

Communication

# Effect of Cu and Cs in the $\beta$ -Mo<sub>2</sub>C system for CO<sub>2</sub> hydrogenation to Methanol

A.B.Dongil<sup>1\*</sup>, Q.Zhang<sup>2</sup>, L.Pastor-Pérez<sup>2</sup>, T.R.Reina<sup>2</sup>, A.Guerrero-Ruiz<sup>3,4</sup> and I.Rodríguez-Ramos<sup>1,3</sup>

<sup>1</sup> Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie No. 2, Cantoblanco, 28049 Madrid, Spain;

<sup>2</sup> Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom;

<sup>3</sup> Dpto. Química Inorgánica y Técnica, Facultad de Ciencias UNED, Senda del Rey 9, 28040 Madrid Spain.

<sup>4</sup> UA UNED-ICP(CSIC), Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, Madrid, Spain

\* Correspondence: a.dongil@csic.es;

**Abstract:** Mitigation of Anthropogenic CO<sub>2</sub> emissions possess a major global challenge for modern societies. Herein catalytic solutions are meant to play a key role. Among the different catalysts for CO<sub>2</sub> 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  $\beta$ -Mo<sub>2</sub>C catalysts and compare the results with those of Cu/Mo<sub>2</sub>C, Cs/Mo<sub>2</sub>C and Cu/Cs/Mo<sub>2</sub>C in CO<sub>2</sub> 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 Mo<sup>0</sup> 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/Mo<sub>2</sub>C 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 CO<sub>2</sub> transformations has increased significantly due to the need of diminishing its atmospheric emissions. The possibility of using CO<sub>2</sub> 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, CO<sub>2</sub> 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 CO<sub>2</sub>. 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 methanol, dry reforming of methane or CO hydrogenation [4]. Some transition metal carbides can adsorb CO<sub>2</sub> 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 CO<sub>2</sub> hydrogenation was studied by using several metals (Ni, Co, Cu) supported on Mo<sub>2</sub>C 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 CO<sub>2</sub> 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-Mo<sub>2</sub>C/γ-Al<sub>2</sub>O<sub>3</sub> 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<sub>x</sub>O/Cu(111), potassium enhances the selectivity to methanol from carbon dioxide favouring a different mechanism in which a methanediol [H<sub>2</sub>C(OH)<sub>2</sub>]-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 CO<sub>2</sub> as previously reported elsewhere [12,13]. We recently evaluated the promoter effect of cesium and copper in the Mo<sub>2</sub>C 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 Cu<sup>0</sup> or Cu<sup>+</sup>. 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].

