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

D.H Carrales-Alvaradoa, A.B. Dongil*a, J.M. Fernández-Moralesb, M. Fernández-Garcíaa,c, A.Guerrero-Ruizb,c, I. Rodríguez-Ramosa,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, H200 (200 m2/g) and H400 (400 m2/g). Particular attention is paid to the effect of Mo loading. The catalysts were prepared in situ using a mixture of CH2 and H2 up to 700°C. Under these conditions carburization was mostly complete. We observed, that the support influenced the Mo:C 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-MoC phase was obtained over activated carbon and over H200. In contrast MoOxC, was obtained over H400. 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 CO 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 H2. Also, changes in the molybdenum phases were observed on the spent catalyst.

Some redox transformations during reaction were responsible for the transformation of β-MoOxC into oxycarbide MoOxCy. In summary, the results of catalytic performance indicated that β-Mo:C 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 Fe3O4, 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
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 CH₄ and H₂ 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 S\textsubscript{BET} of the parent supports is 950, 400 and 200 m²/g for AC, H\textsubscript{200} and H\textsubscript{400} respectively. It can be observed that S\textsubscript{BET} decreases as the amount of carbide increases. The reduction of S\textsubscript{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 pore-blocking 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\textsubscript{BET} (m²/g) | d\textsubscript{BET} (nm) | Mo/C (wt%) | Activity (mol CO₂/mol Mo h\textsuperscript{-1}) |
|---------------|-----------------------------|---------------------------|------------|---------------------------------------------|
| 5MoxC/H\textsubscript{200} | 217                         | 2.0                       | 0.0049     | 85                                          |
| 10MoxC/H\textsubscript{200} | 213                         | 2.2                       | 0.0103     | 112                                         |
| 20MoxC/H\textsubscript{200} | 204                         | 3.8                       | 0.0105     | 73                                          |
| 10MoxC/H\textsubscript{400} | 107                         | na                        | -          | 61                                          |
| 20MoxC/H\textsubscript{400} | 72                          | 8.1                       | -          | 10                                          |
| 10MoxC/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 10MoxC/AC and 20MoxC/H\textsubscript{200} show quite sharp diffractions at 2θ of 34.4°, 37.7°, 39.4° and 61.5°. On the other hand, the catalysts prepared over H\textsubscript{400}, 5-20 wt% Mo and 10MoxC/H\textsubscript{200} display similar XRD profiles showing wide diffractions with maxima shifted to lower angles, ca. 2θ of 36.7°-36.9°, compared to 20MoxC/H\textsubscript{200} and 10MoxC/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 H\textsubscript{400} and AC display diffractions of the oxide phases. This confirming that the carburization treatment was mostly effective. Nonetheless, the XRD pattern of the catalyst 20MoxC/H\textsubscript{200} shows two small diffraction peaks at 2θ of 23.7° and 49.1° corresponding to MoO\textsubscript{3} (JCPDS-PDF 05-0508 and 76-1003).

![Fig. 1 XRD patterns of the catalysts. Dotted lines represent β-MoC (red) graphite](image)

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 10MoxC/H\textsubscript{200} using in situ Mo K-edge X-ray absorption near-edge spectroscopy (XANES). The Mo K-edge spectra, in Fig. S1, show the evolution of molybdenum species under the CH\textsubscript{4}/H\textsubscript{2}/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...
Based on XANES experiments we can now assign the XRD peaks as follows. The diffraction peaks observed for the catalyst 10MoₓC/AC correspond to the (100), (002), (101) and (110) planes of the β-MoₓC 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 MoₓCₓ 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-MoₓC on the selected 10MoₓC/H₄₀₀ sample than what is observed by XRD. This can be attributed to the small size of the 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. S14, confirmed. On the contrary for 10MoₓC/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-MoₓC (101) planes are observed in particles as small as 2 nm. Similar findings are observed for 10MoₓC/H₄₀₀ for which also β-MoₓC (101) is observed in small particles.

Hence, it can as well be inferred that larger particles are more difficult to carburese. This is agreement with the diffraction peaks ascribed to MoO₃ observed on 20MoₓC/H₂₀₀ which is the sample with the largest particle size, ca. 8.1 nm as estimated by TEM in Table 1.
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 $\beta$-Mo$_2$C. b) Alternatively, after MoO$_3$ formation, this oxide may suffer a partial carburization to an oxycarbide MoO$_x$C$_y$, which is eventually transformed into $\beta$-Mo$_2$C [19]. This latter path proposed in literature, agrees quite well with the XANES results obtained in the present work, where both oxycarbide and $\beta$ phases are observed.

