Communication

Effect of Cu and Cs in the β-Mo₂C system for CO₂ hydrogenation to Methanol

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Abstract: Mitigation of Anthropogenic CO₂ emissions possess a major global challenge for modern societies. Herein catalytic solutions are meant to play a key role. Among the different catalysts for CO₂ conversion Cu supported on molybdenum carbide is receiving increasing attention. Hence, in the present communication we show the activity, selectivity and stability of fresh-prepared β-Mo₂C catalysts and compare the results with those of Cu/Mo₂C, Cs/Mo₂C and Cu/Cs/Mo₂C in CO₂ hydrogenation reactions. The results showed that all the catalysts were active and the main reaction product was methanol. The results showed that copper-cesium and molybdenum effectively interact and that cesium promoted the formation of metallic Mo. While, the incorporation of copper is positive to improve the activity and selectivity to methanol, the presence of Mo⁰ phase was detrimental for the conversion and selectivity. Moreover, the catalysts promoted by cesium underwent redox surface transformations during the reaction that diminished their catalytic performance. The molybdenum phase in Cu/Mo₂C changes during reaction leading to metallic molybdenum and tuning the catalytic activity.

Keywords: carbon dioxide; molybdenum carbide; methanol; copper; alkali; dopant

1. Introduction

The study of CO₂ transformations has increased significantly due to the need of diminishing its atmospheric emissions. The possibility of using CO₂ as raw material is a convenient way from an economic and industrial point of view, so conversion to fuels such as methane, or syn-gas which could be later used in the Fisher-Tropsch for the synthesis of fuels or other chemicals, have received renewed attention. Among them, CO₂ hydrogenation to methanol is an appealing alternative since it can be used directly in fuel cells [1].

Despite being an interesting approach, the main challenge of these reactions is the chemical inertness of CO₂. The most studied system is Cu-ZnO for which copper has proven to be critical when it is loaded onto oxides supports such as ceria or alumina. Unfortunately, these catalysts suffer deactivation due to the oxidation and sintering of copper upon reaction conditions [2,3]. Transition metal carbides (TMCs) have received a lot of attention since they display excellent catalytic behavior in transformations such as steam reforming of methane, dry reforming of methane or CO hydrogenation [4]. Some transition metal carbides can adsorb CO₂ and favor the C-O scission by themselves or aided by hydrogen. Among them, molybdenum carbide actually holds catalytic properties similar to those of noble metals [4,5]. Besides, their catalytic properties as active phase, the TMC can also avoid metal sintering being excellent support to disperse metals.

In this sense, methanol synthesis via CO₂ hydrogenation was studied by using several metals (Ni, Co, Cu) supported on MoC and it was observed that copper was the best promoter to selectively obtain methanol, since copper activates hydrogen better than the other metals [6,7].
Furthermore, it has been reported that alkali promoters can improve the adsorption of CO₂ to obtain alcohols or CO and the beneficial effect to higher alcohols followed the trend Cs > Rb > K > Na > Li [8]. Also, potassium has been used to keep the reduced phases of molybdenum in K-MoC/γ-Al₂O₃ system that was used in the reverse water gas shift reaction [9] and similar effects were observed for transition metal nitrides [10]. Potassium has also been successfully used as dopant in the Cu/ZnO system for which it seems that positively charged K can be the active site to adsorb the reactants. Indeed, on a model system of Cu/O/Cu(111), potassium enhances the selectivity to methanol from carbon dioxide favouring a different mechanism in which a methanediol [H₂C(OH)₂]-mediated formate path takes place [11].

Since cesium owns a larger ionic radius than potassium, it is expected to be a better electron donor which could eventually enhance the hydrogenation of CO₂ as previously reported elsewhere [12,13]. We recently evaluated the promoter effect of cesium and copper in the Mo₅C system for reverse water gas shift (RWGS) reaction (1), which can take place simultaneously to reaction 2, and found that both activity and selectivity is significantly improved by the addition of such promoters. We demonstrated that copper provides active sites to the system in the form of Cu⁰ or Cu⁺. On the other hand, cesium provokes electronic changes derived from its high electropositive nature that improved the catalytic behavior. More importantly, cesium was key in assessing highly stable catalysts since the Cs-doped catalyst seemed to be in-situ activated by re-carburization [14].

In the present communication, we investigate the effect of copper and cesium as promoters for methanol synthesis (reaction 3), and evaluate the stability of the catalysts under reaction conditions for CO₂ hydrogenation to methanol without in situ carburization which, to the best of our knowledge, has not been yet reported. These conditions imply higher pressure and milder temperatures, i.e. 20 bar and 150 ºC, compared to those of RWGS reaction.