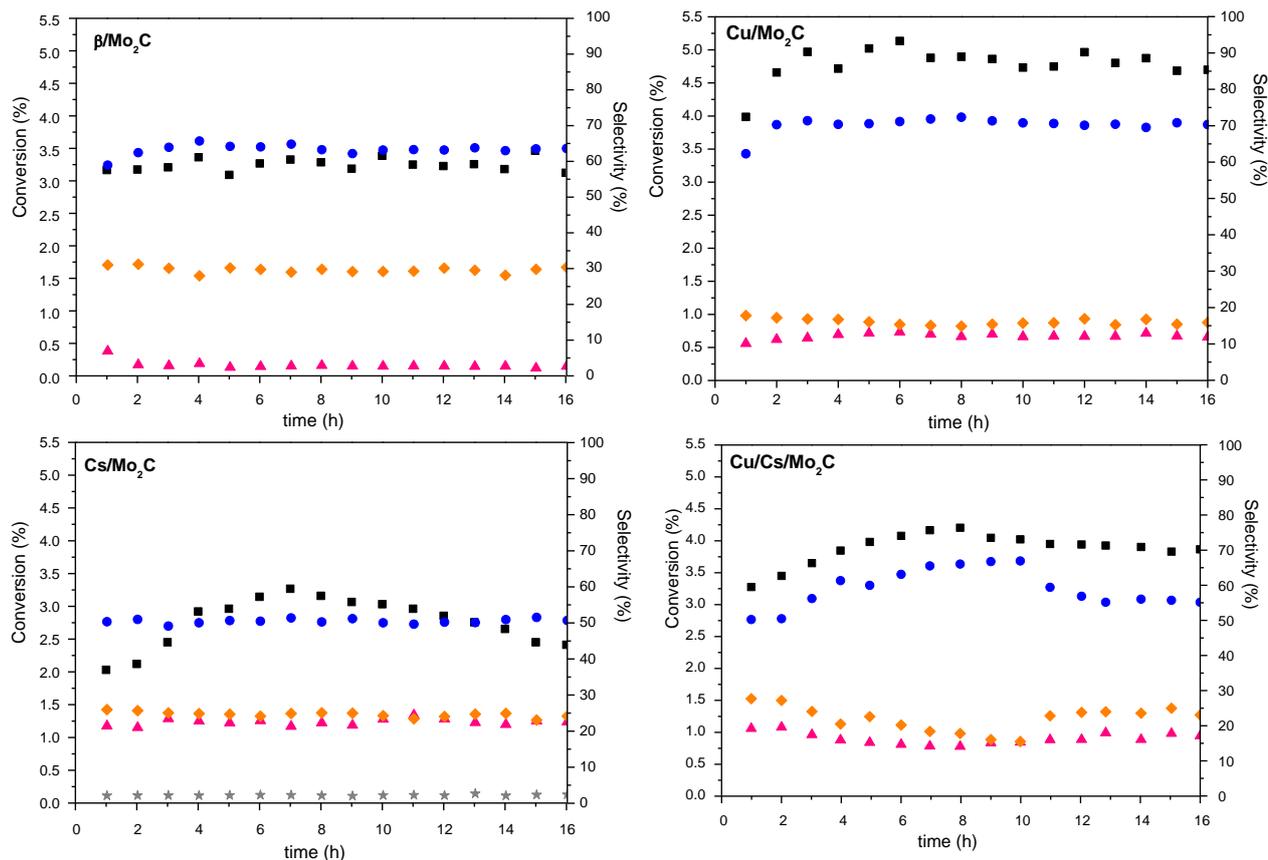
In the present communication, we investigate the effect of copper and cesium as promoters for methanol synthesis (reaction 3), and evaluate the stability of the catalysts under reaction conditions for CO<sub>2</sub> hydrogenation to methanol without in situ carburization which, to the best of our knowledge, 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 CO<sub>2</sub> hydrogenation at 150 °C 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-Mo<sub>2</sub>C 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/Mo<sub>2</sub>C > Cu/Cs/Mo<sub>2</sub>C > β-Mo<sub>2</sub>C > Cs/Mo<sub>2</sub>C 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/Mo<sub>2</sub>C > β-Mo<sub>2</sub>C > Cu/Cs/Mo<sub>2</sub>C > Cs/Mo<sub>2</sub>C. Unlike the conversion behavior, the selectivity profiles were quite stable for all the catalysts except for the sample Cu/Cs/Mo<sub>2</sub>C. The other detected products were CO and CH<sub>4</sub>, with minor contributions of ethanol which was below 0.2% except for the catalyst Cs/Mo<sub>2</sub>C that was around 2% and it is included in the Fig.1. The selectivity to the products CO and CH<sub>4</sub> was similar for the Cu-containing catalysts, Cu/Mo<sub>2</sub>C, Cs/Mo<sub>2</sub>C and Cu/Cs/Mo<sub>2</sub>C which reached values of ca. 12 and 17%, 22 and 25%, and 17 and 22%, respectively. However, over β-Mo<sub>2</sub>C the selectivity of the secondary products was quite different with selectivities of 30% and 5% for CH<sub>4</sub> and CO respectively.

CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH 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<sub>3</sub>OH [16].



**Figure 1.** Conversion (■) and Selectivity to CH<sub>3</sub>OH (●) CO (◆) CH<sub>4</sub> (▲) and C<sub>2</sub>H<sub>5</sub>OH (★). Reaction conditions: T= 150 °C, P= 20 bar, CO<sub>2</sub>:H<sub>2</sub> (1:3), GHSV 7600 mL/(h<sup>-1</sup> g) . .