With the aim of gaining more information on the synthesis mechanism and the effect of the support, additional XANES experiments were performed with 20Mo$_x$C/H$_{400}$ sample but using a H$_2$/He atmosphere. The analysis of the in situ Mo k-edge XANES spectra (Figure SI5) showed that the same MoO$_3$, MoOxCy and $\beta$-Mo$_2$C species are obtained as when CH$_4$/H$_2$/He is employed over the 10Mo$_x$C/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$_x$C/H$_{400}$ 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$_x$C/H$_{400}$ 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 $\beta$-Mo$_2$C. 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. S16, used in the present work show that I$_D$/I$_G$ ratio follows the trend AC > H$_{400}$ > H$_{200}$. Since external CH$_4$ does not seem to be involved on the carburisation mechanism, we performed H$_2$-TPR experiments coupled to mass spectrometry of the impregnated samples 10Mo$_x$C/H$_{400}$ and 10Mo$_x$C/AC to assess for differences among the supports. The masses corresponding to the main fragments of H$_2$O (m/z 18), CO (m/z 28), CO$_2$ (m/z 44) and NH$_3$ (m/z 17) and the secondary of CH$_4$ (m/z 14) were followed along with other secondary fragments of H$_2$O and NH$_3$ (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$_2$O. 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$_x$C/AC. This sample, shows a maximum at 400°C in which contributions...
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 10MoxC/H₄₀₀ and 10MoxC/H₆₀₀ 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).

$$\text{MoO}_3 + C^+ + H_2 \rightarrow \text{MoO}_2C \_ y + H_2O \rightarrow \beta-\text{Mo}_2C + CO \quad (1)$$

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 H₄₀₀ 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 Mo₂C phase [24]. We observed that samples with different loading, mainly 10MoxC/H₂₀₀ and 20MoxC/H₂₀₀ 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 carbon is the support itself. Also, the fact that the support is the source of carbon is in agreement with the easiness carburisation of smaller particles that would be in closer contact with the support.

### 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 10MoxC/H₄₀₀, 20MoxC/H₄₀₀ and 10MoxC/AC, while those of 5MoxC/H₄₀₀, 10MoxC/H₂₀₀ and 20MoxC/H₂₀₀ shifted to higher temperatures.

![Figure 6] A) Conversion of FA vs T and b) CO selectivity vs T. Reaction conditions: 1 bar, GHSV= 20000 h⁻¹.
wt% and 20 wt%. According to the microscopy, carbide nanoparticles are larger on the sample with higher loading, 20MoC/\(\text{H}_2\text{O}_{400}\), in agreement with the similar Mo/C surface ratio obtained by XPS for 10MoC/\(\text{H}_2\text{O}_{400}\) and 20MoC/\(\text{H}_2\text{O}_{400}\) shown in Table 1. This can explain straightforward the lower activity of 20MoC/\(\text{H}_2\text{O}_{400}\) 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 \(\text{H}_2\text{O}_{400}\).

The selectivity to \(\text{CO}_2\) at each temperature, Fig 6B, was estimated considering the total concentration of \(\text{CO}_2\) and \(\text{CO}\) as the only detected products and revealed significant differences. The catalysts displayed maximum selectivity in the range 85.0-96.5%, the catalyst 10MoC/AC offering the best selectivity among the tested systems. This also points to a beneficial effect of \(\beta\)-MoC phase compared to MoO\(_x\)Cy.

Indeed, if we compare the selectivity achieved with the catalysts 10MoC/AC and 10MoC/\(\text{H}_2\text{O}_{400}\), it is clear that the different phase influences the concentration of \(\text{H}_2\) in the products. While with 10MoC/AC selectivity to \(\text{CO}_2\) reached 96.5% at conversions above 50%, with 10MoC/\(\text{H}_2\text{O}_{400}\) 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, \(\alpha\)-Fe\(_2\text{O}_3\) for which maximum conversion was around 24% at temperatures of 200°C with low selectivity to \(\text{H}_2\) [27,7] and other systems where Ag and Mg were used as dopants for MoC 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 20MoC/\(\text{H}_2\text{O}_{400}\) 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 20MoC/\(\text{H}_2\text{O}_{400}\) that showed 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 \(\rightarrow\) \(\text{H}_2 + \text{CO}_2\)) and dehydration (HCOOH \(\rightarrow\) \(\text{CO} + \text{H}_2\text{O}\)). Also, water gas shift and/or the reverse reaction may take place producing \(\text{CO}_2\)+\(\text{H}_2\) or \(\text{CO}\) and \(\text{H}_2\text{O}\) respectively [1].

According to DFT studies described in literature, the surface of molybdenum carbide leads exclusively to the formation of \(\text{CO}_2\) and \(\text{H}_2\) since both Mo and C sites can chemisorb oxygen and eliminate it as \(\text{CO}_2\) [8]. Also, the simulations performed in that investigation suggested that molybdenum carbide decreased the rate of dehydration (undesired reaction to form \(\text{CO} + \text{H}_2\text{O}\)).

Regarding WGS reaction, theoretical studies reported that neither Mo\(_5\) or Mo-terminated MoC are active on the WGS reaction [29]. However, oxygen covering C-terminated surfaces, O-C-MoC, were active on WGS apparently due to the formation of oxycarbide species as a consequence of the presence of \(\text{H}_2\text{O}\). Moreover, we performed additional reaction tests using molybdenum oxide supported on \(\text{H}_2\text{O}_{400}\) and tested in the FA decomposition. The results indicated that molybdenum oxide is active above 190°C when conversion reached 16% but selectivity to \(\text{CO}_2\) was 22% (see Fig S17).