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ = +41 \text{ kJ mol}^{-1} \quad (1)
\]

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H^\circ = -165 \text{ kJ mol}^{-1} \quad (2)
\]

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3 \text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ = -50 \text{ kJ mol}^{-1} \quad (3)
\]

2. Results

We have studied CO₂ hydrogenation at 150 ºC and 20 bar for 16 hours and the conversion and selectivity profiles are included in Fig. 1. As regards to the conversion, it can be observed that while β-Mo₅C catalysts showed a quite stable profile, the other samples displayed some changes along time on stream. The conversion obtained was in the range 3-5 % and the values followed the trend Cu/Mo₅C > Cu/Cs/Mo₅C > β-Mo₅C > Cs/Mo₅C which are in fair agreement with the reported conversion levels for this challenging reaction [15]. Moreover, the main compound obtained was methanol and the selectivity reached 50-65 % following a slightly different trend to that of the conversion: Cu/Mo₅C > β-Mo₅C > Cu/Cs/Mo₅C > Cs/Mo₅C. Unlike the conversion behavior, the selectivity profiles were quite stable for all the catalysts except for the sample Cu/Cs/Mo₅C. The other detected products were CO and CH₄, with minor contributions of ethanol which was below 0.2% except for the catalyst Cs/Mo₅C that was around 2% and it is included in the Fig.1. The selectivity to the products CO and CH₄ was similar for the Cu-containing catalysts, Cu/Mo₅C, Cs/Mo₅C and Cu/Cs/Mo₅C which reached values of ca. 12 and 17%, 22 and 25%, and 17 and 22%, respectively. However, over β-Mo₅C the selectivity of the secondary products was quite different with selectivities of 30% and 5% for CH₃OH and CO respectively.

CO₂ hydrogenation to CH₃OH can take place through direct hydrogenation, or following an intermediate path producing CO through the reverse water gas shift reaction which eventually can be transformed into the alcohol. Alternatively, formate and formaldehyde intermediate species can be formed on the surface followed by subsequent hydrogenation to CH₃OH [16].
Figure 1. Conversion (■) and Selectivity to CH\textsubscript{3}OH (●) CO (▲) CH\textsubscript{3} (▲) and C\textsubscript{2}H\textsubscript{5}OH (★). Reaction conditions: T= 150 °C, P= 20 bar, CO\textsubscript{2}:H\textsubscript{2}: (1:3), GHSV 7600 mL/(h\textsuperscript{-1} g).

The selectivity profiles obtained for β-Mo\textsubscript{2}C suggest that the RWGS path plays a key role, and for this reaction molybdenum carbide has been reported to be highly active [17].

The improved catalytic performances of Cu/Mo\textsubscript{2}C confirm that the addition of copper benefits both the conversion and selectivity to methanol on the molybdenum carbide system as already described. It was reported that this improvement is related to the different paths followed when the copper-molybdenum carbide interface exists since the carbide can modify the electronic density of the metal [16,18].

The copper was well-dispersed over molybdenum in the Cu/Mo\textsubscript{2}C catalyst, as assessed by EDS mapping in Fig. 2b, this suggesting high interaction between Cu and Mo. Also, the elemental analyses showed that the concentration of Mo and C agrees quite well, within the experimental error, with the Mo\textsubscript{2}C stoichiometry. In addition, the mapping of the Cs-doped sample, in Fig. 2a, confirms the interaction between Cu, Cs and Mo\textsubscript{2}C and it seems that copper is well dispersed, which would allow better interaction with molybdenum than the Cs free sample.

Besides, the positive effect of copper can also be related to its ability to activate hydrogen which eventually reacts with CO\textsubscript{2} adsorbed on the molybdenum carbide.

We expected to observe some improvement in the catalytic performance by adding an alkali as dopant since it has been shown to improve the activation of the CO\textsubscript{2} molecule [8]. However, the opposite tendency was indeed observed, and both conversion and selectivity to methanol are diminished, which for the catalyst without copper are even lower than the values achieved with the bare β-Mo\textsubscript{2}C.
Figure 2. STEM images with the corresponding elemental mapping A) Cu/Cs/Mo:C and B) Cu/Mo:C.

It has been suggested that different crystal phases or Mo/C ratios can influence the selectivity on CO₂ hydrogenation [19]. However, in the studied system, we only detected one carbide phase, so the reason must be found in another feature.