The selectivity profiles obtained for  $\beta$ -Mo<sub>2</sub>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<sub>2</sub>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<sub>2</sub>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<sub>2</sub>C stoichiometry. In addition, the mapping of the Cs-doped sample, in Fig. 2a, confirms the interaction between Cu, Cs and Mo<sub>2</sub>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<sub>2</sub> 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<sub>2</sub> 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  $\beta$ -Mo<sub>2</sub>C

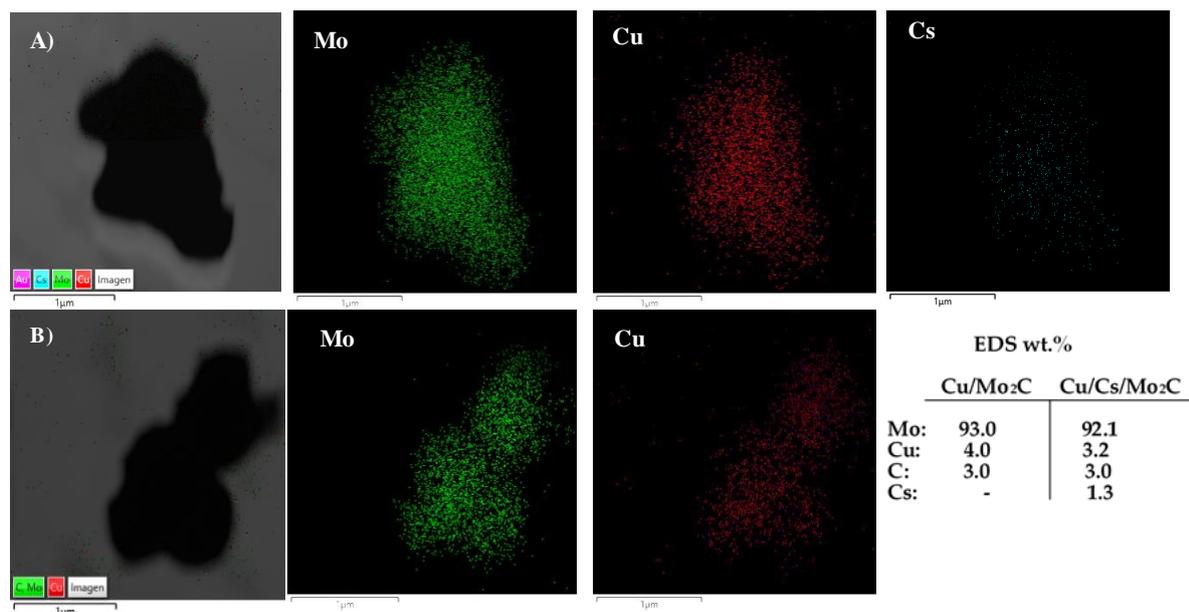


Figure 2. STEM images with the corresponding elemental mapping A) Cu/Cs/Mo<sub>2</sub>C and B) Cu/Mo<sub>2</sub>C.

It has been suggested that different crystal phases or Mo/C ratios can influence the selectivity on CO<sub>2</sub> hydrogenation [19]. However, in the studied system, we only detected one carbide phase, so the reason must be found in another feature.

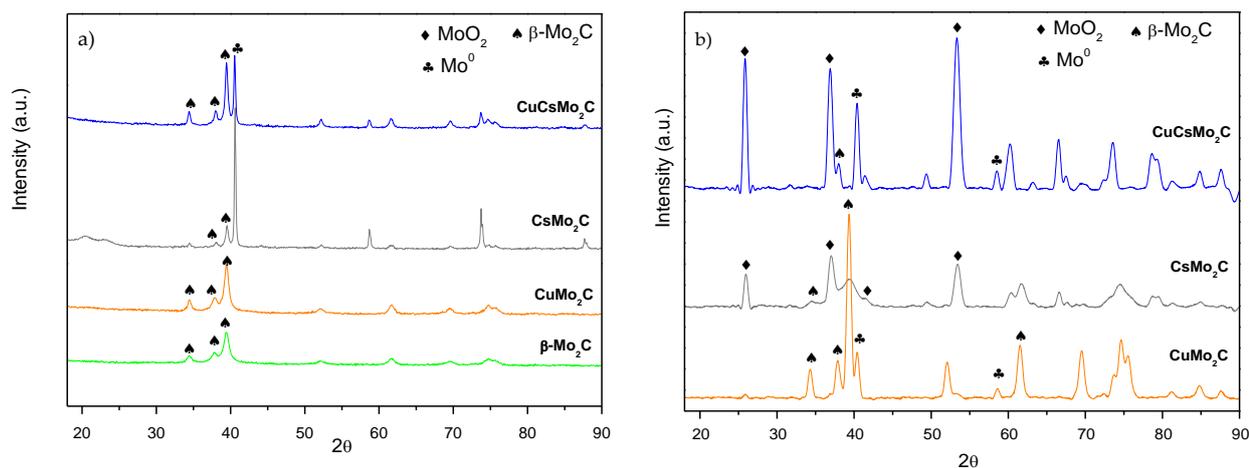
In order to understand the results, we evaluated the XRD patterns of the fresh and spent catalysts. The diffractograms showed that all the fresh catalysts, in Fig. 3a, displayed the characteristics peaks of  $\beta$ -Mo<sub>2</sub>C with hexagonal closet packing crystal structure (JCPDS 35-0787) at  $2\theta$  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  $2\theta$  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 Mo<sup>0</sup> 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 Mo<sup>0</sup> has poorer activation ability towards the CO<sub>2</sub> molecule. It has been reported that, when Mo<sup>0</sup> adsorbs CO<sub>2</sub>, HO<sub>2</sub>C–Mo species are formed which do not favor the scission of the C–O bond [20]. In contrast, dissociation of CO<sub>2</sub> over  $\beta$ -Mo<sub>2</sub>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<sub>3</sub>OH. Also, since the adsorption and activation of CO<sub>2</sub> molecule can occur on both Cu and Mo<sub>2</sub>C surfaces, the negative effect of the Mo<sup>0</sup> phase was not so relevant in the catalytic performance of the Cu/Cs/Mo<sub>2</sub>C as it is on the copper free sample, Cs/Mo<sub>2</sub>C [21].

