts will be labelled according to the metal composition, loading and support.

3.2 Characterization

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Textural properties were measured from the adsorption isotherm of N₂ at -196°C using a 3Flex instrument from Micromeritics. Around 100 mg were previously degassed at 4 h at 110°C under vacuum using a SmartVacPrep instrument from Micromeritics. The surface area was calculated from the adsorption branch in the range $0.02 \le p/p_0 \le 0.25$ using the Brunauer-Emmett-Teller (BET) theory. Total pore volume was defined as the single-point pore volume at $p/p_0=0.99$.

X-ray diffraction (XRD) patterns of the passivated catalysts were acquired in the 20 range between 4° and 90° with a step of 0.04°/s using a Polycristal X'Pert Pro PANalytical diffractometer with Ni-filtered Cu K α radiation (λ = 1.54 Å) operating at 45 kV and 40 mA.

XPS measurements were performed with an energy analyser (PHOIBOS 150 9MCD, SPECS GmbH) using non-monochromatic Al radiation (200 W, 1486.61 eV). The samples were pelletized and transferred to the outgassed chamber. Prior to the experiments, samples were outgassed in-situ for 24 h to achieve a dynamic vacuum below 10-10 mbar. The binding energy (BE) was measured by reference to the C 1s peak at 284.6 eV, with an equipment error of less than 0.01 eV in the energy determinations.

Information about the supported metal particles was acquired by TEM in a JEOL 2100F field emission gun electron microscope operated at 200 kV and equipped with an Energy-Dispersive X-Ray detector. The sample was ground until powder and a small amount was suspended in ethanol solution using an ultrasonic bath. Some drops were added to the copper grid (Aname, Lacey carbon 200 mesh) and the ethanol was evaporated at room temperature before introduce in the microscope. The Scanning Transmission Electron Microscopy (STEM) was done using a spot size of 1 nm. Average particle size area (d_{TEM}) was calculated as

$$d_{\text{TEM}} = \frac{\sum n_i \ d_i^3}{\sum n_i \ d_i^2}$$

Mo K-edge (20.000 eV) X-ray absorption near edge spectra (XANES) were recorded in dispersive mode at the BM23 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The catalysts were pressed into pellets and sieved to a size between 0.090 and 0.140 mm. The samples (ca. 15 mg) were loaded in a quartz plug-flow microreactor system developed at BM23. The reactor was continuously fed with: a) 30 mL min⁻¹ of the mixture composition 20/5/75 of H₂/CH₄/He for the temperature-programmed carburization experiment or b) 30 mL min⁻¹ of 20% hydrogen in helium during temperatureprogrammed reduction experiment. The temperature was raised by 3 °C min⁻¹ up to 700 °C. XANES spectra were collected every 30 °C or 10 min during the heating.

3.3 Reaction

The measurements of the catalyst activity in vapor phase formic acid decomposition were carried out in a fixed-bed flow reactor. The catalysts (0.075 g) were placed in a U-tube reactor with an internal diameter of 4 mm. All the samples were in situ carburized in CH₄/H₂ (20:80 vol) at 700 °C for 2 h and cooled in N_2 to a reaction temperature prior to testing (in situ reduction). The mixture of 5.5 vol % formic acid/ N_2 at a total flow rate of 25 cm³ (STP)/ min was fed to the reactor by a saturator. The reactants and products were analysed by a gas chromatograph (Varian 3400) fitted with a 60/80 Carboxen TM 1000 column and a thermal conductivity detector. At each temperature, a few measurements were performed to be sure in reaching of steady-state activity. During the test, the unique products determined were CO, CO₂ and H₂. The concentrations of these compounds were calculated by following equations.

$$[H_2] = \frac{\text{Area } H_2}{\text{RF}} \quad [CO_2] = \frac{\text{Area } CO_2}{\text{RF}} \quad [CO] = \frac{\text{Area } CO}{\text{RF}}$$

As the formation of products different from those indicated was negligible, the total conversion of formic acid was determined as the sum of CO and CO₂ concentrations related to the initial concentration of formic acid.

 $[HCOOH]_0 = [CO]_m + [CO_2]_m$ at T_{max} to obtain a complete conversion of HCOOH

To determinate the conversion of formic acid, it was necessary to calculate the concentration of CO and CO₂ and using the equation (1).

$$X_{\text{HCOOH}} = \frac{[\text{CO}] + [\text{CO}_2]}{[\text{HCOOH}]_0} \times 100 \quad (1)$$

In addition, the selectivity to CO₂ was calculated. The catalysts were studied in two heating cycles. The stability of the catalyst was evaluated during 18 hours at a selected temperature.

