

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 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 show that all the catalysts were active, and the main reaction product was methanol. Copper, cesium and molybdenum interaction is observed, and cesium promoted the formation of metallic Mo on the fresh catalyst. The incorporation of copper is positive and improves the activity and selectivity to methanol. Additionally, the addition of cesium favored the formation of Mo⁰ phase, which for the catalysts Cs/Mo₂C seemed to be detrimental for the conversion and selectivity. Moreover, the catalysts promoted by copper and/or cesium underwent redox surface transformations during the reaction, these were more obvious for cesium doped catalysts, which diminished their catalytic performance.

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

1. Introduction

The study of CO₂ transformations has increased significantly due to the need to diminish its atmospheric emissions. The possibility of using CO₂ as a raw material is a convenient way from an economic and industrial point of view, therefore conversion to fuels such as methane, or syn-gas, which could be later used in the Fisher–Tropsch process 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 oxide 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 methanol, dry reforming of methane or CO hydrogenation [4]. Some transition metal carbides can adsorb CO₂ and favor the C–O scission

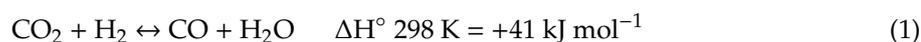
by themselves or aided by hydrogen. Among them, molybdenum carbide actually holds catalytic properties similar to those of noble metals [4,5]. In addition to their catalytic properties as active phase, the TMC can also avoid metal sintering, being excellent support to disperse metals.

Methanol synthesis via CO₂ hydrogenation has been studied by using several non-noble metals (Ni, Co, Cu) supported on Mo₂C 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]. The selectivity to methanol obtained in liquid phase at 1% conversion with a catalyst of ca. 5 wt.% Cu loading onto Mo₂C at 135 °C and 40 bar was 93%, just slightly lower than that achieved with 5 wt.% Pd on Mo₂C, which was 95% [6].

Furthermore, it has been reported that alkali promoters can improve the adsorption of CO₂ to obtain alcohols or CO and the beneficial effect for higher alcohols followed the trend Cs > Rb > K > Na > Li [8]. Additionally, potassium has been used to keep the reduced phases of molybdenum in a K-Mo₂C/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_xO/Cu(111), potassium enhances the selectivity to methanol from carbon dioxide, favoring 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 Mo₂C system for reverse water gas shift (RWGS) reaction (1), which can take place simultaneously to reaction two, 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, which 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 three), 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 °C, compared to those of RWGS reaction.



2. Results

We have studied four catalysts based on Mo₂C with 1 wt.% loading of each metal and they are labelled as follows: β-Mo₂C, Cu/Mo₂C, Cs/Mo₂C and Cu/Cs/Mo₂C. The catalysts were tested in CO₂ hydrogenation at 150 °C and 20 bar for 16 h and the conversion and selectivity profiles are included in Figure 1. In regard to the conversion, it can be observed that while β-Mo₂C 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/Mo₂C > Cu/Cs/Mo₂C > β-Mo₂C > Cs/Mo₂C, 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/Mo₂C > β-Mo₂C > Cu/Cs/Mo₂C > Cs/Mo₂C. Unlike the conversion behavior, the selectivity profiles were quite stable for all the catalysts except for the sample Cu/Cs/Mo₂C. The other detected products were CO

and CH_4 , with minor contributions of ethanol, which was below 0.2% except for the catalyst $\text{Cs}/\text{Mo}_2\text{C}$ that was around 2% and is included in Figure 1. The selectivity of the main secondary products, i.e., CH_4 and CO , over $\beta\text{-Mo}_2\text{C}$ was quite different with values of 30% and 5%, respectively. However, the selectivity to those products obtained for each catalyst was more similar for $\text{Cu}/\text{Mo}_2\text{C}$, $\text{Cs}/\text{Mo}_2\text{C}$ and $\text{Cu}/\text{Cs}/\text{Mo}_2\text{C}$, for which the values differ between 3%–5% when comparing CO and CH_4 selectivity of every catalyst.