The diffractograms of the spent catalyst, in Fig. 3b, showed that Cu/Mo<sub>2</sub>C preserved the  $\beta$ -Mo<sub>2</sub>C crystal structure and, surprisingly, it also showed the typical diffractions of Mo<sup>0</sup> 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 Mo<sub>2</sub>C 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  $\text{Mo}^0$  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  $\text{MoO}_2$  or  $\text{MoO}_3$  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.

On the other hand, the XRD patterns of spent catalysts with cesium display diffractions at  $2\theta$  of  $26.0^\circ$ ,  $37.1^\circ$  and  $53.3^\circ$  which correspond to the  $\text{MoO}_2$  crystal phase (JCPDS 32-671). Furthermore, the diffractions due to the  $\text{Mo}_2\text{C}$  phase mostly disappear and just a broad hump with maximum at  $2\theta$  of  $39.4^\circ$  can be envisaged on the catalyst  $\text{Cs}/\text{Mo}_2\text{C}$ . This broad peak probably includes just the contributions of  $\text{Mo}_2\text{C}$  and  $\text{Mo}_x\text{O}$ , since no diffraction at  $2\theta$  of  $58^\circ$  corresponding to  $\text{Mo}^0$  is observed. On the contrary, the spent catalyst  $\text{Cu}/\text{Cs}/\text{Mo}_2\text{C}$ , despite having mostly lost the typical diffractions of  $\text{Mo}_2\text{C}$ , it still displayed the diffractions ascribed to metallic  $\text{Mo}$ .

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  $\text{Cu}/\text{Mo}_2\text{C}$ , 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  $\text{Cu}/\text{Mo}_2\text{C}$ , conversion was then stable after the first 4 h, this is not true for  $\text{Cu}/\text{Cs}/\text{Mo}_2\text{C}$  and  $\text{Cs}/\text{Mo}_2\text{C}$  for which an apparent deactivation occurred, this effect being more pronounced for the  $\text{Cs}/\text{Mo}_2\text{C}$  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,  $\text{MoO}_x\text{C}_y$ , and/or to reduce  $\text{Mo}$  oxide layers [24, 25]. Then, for the  $\text{Cu}/\text{Cs}/\text{Mo}_2\text{C}$  and  $\text{Cs}/\text{Mo}_2\text{C}$ , 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  $\text{Cs}/\text{Mo}_2\text{C}$ .