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Tests with the bare supports proved that conversion was negligible.

Conclusions

The synthesis of molybdenum carbide by the TPR method using a CH₄/H₂ feed was performed successfully over activated carbon and two high surface area graphites, H₂₀₀ and H₄₀₀, of different graphitic layer dimension. The formed carbide nanoparticles were between 2.0 and 8.1 nm size which depended on the surface area and metal loading. Also, the characterization showed that the carbide phase was influenced by the support. Accordingly, when activated carbon was used, the β -Mo₂C phase was obtained mostly exclusively. However, over H₄₀₀ and H_{200} the oxycarbide phase, MoO_xC_y was also observed. We explained the differences based on the graphitic layer size. This is related to the availability of defective carbon which in turn favours the carburisation. Interestingly, XANES experiments showed that even under a CH_4/H_2 atmosphere the main source of carbon is the support itself. This also implies that smaller particles, which are in closer contact with the support, are more easily carburised.

The different molybdenum carbide phase influences the catalytic performance. The results showed that the $\beta-Mo_2C$ phase is more active and selective than the MoO_xC_y . However, since MoO_xC_y is also active on the WGS reaction, the selectivity to CO_2 increases during the reaction. Moreover, $\beta-Mo_2C$ supported on activated carbon proved to be stable under reaction conditions.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 B. Dou, H. Zhang, Y. Song, L. Zhao, B. Jiang, M. He, C. Ruan, H. Chen, Y. Xu, Sustainable Energy Fuels, 2019, 3, 314.
- 2 a) D.J. Hayes, S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, The Biofine Process – Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks in Biorefineries— Industrial Processes and Products: Status Quo and Future Directions, (Eds.: B. Kamm, P. R. Gruber, M. Kamm), Wiley-VCH, Weinheim, 2006, pp. 139–164. b) A.Kumar Singh, S.Singh and A.Kumar CatalSciEng 2016, 6, 12-40.
- 3 J. Wang, J. Zheng, J. Cao, X. Hao, Z. Wang, A. Abudula, G. Guan, Energy conversion and management, 2018, 164, 122. c) Energy conversion and management, 2017, 147, 166. D) J power sources, 2014, 246, 48x