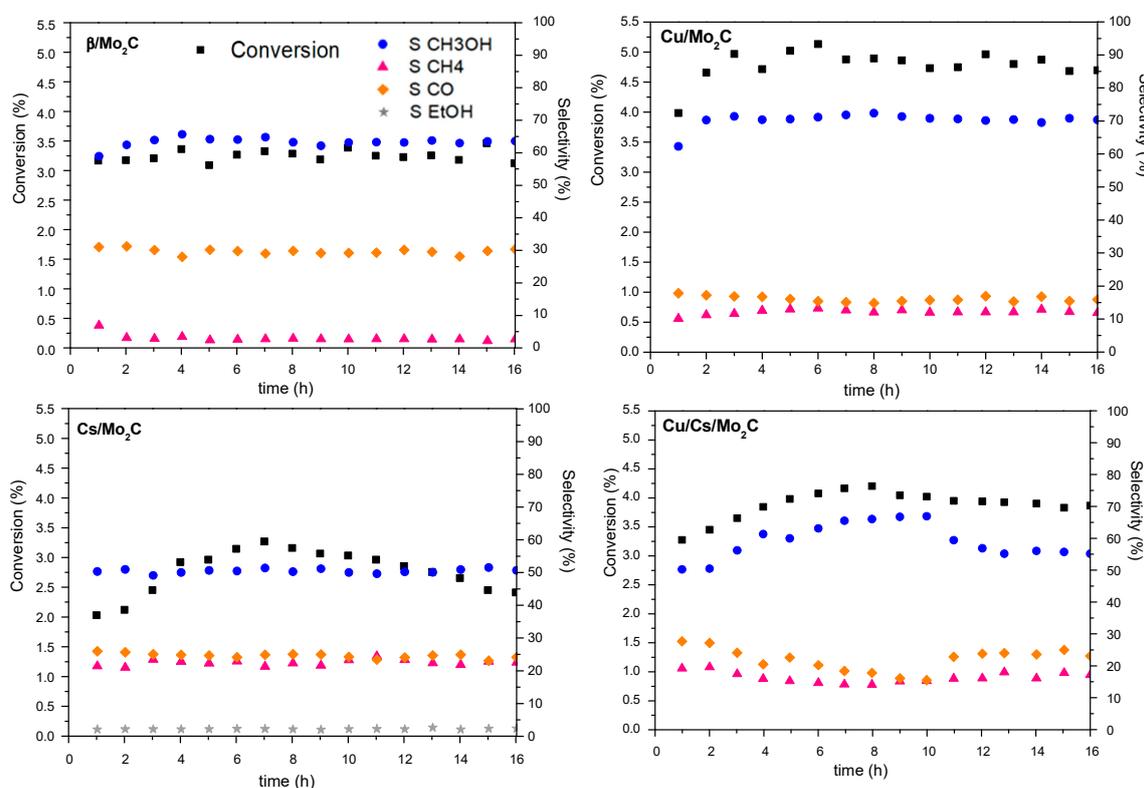


Figure 1. Conversion and selectivity to CH_3OH , CO , CH_4 , and $\text{C}_2\text{H}_5\text{OH}$. Reaction conditions: $T = 150\text{ }^\circ\text{C}$, $P = 20\text{ bar}$, $\text{CO}_2:\text{H}_2$ (1:3), GHSV $7600\text{ mL}/(\text{h}^{-1}\text{ g})$.

CO_2 hydrogenation to CH_3OH 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 CH_3OH [16].

The selectivity profiles obtained for $\beta\text{-Mo}_2\text{C}$ 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 $\text{Cu}/\text{Mo}_2\text{C}$ 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 elemental analyses showed that the concentration of Mo and C agrees quite well, within the experimental error, with the Mo_2C stoichiometry. In addition, the mapping of the Cs-doped sample, in Figure 2A, confirms the interaction between Cu, Cs and Mo_2C .