The explanation of the oxidation of the alkali-doped samples, could be that reverse water-gas-shift reaction (RWGS) ( $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ ) 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<sub>2</sub>C and Cs/Mo<sub>2</sub>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<sub>2</sub> 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<sub>2</sub>O<sub>3</sub> catalysts, with a worldwide demand of ~50 Mtons year<sup>-1</sup> [28]. Therefore, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> series still attract numerous attentions [32]. As shown in table 1, the CO<sub>2</sub> conversion and methanol selectivity towards Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> are highly depend on the temperatures. The CO<sub>2</sub> conversion and CH<sub>3</sub>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<sub>2</sub> [33,34]. For comparison's sake, the performances of other Mo<sub>2</sub>C related catalysts have also been listed in table 1 [29, 30]. As can be seen, although Cu-based catalysts are suitable for CO<sub>2</sub> 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 1.** Performance of catalysts towards methanol synthesis.

Catalysts	Reaction condition				CO <sub>2</sub> Conversion(%)	Methanol selectivity (%)	Ref
	P (bar)	T (°C)	H <sub>2</sub> /CO <sub>2</sub>	GHSV			
β-Mo <sub>2</sub> C					3.25%	60%	
Cu-Mo <sub>2</sub> C	20bar	150°C	3/1	120	5%	70%	This
Cs-Mo <sub>2</sub> C				ml min <sup>-1</sup> g <sup>-1</sup>	3%	50%	work
CuCs-Mo <sub>2</sub> C					4%	55%	
MoC/TiO <sub>2</sub> -P					2.5%	3%	
MoC/TiO <sub>2</sub> -D	20 bar	250°C	5/1	75	2.2%	11%	[29]
MoC <sub>2</sub> /ZrO <sub>2</sub>				ml min <sup>-1</sup> g <sup>-1</sup>	1.7%	4%	
Mo <sub>2</sub> C				170	2.8%	8%	
MoC <sub>1-x</sub>	20 bar	240°C	16/3	ml min <sup>-1</sup> g <sup>-1</sup>	8%	3%	[30]
Mo <sub>x</sub> C <sub>y</sub> /SiO <sub>2</sub>					4%	12%	
Cu/Mg/Al	20 bar	200°C	2.8/1	2000 h <sup>-1</sup>	3%	30%	[31]
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	20 bar	200°C	3/1	2000h <sup>-1</sup>	5.19%	67%	[32]
		250°C			13.4%	13%	
Cu/ZnO/ZrO <sub>2</sub>	30 bar	250°C	3/1	400	8%	45%	[33]
Cu/ZnO@SBA-15	30 bar	250°C	3/1	44000	10%	25-30%	[34]
Cu/ZnO/ZrO <sub>2</sub> @SBA-15				ml h <sup>-1</sup> g <sup>-1</sup>	20-25%	30%	

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 °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  $\beta$ -Mo<sub>2</sub>C catalyst was obtained through TPC procedure using ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O Sigma-Aldrich) as reported before [28]. Briefly, the precursor was calcined heated at a rate of 5 °C/min up to 500 °C and maintained for 4 h to get MoO<sub>3</sub>. Then, the oxide precursor was placed under an atmosphere composed of 20% CH<sub>4</sub> and 80% H<sub>2</sub> 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/Mo<sub>2</sub>C, Cu/Mo<sub>2</sub>C and Cu/Cs/Mo<sub>2</sub>C catalysts were prepared using the corresponding amounts of the same molybdenum precursor and Cu(NO<sub>3</sub>)<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub>/Cs<sub>2</sub>CO<sub>3</sub> 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 (CO<sub>2</sub>:H<sub>2</sub>: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:

$$X_{\text{CO}_2} = \frac{\sum_i n_i \times \text{moli}}{\sum_i n_i \times \text{moli} + \text{mol CO}_2\text{-un}} \times 100 \quad (1)$$

$$S_i = \frac{n_i \times \text{moli}}{\sum_i n_i \times \text{moli}} \times 100 \quad (2)$$

n<sub>i</sub>: number of carbon atoms of i.

moli: number of moles i,

mol CO<sub>2</sub>-un: mol of unreacted CO<sub>2</sub>.

X-ray diffraction (XRD) patterns of the catalysts were acquired using a Polycrystal X'Pert Pro PANalytical diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) operating at 45 kV and 40 mA. The 2 $\theta$  range 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 in the microscope.

**Supplementary Materials:** The following are available online at [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1), Figure S1: title, Table S1: title, Video S1: title.

#### Author Contributions:

A.B.Dongil: Conception, investigation, funding acquisition and writing—original draft preparation;

Q.Zhang methodology, review and editing

L.Pastor-Pérez: resources, review and editing

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.