- a) Sustainable Energy Fuels, 2019, 3, 1042. b) We. Gan, P. J. Dyson and G. Laurenczy, ChemCatChemo 2013 57/5124 00 We Gan, P. J. Dyson and G. Laurenczy, React. Kinet. Catal. Lett., 2009, 98, 205. d) Y. Zhao, L. Deng, S.-Y. Tang, D.-M. Lai, B. Liao, Y. Fu and Q.-X. Guo, Energy Fuels, 2011, 25, 3693.
- 5 G. H. Gunasekar, H. Kim and S. Yoon, Sustain. Energy Fuels, 2019, 3, 1042–1047.
- 6 I. E. Wachs and D. E. Fein, J. Catal., 2002, 210, 241–254.
- 7 S. A. Halawy, S. S. Al-Shihry and M. A. Mohamed, Catal. Letters, 1997, 48, 247–251.
- 8 a) Á. Koós and F. Solymosi, Catal. Letters, 2010, 138, 23–27.
 b) Q. Luo, T. Wang, G. Walther, M. Beller and H. Jiao, J. Power Sources, 2014, 246, 548–555.
- 9 Y. Ma, G. Guan, X. Hao, J. Cao and A. Abudula, Renew. Sustain. Energy Rev., 2017, 75, 1101–1129.
- 10 D. W. Flaherty, S. P. Berglund and C. B. Mullins, J. Catal., 2010, 269, 33–43.
- 11 J. Cao, J. Wang, Y. Ma, X. Li, P. Xiaokaiti, X. Hao, A. Abudula and G. Guan, J. Alloys Compd., 2018, 735, 1463–1471.
- 12 J. Q. Chi, K. L. Yan, W. K. Gao, B. Dong, X. Shang, Y. R. Liu, X. Li, Y. M. Chai and C. G. Liu, J. Alloys Compd., 2017, 714, 26–34.
- 13 a) P. Liang, H. Gao, Z. Yao, R. Jia, Y. Shi, Y. Sun, Q. Fan and H. Wang, Catal. Sci. Technol., 2017, 7, 3312–3324; c) H. Gao, Z. Yao, Y. Shi and S. Wang, Catal. Sci. Technol., 2018, 8, 697–701.
- 14 H. Wang, S. Liu and K. J. Smith, Energy and Fuels, 2016, 30, 6039–6049.
- 15 a) C. Máirquez-Alvarez, I. Rodríguez-Ramos, A. Guerrero-Ruiz, G.L. Haller, M.J.Fernáindez-García, Am. Chem. Soc. 1997, 19 2905–2914. b) F.R. García-García, M. Fernández-García, M.A. Newton, I. Rodríguez-Ramos, A. Guerrero-Ruiz, ChemCatChem 2013, 5, 2446–2452.
- 16 A. Tougerti, E. Berrier, A.-S. Mamede, C. La Fontaine, V. Briois, Y. Joly, E. Payen, J.-F. Paul, S. Cristol, Angew. Chem. Int. Ed. 2013, 52, 6440-6444.
- 17 S. T Oyama,. P. Delporte,; C. Pham-Huu; Ledoux, Chem.Lett. 1997 949-950.
- 18 A. Hanif, T. Xiao, A. P. E. York, J. Sloan, M. L. H. Green, Chem. Mater. 2002, 14, 1009-1015.
- 19 C. Bouchy, C. Pham-huu and M. J. Ledoux, J. Mol. Catal. A Chem., 2000, 162, 317–334.
- 20 A. B. Dongil, L. Pastor-Pérez, A. Sepúlveda-Escribano and P. Reyes, Appl. Catal. A Gen., 2015, 505, 98–104.
- 21 L.Souza Macedo, R. R. Oliveira, T. van Haasterecht, V. Teixeira da Silva, H. Bitter, Appl. Catal B: Environ, 2019, 241, 81.
- 22 E. F. Mai, M. A. Machado, T. E. Davies, J. A. Lopez-Sanchez and V. T. da Silva. Green Chemistry 2014, 16, 4092-4097.
- 23 B. Frank, Z. L. Xie, K. F. Ortega, M. Scherzer, R. Schlögl, and A. Trunschke. Catalysis Science & Technology 2016, 6, 3468-3475.
- 24 J. Han, J. Duan, P. Chen, H. Lou, X. Zheng, and H. Hong, ChemSusChem 2012, 5, 727-733.
- 25 A. B. Dongil, L. Pastor-Pérez, N. Escalona, and A Sepúlveda-Escribano, Carbon 2016, 101, 296-304.
- 26 Tao, Y., L. Tao, Z. Pan, S. Qiu, and X. Shen, Fuel 2018, 217, 106-110.
- 27 D. E. J Fein and I. E. Wachs, J. Catal. 2002, 210, 241-254.
- 28 J. Wang, J. Cao, Y. Ma, X. Li, P. Xiaokaiti, X. Hao and G. Guan, Energy Conversion and Management 2017, 147, 166-173.
- 29 P. Liu, JA. Rodriguez, J Phys Chem. B., 2006,110, 19418-19425.
- 30 P. Delporte, C. Pham-Huu, P. Vennegues, M. J. Ledoux and J. Guille, Catalysis Today 1995, 23, 251-267.
- 31 M. Tsuji, T. Miyao, S. Naito, Catal. letters, 2000, 69,195-198.
- 32 J.B. Claridge, A.P.E. York, A.J. Brungs, C. Marquez-Alvarez, J. Sloan, S.C. Tsang and M.L.H. Green, J. Catal. 1998, 180, 85-100.
- 33 B. Frank, K. Friedel, F. Girgsdies, X. Huang, R. Schlögl and A Trunschke, ChemCatChem 2013, 5, 2296-2305.

Journal Name

View Article Online DOI: 10.1039/D0CY01088J

- 34 J. T. Gray, S. W. Kang, J. I. Yang, N. Kruse, J. S. McEwen, J. C. Park and S. Ha, Appl. Catal. B: Environ. 2020, 264, 118478.
- 35 T. Wang, X. Tian, Y. Yang, Y. W. Li, J. Wang, M. Beller and H. Jiao Physical Chemistry Chemical Physics 2015, 17, 1907-1917.

10 | J. Name., 2012, **00**, 1-3

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