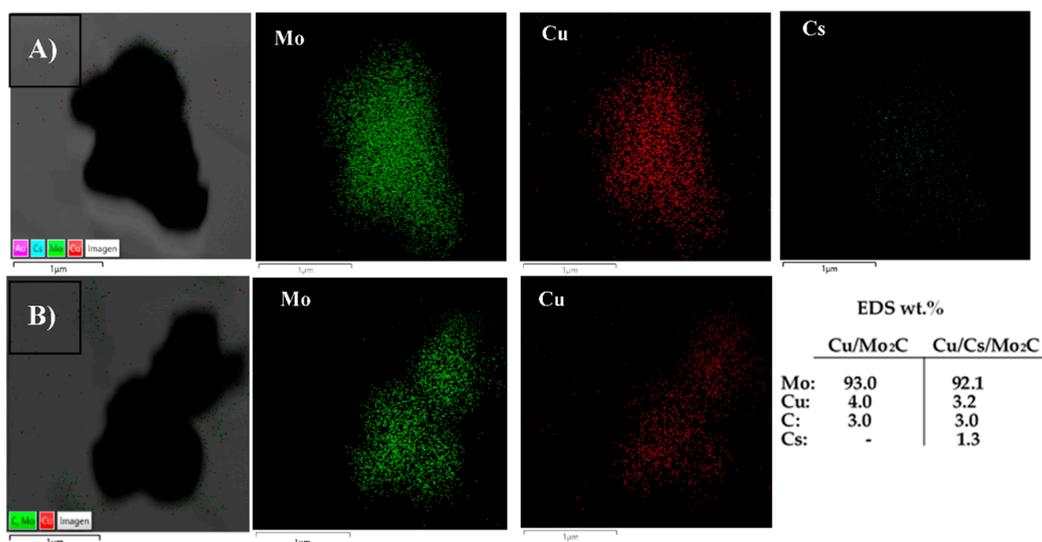


Figure 2. STEM images with the corresponding elemental mapping (A) Cu/Cs/Mo₂C and (B) Cu/Mo₂C.

Additionally, the positive effect of copper can also be related to its ability to activate hydrogen, which eventually reacts with CO₂ 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 CO₂ molecule [8]. However, the opposite tendency was indeed observed, and both conversion and selectivity to methanol are diminished, which for the catalyst Cs/Mo₂C are even lower than the values achieved with the bare β-Mo₂C.

It has been suggested that different crystal phases or Mo/C ratios can influence the selectivity of CO₂ hydrogenation [19]. However, in the studied system, we only detected one carbide phase, therefore 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, as shown in Figure 3a, displayed the characteristic peaks of β-Mo₂C with hexagonal closet 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. Additionally, 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 can be observed, the relative contribution of Mo⁰ is more relevant on the sample Cs/Mo₂C.

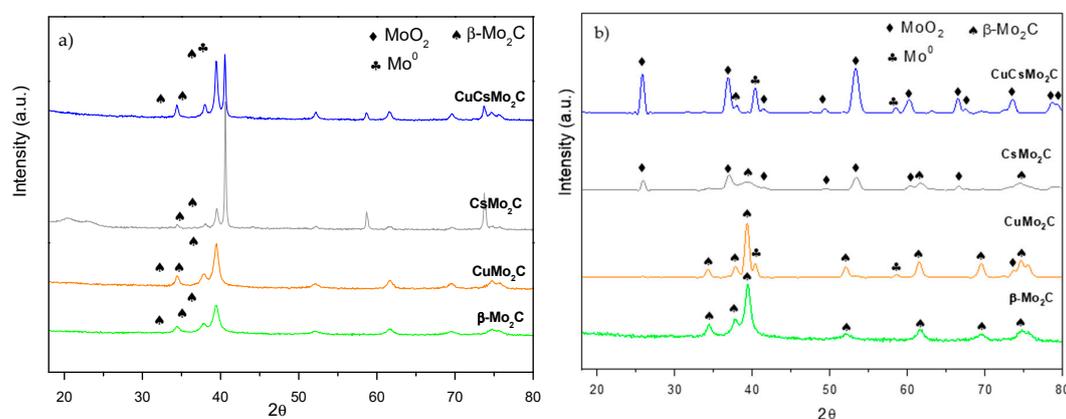


Figure 3. XRD patterns of the catalysts (a) fresh samples; (b) spent samples.