**Funding:** "This research was funded by Fundación General del CSIC ComFuturo programme, and "The APC was funded by iLink project N° 20211 from CSIC". The team at Surrey acknowledges the funding from CO2ChemUK via the EPSRC grant EP/P026435/1.

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

## References

1. Ahmad Galadima Oki Muraza. "Catalytic thermal conversion of CO<sub>2</sub> into fuels: Perspective and challenge". *Renewable and Sustainable Energy Reviews*, Volume 115, 2019, 109333-109353. <https://doi.org/10.1016/j.rser.2019.109333>
2. Nicola Scotti, Filippo Bossola, Federica Zaccheria and Nicoletta Ravasio. "Copper–Zirconia Catalysts: Powerful Multifunctional Catalytic Tools to Approach Sustainable Processes" *Catalysts*, Volume 10 (2), 2020, 168-188; <https://doi.org/10.3390/catal10020168>
3. Israf Ud Dina, Maizatul S. Shaharunb, Mshari A. Alotaibia, Abdulrahman I. Alharthia, A. Naeem Recent developments on heterogeneous catalytic CO<sub>2</sub> reduction to methanol. *Journal of CO<sub>2</sub> Utilization*, Volume 34, 2019, 20–33. <https://doi.org/10.1016/j.jcou.2019.05.036>
4. Carine E. Chan-Thaw and Alberto Villa "Metal Carbides for Biomass Valorization" *Appl. Sci.* Volume 8(2), 2018, 259-278; <https://doi.org/10.3390/app8020259>
5. Henry H. Hwu and Jingguang G. Chen. "Surface Chemistry of Transition Metal Carbides". *Chem. Rev.* Volume 105, 2005, 185-212. <https://doi.org/10.1021/cr0204606>
6. C. Panzone, R. Philippe, A. Chappaz, P. Fongarland, A. Bengaouer. "Power-to-Liquid catalytic CO<sub>2</sub> valorization into fuels and chemicals: focus on the Fischer-Tropsch route". *Journal of CO<sub>2</sub> Utilization* Volume 38, 2020, 314-347. <https://doi.org/10.1016/j.jcou.2020.02.009>
7. S. Posada Pérez, P. J. Ramirez Ramon A Gutierrez and J. A. Rodriguez. "The Conversion of CO<sub>2</sub> to Methanol on orthorhombic β-Mo<sub>2</sub>C and Cu/β-Mo<sub>2</sub>C Catalysts: Mechanism for Admetal Induced Change in the Selectivity and Activity". *Catalysis Science & Technology* Volume 6(18), 2016, 6766-6777. <https://doi.org/10.1039/C5CY02143J>
8. Xiaowa Nie, Wenhui Li, Xiao Jiang, Xinwen Guo, Chunshan Song. Recent advances in catalytic CO<sub>2</sub> hydrogenation to alcohols and hydrocarbons. In *Advances in Catalysis*, Volume 65, 1<sup>st</sup> ed.; Editor: Chunshan Song, Elsevier, United States, 2019; Volume 1, pp. 121-231.
9. MD. Porosoff, J.W. Baldwin, X. Peng, G. Mpourmpakis, HD. Willauer, "Alkali promoted tungsten carbide as a selective catalyst for the reverse water gas shift reaction". *ChemSusChem*, Volume 10, 2408-2415, <https://doi.org/10.1002/cssc.201700412>.
10. A.B. Dongil. "Recent progress on transition metal nitrides nanoparticles as heterogeneous catalysts" *Nanomaterials*, 2019, Volume 9, 1111-1129. <https://doi.org/10.3390/nano9081111>
11. Wenjie Liao and Ping Liu. "Methanol Synthesis from CO<sub>2</sub> Hydrogenation over a Potassium-Promoted Cu<sub>x</sub>O/Cu(111) (x ≤ 2) Model Surface: Rationalizing the Potential of Potassium in Catalysis". *ACS Catal.* Volume 20, 2020, <https://doi.org/10.1021/acscatal.9b05226>
12. L. Pastor-Pérez, F. Baibars, E. Le Sache, H. Arellano-García, S. Gu, T.R. Reina. "CO<sub>2</sub> valorisation via Reverse Water-Gas Shift reaction using advanced Cs doped Fe-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts". *Journal of CO<sub>2</sub> utilization* 21 (2017) 423-428; <https://doi.org/10.1016/j.jcou.2017.08.009>
13. L. Pastor Perez, M. Saha, E. Le Saché, T.R. Reina "Improving Fe/Al<sub>2</sub>O<sub>3</sub> Catalysts for the Reverse Water-Gas Shift Reaction: On the Effect of Cs as Activity/Selectivity Promoter". *Catalysts* 2018, 8, 608-622; <https://doi.org/10.3390/catal8120608>
14. Q. Zhang, L. Pastor-Pérez, W. Jin, S. Gu, T.R. Reina. "Understanding the promoter effect of Cu and Cs over highly effective β-Mo<sub>2</sub>C catalysts for the reverse water-gas shift reaction". *Applied Catalysis B: Environmental* Volume 244, 2019, 889–898. <https://doi.org/10.1016/j.apcatb.2018.12.023>