In order to understand the results, we evaluated the XRD patterns of the fresh and spent catalysts. The diffractograms showed that all the fresh catalysts, in Fig. 3a, displayed the characteristic peaks of β-Mo₂C with hexagonal closest packing crystal structure (JCPDS 35-0787) at 2θ of 34.4°, 38°, 39.4°, 52.1°, 61.5°, 69.6° and 74.6°, and that no copper or cesium is observed likely due to the small percentage of these elements. Also, the absence of the characteristic peaks of molybdenum oxides, confirmed the successful carburization. Moreover, the alkali-doped samples also displayed peaks at 2θ of 40.6° and 58.7° which corresponds to metallic Mo (JCPDS 42-1120) and whose formation has already been explained as a result of the negative charge transfer of Cs to molybdenum [14]. As it can be observed, the relative contribution of Mo⁰ is more relevant on the sample without copper.

Hence, the presence of this metallic molybdenum phase could explain the worse catalytic performance of Cs-doped samples since Mo⁰ has poorer activation ability towards the CO₂ molecule. It has been reported that, when Mo⁰ adsorbs CO₂, HO₂C–Mo species are formed which do not favor the scission of the C-O bond [20]. In contrast, dissociation of CO₂ over β-Mo₂C is relatively easy and it may take place through a previous hydrogenation to CO followed by formation of HCO followed by hydrogenation to CH₃OH. Also, since the adsorption and activation of CO₂ molecule can occur on both Cu and Mo₂C surfaces, the negative effect of the Mo⁰ phase was not so relevant in the catalytic performance of the Cu/Cs/Mo₂C as it is on the copper free sample, Cs/Mo₂C [21].

The diffractograms of the spent catalyst, in Fig. 3b, showed that Cu/Mo₂C preserved the β-Mo₂C crystal structure and, surprisingly, it also showed the typical diffractions of Mo⁰ which were not observed in the fresh catalysts. This is an interesting finding and there is not obvious reason for the formation of such a phase under the reaction conditions used. As observed by previous characterization by XRD and XPS of these samples, the fresh catalyst does not display metallic molybdenum, so we can tentatively rule out that these peaks appear as a consequence of sintering of molybdenum during the reaction [14]. Another possibility is that the reaction conditions could somehow favour the formation of metallic molybdenum. The reduction of metals by Mo₂C has been already reported to occur. Some authors have observed that metal precursors of Pt, Pd and Cu were spontaneously reduced when deposited onto unpassivated molybdenum carbide [22,23]. This was explained by a redox phenomenon on the surface which probably implied the oxidation of
molybdenum, since it is in a highly reduced state. However, this is not observed in most of the literature because molybdenum carbide is frequently passivated, and this surface layer might prevent the oxidation-reduction reactions [24]. A plausible explanation is that the same happens with molybdenum, so that redox transformations during reaction could be the reason for the chemical state of the spent catalyst. Nevertheless, the possibility of a molybdenum oxide passivation layer on Mo\(^6\) nanoparticles of the fresh catalysts cannot be totally disregarded. However, conventional ex situ XPS cannot be used to assess for the effect of the reaction conditions on the crystal phase changes, and further in situ studies would be required, which are beyond this proof-of-concept work.

Finally, no diffractions ascribed to MoO\(_2\) or MoO\(_3\) are observed, this indicating a good stability towards oxidation under the tested conditions.

![Figure 3. XRD patterns of the catalysts (a) Fresh samples; (b) Spent samples.](image)

On the other hand, the XRD patterns of spent catalysts with cesium display diffractions at 2\(\theta\) of 26.0°, 37.1° and 53.3° which correspond to the MoO\(_2\) crystal phase (JCPDS 32-671). Furthermore, the diffractions due to the MoC phase mostly disappear and just a broad hump with maximum at 2\(\theta\) of 39.4° can be envisaged on the catalyst Cs/MoC. This broad peak probably includes just the contributions of MoO\(_2\) and MoO\(_2\), since no diffraction at 2\(\theta\) of 58° corresponding to Mo\(^6\) is observed. On the contrary, the spent catalyst Cu/Cs/MoC, despite having mostly lost the typical diffractions of MoC, it still displayed the diffractions ascribed to metallic Mo.