Hence, the presence of this metallic molybdenum phase could explain the worse catalytic performance of Cs-doped samples since Mo^0 has a poorer activation ability towards the CO_2 molecule. It has been reported that when Mo^0 adsorbs CO_2 $\text{HO}_2\text{C-Mo}$ species are formed, which do not favor the scission of the C-O bond [20]. In contrast, dissociation of CO_2 over $\beta\text{-Mo}_2\text{C}$ is relatively easy and it may take place through a previous hydrogenation to CO followed by formation of HCO followed by hydrogenation to CH_3OH . Furthermore, since the adsorption and activation of CO_2 molecules can occur on both Cu and Mo_2C surfaces, the negative effect of the Mo^0 phase was not so relevant in the catalytic performance of the Cu/Cs/ Mo_2C as it is on the copper free sample, Cs/ Mo_2C [21].

The diffractograms of the spent catalyst, as shown in Figure 3b, showed that Cu/ Mo_2C preserved the $\beta\text{-Mo}_2\text{C}$ crystal structure and surprisingly it also showed the typical diffractions of Mo^0 , which were not observed in the fresh catalysts. This is an interesting finding and there is not an 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, therefore we can tentatively rule out that these peaks appear as a consequence of the sintering of molybdenum during the reaction [14]. Another possibility is that the reaction conditions could somehow favor the formation of metallic molybdenum. The reduction of metals by Mo_2C 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, therefore redox transformations during the reaction could be the reason for the chemical state of the spent catalyst. Nevertheless, the possibility of a molybdenum oxide passivation layer on Mo^0 nanoparticles of the fresh catalysts cannot be totally disregarded. However, conventional ex situ XPS cannot be used to assess 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 indicates a good stability towards oxidation under the tested conditions.

On the other hand, the XRD patterns of spent catalysts Cu/Cs/ Mo_2C and Cs/ Mo_2C display diffractions at 2θ 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 Mo_2C phase mostly disappear and just a broad hump with maximum at 2θ of 39.4° can be envisaged on the catalyst Cs/ Mo_2C . This broad peak probably includes just the contributions of Mo_2C and MoO_x , since no diffraction at 2θ of 58° corresponding to Mo^0 is observed. On the contrary, the spent catalyst Cu/Cs/ Mo_2C , despite having mostly lost the typical diffractions of Mo_2C , still displayed the diffractions ascribed to metallic Mo.

The conversion and selectivity profiles can be partially explained by the XRD patterns. The catalyst $\beta\text{-Mo}_2\text{C}$, despite displaying lower conversion and selectivity than the catalyst Cu/ Mo_2C , showed a more stable catalytic performance, in agreement with the structure preservation observed by XRD. In addition, it can be observed that Cu/ Mo_2C , Cs/ Mo_2C and Cu/Cs/ Mo_2C catalysts are activated at the beginning of the reaction as the increase in conversion indicates. However, while for Cu/ Mo_2C conversion was then stable after the first 4 h, this is not true for Cu/Cs/ Mo_2C and Cs/ Mo_2C for which an apparent deactivation occurred, this effect being more pronounced for the Cs/ Mo_2C 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 behavior 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_xC_y , and/or to reduce Mo oxide layers [24,25]. Then, for Cu/Cs/ Mo_2C and Cs/ Mo_2C , oxidation of the molybdenum carbide took place, as the XRD shows. Furthermore, the extent of oxidation seems to be in agreement with the deactivation slope, which is more obvious for Cs/ Mo_2C .