15. M.Abou Hamdan, A.Nassereddine, R.Checa, M.Jahjah, C.Pinel, L.Piccolo, N.Perret. "Supported Molybdenum Carbide and Nitride Catalysts for Carbon Dioxide Hydrogenation". *Front. Chem.*, Volume 09, 2020, 452-464. <https://doi.org/10.3389/fchem.2020.00452>
16. S.Posada-Pérez, P.J Ramirez, J. Evans, F. Viñes, P. Liu, F. Illas, and J.A. Rodriguez. "Highly Active Au/#-MoC and Cu/#-MoC Catalysts for the Conversion of CO<sub>2</sub>: The Metal/C Ratio as a Key Factor Defining Activity, Selectivity, and Stability". *J. Am. Chem. Soc.*, Volume 138, 2016, 8269-8278 <https://doi.org/10.1021/jacs.6b04529>.
17. J.L. Dubois, K. Sayama, H. Arakawa. "CO<sub>2</sub> Hydrogenation over Carbide Catalysts". *Chem. Lett.* Volume 21, 1992, 5-8. <https://doi.org/10.1246/cl.1992.5>
18. A.B. Vidal, L.Feria, J. Evans, Y.Takahashi, P. Liu, K. Nakamura, F. Illas, and J.A. Rodriguez. "CO<sub>2</sub> Activation and Methanol Synthesis on Novel Au/TiC and Cu/TiC Catalysts" *J. Phys. Chem. Lett.* Volume 3, 2012, 2275-2280. <https://doi.org/10.1021/jz300989e>
19. W. Xu, P.J. Ramirez, D. Stacchiola, J.A. Rodriguez. "Synthesis of  $\alpha$ -MoC<sub>1-x</sub> and  $\beta$ -MoC<sub>y</sub> Catalysts for CO<sub>2</sub> Hydrogenation by Thermal Carburization of Mo-oxide in Hydrocarbon and Hydrogen Mixtures". *Catal. Lett.* Volume 144, 2014, 1-7. <https://doi.org/10.1007/s10562-014-1278-5>
20. H. Tominaga and M. Nagai. "Density functional study of carbon dioxide hydrogenation on molybdenum carbide and metal". *Applied Catalysis A: General*, Volume 282, 2005, 5-13. <https://doi.org/10.1016/j.apcata.2004.09.041>
21. S.Posada-Pérez, Francesc Viñes, Pedro J. Ramirez Alba B. Vidal, J.A. Rodriguez and Francesc Illas. "The bending machine: CO<sub>2</sub> activation and hydrogenation on  $\delta$ -MoC(001) and  $\beta$ -Mo<sub>2</sub>C(001) surfaces. *Physical Chemistry Chemical Physics*, Volumen 16, 2014, 14912-14921, <https://doi.org/10/c4cp01943a>
22. J.A. Schaidle, N.M. Schweitzer, O.T. Ajenifujah, L.T. Thompson "On the preparation of molybdenum carbide-supported metal catalysts". *Journal of Catalysis*, Volume 289, 2012, 210-217. <https://doi.org/10.1016/j.jcat.2012.02.012>
23. Brian M. Wyvratt, Jason R. Gaudet, Levi T. Thompson. "Effects of passivation on synthesis, structure and composition of molybdenum carbide supported platinum water-gas shift catalysts". *Journal of Catalysis* Volume, 330, 2015, 280-287. <https://doi.org/10.1016/j.jcat.2015.07.023>
24. V.Ve. Rozanov, O.V. Krylov. "Hydrogen spillover in heterogeneous catalysis" *Russ. Chem. Rev.* Volume 66, 1997, 107-119.
25. S. Srinivas, P.K. Rao. "Direct Observation of Hydrogen Spillover on Carbon-Supported Platinum and Its Influence on the Hydrogenation of Benzene" *J. Catalysis*, Volume 148, 1994, 470-477. <https://doi.org/10.1006/jcat.1994.1233>
26. J. R.Morse, M.Juneau, J.W.Baldwin M.D.Porosoff, H.D.Willauer. "Alkali promoted tungsten carbide as a selective catalyst for the reverse water gas shift reaction". *Journal of CO<sub>2</sub> Utilization*, Volume 35, 2020, 38-46. <https://doi.org/10.1016/j.jcou.2019.08.024>
27. X.Yang et al. "Promotion effects of potassium on the activity and selectivity of Pt/zeolite catalysts for reverse water gas shift reaction". *Applied Catalysis B: Environmental*, Volume 216, 2017, 95-105. <https://doi.org/10.1016/j.apcatb.2017.05.067>
28. Behrens, M., Studt, F., Kasatkina, I., Kühn, S., Hävecker, M., Abild-pedersen, F., Zander, S., Girgsdies, F., Kurr, P., Kniep, B., Tovar, M., Fischer, R. W., Nørskov, J. K., & Schlögl, R. (2012). *Industrial Catalysts*. 759(May), 893-898. <https://doi.org/10.1126/science.1219831>
29. Abou Hamdan, M., Nassereddine, A., Checa, R., Jahjah, M., Pinel, C., Piccolo, L., & Perret, N. (2020). Supported Molybdenum Carbide and Nitride Catalysts for Carbon Dioxide Hydrogenation. *Frontiers in Chemistry*, 8(June), 1-12. <https://doi.org/10.3389/fchem.2020.00452>
30. García Blanco, A. A., Furlong, O. J., Stacchiola, D. J., Sapag, K., & Nazzarro, M. S. (2019). Porous Mo<sub>x</sub>C<sub>y</sub>/SiO<sub>2</sub> Material for CO<sub>2</sub> Hydrogenation. *Topics in Catalysis*, 62(12-16), 1026-1034. <https://doi.org/10.1007/s11244-019-01195-w>
31. Dasireddy, V. D. B. C., Štefančíč, N. S., & Likozar, B. (2018). Correlation between synthesis pH, structure and Cu/MgO/Al<sub>2</sub>O<sub>3</sub> heterogeneous catalyst activity and selectivity in CO<sub>2</sub> hydrogenation to methanol *Journal of CO<sub>2</sub> Utilization*, 28(September), 189-199. <https://doi.org/10.1016/j.jcou.2018.09.002>
32. Sun, J. T., Metcalfe, I. S., & Sahibzada, M. (1999). Deactivation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst by sintering. *Industrial and Engineering Chemistry Research*, 38(10), 3868-3872. <https://doi.org/10.1021/ie990078s>