The conversion and selectivity profiles can be partially explained by the XRD patterns. The catalyst β-MoC, despite displaying lower conversion and selectivity than the catalyst Cu/MoC, showed a more stable catalytic performance, in agreement with the structure preservation observed by XRD. In addition, it can be observed that all the copper-containing catalysts are activated at the beginning of the reaction as the increase of conversion indicates. However, while for Cu/MoC, conversion was then stable after the first 4 h, this is not true for Cu/Cs/MoC and Cs/MoC for which an apparent deactivation occurred, this effect being more pronounced for the Cs/MoC catalyst. Nevertheless, the conversion at the end of the experiment was still higher than that observed at the start of the reaction. The reason for this behaviour can be that at the beginning of the reaction the hydrogen flow of the reactants feed is able to reduce the oxide layer of copper which could subsequently activate hydrogen to carburize molybdenum oxycarbide species, MoO\(_x\)C\(_y\), and/or to reduce Mo oxide layers [24, 25]. Then, for the Cu/Cs/MoC and Cs/MoC, oxidation of the molybdenum carbide took place, as the XRD showed. Also, the extent of oxidation seems to be in agreement with the deactivation slope which is more obvious for Cs/MoC.

The explanation of the oxidation of the alkali-doped samples, could be that reverse water-gas-shift reaction (RWGS) (CO\(_2\) + H\(_2\) \(\leftrightarrow\) CO + H\(_2\)O) took place simultaneously. The occurrence of RWGS would not only decrease the selectivity, but it would also increase the amount of water on the reactant stream which could eventually oxidize the molybdenum carbide phase as the XRD of these spent
catalysts showed. The reason for the RWGS reaction being favoured on Cu/Cs/Mo:C and Cs/Mo:C is in agreement with previous literature reporting the effect of alkalis on the RWGS [14,26,27].

Much progress has been made towards the development of viable catalysts for CO$_2$ hydrogenation to methanol. Some recent works related with the performances and reaction conditions of these catalysts have been summarized in Table 1. In industry, methanol is produced from synthesis gas mixtures at elevated pressures P (50 to 100 bar) and temperatures T (200°C to 300°C) over Cu/ZnO/Al$_2$O$_3$ catalysts, with a worldwide demand of ~50 Mtons year$^{-1}$ [28]. Therefore, Cu/ZnO/Al$_2$O$_3$ series still attract numerous attentions [32]. As shown in table 1, the CO$_2$ conversion and methanol selectivity towards Cu/ZnO/Al$_2$O$_3$ are highly depend on the temperatures. The CO$_2$ conversion and CH$_2$OH selectivity reached 5.19% and 67% respectively at 200°C. When the temperature increased to 250°C, the corresponding values changed to 13.4% and 13% respectively. In addition, other combinations of Cu and metal/metal oxides have been explored extensively in methanol synthesis field, such as Cu/Mg/Al [31], Cu/ZnO/ZrO$_2$ [33,34]. For comparison’s sake, the performances of other Mo:C related catalysts have also been listed in table 1 [29,30]. As can be seen, although Cu-based catalysts are suitable for CO$_2$ hydrogenation, an efficient catalyst exhibiting high selectivity, conversion, and functional stability towards methanol synthesis at low pressure (less than 50 bar) has not been developed yet [33].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction condition</th>
<th>CO$_2$ Conversion(%)</th>
<th>Methanol selectivity (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Mo:C</td>
<td>20 bar 150°C 3/1</td>
<td>3.25%</td>
<td>60%</td>
<td>This work</td>
</tr>
<tr>
<td>Cu-Mo:C</td>
<td>20 bar 150°C 3/1</td>
<td>5%</td>
<td>70%</td>
<td>[29]</td>
</tr>
<tr>
<td>Cs-Mo:C</td>
<td>20 bar 150°C 3/1</td>
<td>3%</td>
<td>50%</td>
<td>[29]</td>
</tr>
<tr>
<td>CuCs-Mo:C</td>
<td>20 bar 150°C 3/1</td>
<td>4%</td>
<td>55%</td>
<td>[29]</td>
</tr>
<tr>
<td>Mo:C/TiO$_2$-P</td>
<td>20 bar 250°C 5/1</td>
<td>2.5%</td>
<td>3%</td>
<td>[30]</td>
</tr>
<tr>
<td>Mo:C/TiO$_2$-D</td>
<td>20 bar 250°C 5/1</td>
<td>2.2%</td>
<td>11%</td>
<td>[30]</td>
</tr>
<tr>
<td>MoC$_2$/ZrO$_2$</td>
<td>20 bar 250°C 5/1</td>
<td>1.7%</td>
<td>4%</td>
<td>[30]</td>
</tr>
<tr>
<td>Mo:C</td>
<td>20 bar 240°C 16/3</td>
<td>2.8%</td>
<td>8%</td>
<td>[31]</td>
</tr>
<tr>
<td>MoC$_3$/SiO$_2$</td>
<td>20 bar 240°C 16/3</td>
<td>8%</td>
<td>3%</td>
<td>[31]</td>
</tr>
<tr>
<td>Cu/Mg/Al</td>
<td>20 bar 200°C 2.8/1</td>
<td>3%</td>
<td>30%</td>
<td>[32]</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$</td>
<td>20 bar 200°C 3/1</td>
<td>5.19%</td>
<td>67%</td>
<td>[32]</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO$_2$</td>
<td>30 bar 250°C 3/1</td>
<td>13.4%</td>
<td>13%</td>
<td>[33]</td>
</tr>
<tr>
<td>Cu/ZnO@SBA-15</td>
<td>30 bar 250°C 3/1</td>
<td>8%</td>
<td>45%</td>
<td>[34]</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO@SBA-15</td>
<td>30 bar 250°C 3/1</td>
<td>10%</td>
<td>25-30%</td>
<td>[34]</td>
</tr>
</tbody>
</table>