The oxidation of the alkali-doped samples could be explained by the reverse water-gas-shift reaction (RWGS) ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) taking 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 shows. The reason for the RWGS reaction being favored by Cu/Cs/Mo₂C and Cs/Mo₂C 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 CO₂ 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/Al₂O₃ catalysts, with a worldwide demand of ~50 Mt year⁻¹ [28]. Therefore, Cu/ZnO/Al₂O₃ series still attract numerous attention [29]. As shown in Table 1, the CO₂ conversion and methanol selectivity towards Cu/ZnO/Al₂O₃ highly depend on the temperatures. The CO₂ conversion and CH₃OH 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 the methanol synthesis field, such as Cu/Mg/Al [30], Cu/ZnO/ZrO₂ [31,32]. For comparison's sake, the performances of other Mo₂C related catalysts have also been listed in Table 1 [15,33]. As can be seen, although Cu-based catalysts are suitable for CO₂ 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 [31].

Table 1. Performance of catalysts towards methanol synthesis.

Catalysts	Reaction Condition				CO ₂ Conversion (%)	Methanol Selectivity (%)	Ref
	P (bar)	T (°C)	H ₂ /CO ₂	GHSV			
β-Mo ₂ C	20 bar	150 °C	3/1	120 mL min ⁻¹ g ⁻¹	3.25%	60%	This work
Cu/Mo ₂ C					5%	70%	
Cs/Mo ₂ C					3%	50%	
Cu/Cs-Mo ₂ C					4%	55%	
MoC/TiO ₂ -P	20 bar	250 °C	5/1	75 mL min ⁻¹ g ⁻¹	2.5%	3%	[15]
MoC/TiO ₂ -D					2.2%	11%	
MoC ₂ /ZrO ₂					1.7%	4%	
Mo ₂ C	20 bar	240 °C	16/3	170 mL min ⁻¹ g ⁻¹	2.8%	8%	[33]
MoC _{1-x}					8%	3%	
Mo _x C _y /SiO ₂					4%	12%	
Cu/Mg/Al	20 bar	200 °C	2.8/1	2000 h ⁻¹	3%	30%	[30]
Cu/ZnO/Al ₂ O ₃	20 bar	200 °C	3/1	2000 h ⁻¹	5.19%	67%	[29]
		250 °C			13.4%	13%	
Cu/ZnO/ZrO ₂	30 bar	250 °C	3/1	400 mL min ⁻¹ g ⁻¹	8%	45%	[31]
Cu/ZnO@SBA-15	30 bar	250 °C	3/1	44000 mL h ⁻¹ g ⁻¹	10%	25–30%	[32]
Cu/ZnO/ZrO ₂ @SBA-15					20–25%	30%	

In summary, the results show that for the studied system, alkali doping with cesium is not beneficial for the synthesis of methanol in the studied catalytic system 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 absence of the re-carburization of catalysts in the 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 °C, 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 °C.

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 and heated at a rate

of 5 °C/min up to 500 °C 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 °C/min up to 300 °C. Then, at a rate of 2 °C/min, the temperature was raised up to 700 °C 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)₂ or Cu(NO₃)₂/Cs₂CO₃, using the 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:

$$X_{\text{CO}_2} = \frac{\sum_i n_i \times \text{mol}_i}{\sum_i n_i \times \text{mol}_i + \text{mol CO}_2 - \text{un}} \times 100 \quad (4)$$

$$S_i = \frac{n_i \times \text{mol}_i}{\sum_i n_i \times \text{mol}_i} \times 100 \quad (5)$$

n_i : number of carbon atoms of i .

mol_i : number of moles i .

mol CO₂-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 K α radiation ($\lambda = 1.54 \text{ \AA}$) operating at 45 kV and 40 mA. The 2θ range was between 4° and 90° with a step of 0.04°/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 the microscope.

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

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