33. Marcos, F. C. F., Lin, L., Betancourt, L. E., Senanayake, S. D., Rodriguez, J. A., Assaf, J. M., Giudici, R., & Assaf, E. M. (2020). Insights into the methanol synthesis mechanism via CO<sub>2</sub> hydrogenation over Cu-ZnO-ZrO<sub>2</sub> catalysts: Effects of surfactant/Cu-Zn-Zr molar ratio. *Journal of CO<sub>2</sub> Utilization*, 41(May), 101215. <https://doi.org/10.1016/j.jcou.2020.101215>
34. Mureddu, M., Ferrara, F., & Pettinau, A. (2019). Applied Catalysis B: Environmental Highly efficient CuO / ZnO / ZrO<sub>2</sub> @ SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO<sub>2</sub>. 258(July). <https://doi.org/10.1016/j.apcatb.2019.117941>
35. X. Zhang, X. Zhu, L. Lin, S. Yao, M. Zhang, X. Liu, X. Wang, Y.W. Li, C. Shi, D. Ma, Highly dispersed copper over  $\beta$ -Mo<sub>2</sub>C as an efficient and stable catalyst for the reverse water gas shift (RWGS) reaction, *ACS Catal* Volume 7, 2017, 912–918. <https://doi.org/10.1021/acscatal.6b02991>