Thus, considering the potential reactions and the selectivity profiles we could explain the results as follows. \(\beta\)-MoC would be selective to the dehydrogenation of FA producing mainly \(\text{CO}_2+\text{H}_2\). The presence of small amounts of a different phase other than \(\beta\)-MoC produced during the reaction on 10MoC/AC, i.e. MoOxCy and/or molybdenum oxide, could explain the 96.5% selectivity to \(\text{CO}_2\) obtained with that catalyst.
On the other hand, for the catalysts presenting also MoOₓCᵧ, 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”.

However, different results were observed. On the one hand, 10MoₓCₓ/H₂O-PR displayed diffractions at 2θ 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-MoC phase. On the other hand, 20MoₓCₓ/H₂O-PR shows diffractions at 2θ of 35.2°, 36.7° and at 2θ of 53.5° which can be ascribed to MoO₂ [30].

For 5MoₓCₓ/H₂O-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-MoC or to oxyxocarbide agree with the selectivity profiles observed for 10MoₓCₓ/H₂O-PR and 20MoₓCₓ/H₂O-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 20MoₓCₓ/H₂O. This catalyst initially presented both carbide and oxide phases and the selectivity to CO₂ 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 2θ of 34.4°, 37.8°, and 39.8° from the β-MoC along with peaks at 35.7°, 38.2° and 60.1°. The position of these latter peaks seems to indicate that they correspond to oxyxocarbide. Again, it seems that oxyxocarbide is formed during the reaction and, although β-MoC phase is still detected, the intense and sharp diffraction observed on oxyxocarbide 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 oxyxocarbides species which are active in WGS. However, the larger particle size inferred from the sharp XRD peaks would be responsible of the conversion decrease with time.

In contrast, the XRD pattern of the 10MoₓCₓ/AC sample after reaction also corresponds to the β-MoC 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-Mo.C catalysts due to oxidation to MoO₂ has been reported [32]. Ledoux et al. also found that β-Mo-C changed to MoO₂ while γ-Mo-C was transformed into MoO₂ and eventually to β-MoC [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-MoC [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-MoC 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].

Very recently, the reaction mechanisms of both dehydrogenation 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 H₂ following a Langmuir-Hinshelwood mechanism. On the other hand, the dehydrogenation 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 MoₓCᵧ 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-MoC would be energetically favoured than over MoOₓCᵧ.
3. Experimental

3.1 Synthesis of materials

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 µm 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

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 ≤ p/p0 ≤ 0.25 using the Brunauer-Emmett-Teller ( BET) theory. Total pore volume was defined as the single-point pore volume at p/p0=0.99.

X-ray diffraction (XRD) patterns of the passivated catalysts were acquired in the 2θ range between 4° and 90° with a step of 0.04°/s using a Polycrystalline X’Pert Pro PANalytical diffractometer with Ni-filtered Cu Kα 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 pelleted 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 a ultrasonic bath. Some drops were added to the copper grid (Anance, 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 (dTEM) was calculated as

$$d_{\text{TEM}} = \frac{\sum n_i d_i^2}{\sum n_i d_i^1}$$

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 temperate-programmed 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 N₂ to a reaction temperature prior to testing (in situ reduction). The mixture of 5.5 vol % formic acid/N₂ 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.

$$[\text{H₂}] = \frac{\text{Area } \text{H₂}}{\text{RF}} \quad [\text{CO₂}] = \frac{\text{Area } \text{CO₂}}{\text{RF}} \quad [\text{CO}] = \frac{\text{Area } \text{CO}}{\text{RF}}$$

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.

$$[\text{HCOOH}]_0 = [\text{CO}]_m + [\text{CO₂}]_m \text{ at } T_{\text{max}}$$

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

$$X_{\text{HCOOH}} = \frac{[\text{CO}] + [\text{CO₂}]}{[\text{HCOOH}]_0} \leq 100 \quad (1)$$

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.
Tests with the bare supports proved that conversion was negligible.

Conclusions
The synthesis of molybdenum carbide by the TPR method using a \( \text{CH}_4/\text{H}_2 \) feed was performed successfully over activated carbon and two high surface area graphites, \( \text{H}_{200} \) and \( \text{H}_{400} \), 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 \( \beta-\text{MoC} \) phase was obtained mostly exclusively. However, over \( \text{H}_{400} \) and \( \text{H}_{200} \) the oxycarbide phase, \( \text{MoO}_x\text{C}_y \), 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 \( \text{CH}_4/\text{H}_2 \) 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 \( \beta-\text{MoC} \) phase is more active and selective than the \( \text{MoO}_x\text{C}_y \). However, since \( \text{MoO}_x\text{C}_y \) is also active on the WGS reaction, the selectivity to \( \text{CO}_2 \) increases during the reaction. Moreover, \( \beta-\text{MoC} \) supported on activated carbon proved to be stable under reaction conditions.

Conflicts of interest
There are no conflicts to declare.

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