In summary, the results showed that for the studied system, alkali doping with cesium is not beneficial for the synthesis of methanol and that in situ carburization would be required. This did not happen during the reverse water-gas-shift reaction, for which re-carburization of the active phase was observed during reaction conditions [14]. Hence, the different stability of the catalysts in the RWGS and methanol synthesis is probably due to the different reaction conditions used. The
conditions used in Ref. 14 for RWGS, i.e. atmospheric pressure and 400-750 ºC, could allow the re-carburization of molybdenum during the reaction, in contrast to what is observed in the present work at 20 bar and mild temperature, 150 ºC.

3. Materials and Methods

The β-Mo2C catalyst was obtained through TPC procedure using ((NH4)6Mo7O24·4H2O Sigma-Aldrich) as reported before[28]. Briefly, the precursor was calcined heated at a rate of 5 ºC/min up to 500 ºC and maintained for 4 h to get MoO3. Then, the oxide precursor was placed under an atmosphere composed of 20% CH4 and 80% H2 and submitted to thermal treatment at a heating rate of 5 ºC/min up to 300 ºC. Then at a rate of 2 ºC/min the temperature was raised up to 700 ºC and kept for 2 h. The Cs/Mo2C, Cu/Mo2C and Cu/Cs/Mo2C catalysts were prepared using the corresponding amounts of the same molybdenum precursor and Cu(NO3)3 or Cu(NO3)2/Cs2CO3 using co-precipitation method as described previously[14]. The nominal loading of copper and cesium was 1 wt% for each element. Then, the same TPC process was used to prepare.

The catalytic tests were done in a stainless steel fixed-bed flow reactor of 3/8” internal diameter. Around 0.25 g of catalyst was used as prepared. Before the measurements, 20 bar was reached in the reactor with a reactant mixture of (CO2:H2:He = 3:9:18 vol) and a total flow of 30 ml/min. The compounds were analyzed by gas chromatographs (Varian CP 3400) with FID and TCD detectors and fitted with a column SupelQ Plot and 60/80 Carboxen-1000 column, respectively. The carbon balance was over 95% in all cases. The conversion and products selectivity were obtained according to the following equations:

\[
X_{CO2} = \frac{\sum_{i} n_i \times mol_i}{\sum_{i} n_i \times mol_i + mol CO_2-un} \times 100\quad (1)
\]

\[
S_i = \frac{n_i \times mol_i}{\sum_{i} n_i \times mol_i} \times 100\quad (2)
\]

\(n_i\): number of carbon atoms of \(i\).
\(mol_i\): number of moles \(i\),
\(mol CO_2-un\): mol of unreacted CO2.

X-ray diffraction (XRD) patterns of the catalysts were acquired using a Polycrystal X’Pert Pro PANalytical diffractometer with Ni-filtered Cu Kα radiation (\(\lambda = 1.54\) Å) operating at 45 kV and 40 mA. The 2θ range between 4º and 90º with a step of 0.04º/s

XEDS-mapping analysis was performed in STEM mode with a probe size of ~1 nm using the INCA x-sight (Oxford Instruments) detector. To prepare the samples, small amounts of the samples were ground and dissolved in acetone solution under sonication. Small drops were added to the gold grid (Aname, Lacey carbon 200 mesh) and the acetone was evaporated at room temperature before introducing in the microscope.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: title, Table S1: title, Video S1: title.

Author Contributions:

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T.R.Reina: resources, review and editing
A.Guerrero-Ruiz: resources, review and editing
I.Rodríguez-Ramos: resources, review and editing
All authors have read and agreed to the published version of the manuscript.”, please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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Conflicts of Interest: The authors declare no conflict of interest.

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