Effect of Cu and Cs in the $\beta$-Mo$_2$C System for CO$_2$ Hydrogenation to Methanol

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Abstract: Mitigation of anthropogenic CO$_2$ 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$_2$ conversion, Cu supported molybdenum carbide is receiving increasing attention. Hence, in the present communication, we show the activity, selectivity and stability of fresh-prepared $\beta$-Mo$_2$C catalysts and compare the results with those of Cu/Mo$_2$C, Cs/Mo$_2$C and Cu/Cs/Mo$_2$C in CO$_2$ 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 Mo$_0$ phase, which for the catalysts Cs/Mo$_2$C 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 CO$_2$ transformations has increased significantly due to the need to diminish its atmospheric emissions. The possibility of using CO$_2$ as a raw material is a convenient way from an economic and industrial point of view, therefore conversion to fuels such as methane, or syngas, which could be later used in the Fisher–Tropsch process for the synthesis of fuels or other chemicals, have received renewed attention. Among them, CO$_2$ 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$_2$. 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 CO$_2$ 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 that 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 Cu₉O/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.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ \text{ 298 K} = +41 \text{ kJ mol}^{-1} \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H^\circ \text{ 298 K} = -165 \text{ kJ mol}^{-1} \\
\text{CO}_2 + 3\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ \text{ 298 K} = -50 \text{ kJ mol}^{-1}
\end{align*}
\]

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 CH₄, with minor contributions of ethanol, which was below 0.2% except for the catalyst Cs/Mo₂C that was around 2% and is included in Figure 1. The selectivity of the main secondary products, i.e., CH₄ and CO, over β-Mo₂C was quite different with values of 30% and 5%, respectively. However, the selectivity to those products obtained for each catalyst was more similar for Cu/Mo₂C, Cs/Mo₂C and Cu/Cs/Mo₂C, for which the values differ between 3%–5% when comparing CO and CH₄ selectivity of every catalyst.

![Figure 1](image_url)

**Figure 1.** Conversion and selectivity to CH₃OH, CO, CH₄, and C₂H₅OH. Reaction conditions: T = 150 °C, P = 20 bar, CO₂:H₂ (1:3), GHSV 7600 mL/(h⁻¹ g).

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].

The selectivity profiles obtained for β-Mo₂C 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/Mo₂C 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 Mo₂C stoichiometry. In addition, the mapping of the Cs-doped sample, in Figure 2A, confirms the interaction between Cu, Cs and Mo₂C.
Additionally, the positive effect of copper can also be related to its ability to activate hydrogen, which eventually reacts with CO$_2$ 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$_2$ molecule [8]. However, the opposite tendency was indeed observed, and both conversion and selectivity to methanol are diminished, which for the catalyst Cs/Mo$_2$C are even lower than the values achieved with the bare β-Mo$_2$C.

It has been suggested that different crystal phases or Mo/C ratios can influence the selectivity of CO$_2$ 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 characteristics peaks of β-Mo$_2$C 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 Mo$^0$ is more relevant on the sample Cs/Mo$_2$C.
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\(_2\) HO\(_2\)C-Mo species are formed, which do not favor the scission of the C-O bond [20]. In contrast, dissociation of CO\(_2\) over \(\beta\)-Mo\(_2\)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\(_3\)OH. Furthermore, since the adsorption and activation of CO\(_2\) molecules can occur on both Cu and Mo\(_2\)C surfaces, the negative effect of the Mo\(^0\) phase was not so relevant in the catalytic performance of the Cu/Cs/Mo\(_2\)C as it is on the copper free sample, Cs/Mo\(_2\)C [21].

The diffractograms of the spent catalyst, as shown in Figure 3b, showed that Cu/Mo\(_2\)C preserved the \(\beta\)-Mo\(_2\)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\(_2\)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, 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/CsMo\(_2\)C and Cs/Mo\(_2\)C display diffractions at 2\(\theta\) of 26.0\(^\circ\), 37.1\(^\circ\) and 53.3\(^\circ\), which correspond to the MoO\(_2\) crystal phase (JCPDS 32-671). Furthermore, the diffractions due to the Mo\(_2\)C phase mostly disappear and just a broad hump with maximum at 2\(\theta\) of 39.4\(^\circ\) can be envisaged on the catalyst Cs/Mo\(_2\)C. This broad peak probably includes just the contributions of Mo\(_2\)C and MoO\(_x\), since no diffraction at 2\(\theta\) of 58\(^\circ\) corresponding to Mo\(^0\) is observed. On the contrary, the spent catalyst Cu/Cs/Mo\(_2\)C, despite having mostly lost the typical diffractions of Mo\(_2\)C, still displayed the diffractions ascribed to metallic Mo.

The conversion and selectivity profiles can be partially explained by the XRD patterns. The catalyst \(\beta\)-Mo\(_2\)C, despite displaying lower conversion and selectivity than the catalyst Cu/Mo\(_2\)C, showed a more stable catalytic performance, in agreement with the structure preservation observed by XRD. In addition, it can be observed that Cu/Mo\(_2\)C, Cs/Mo\(_2\)C and Cu/Cs/Mo\(_2\)C catalysts are activated at the beginning of the reaction as the increase in conversion indicates. However, while for Cu/Mo\(_2\)C conversion was then stable after the first 4 h, this is not true for Cu/Cs/Mo\(_2\)C and Cs/Mo\(_2\)C for which an apparent deactivation occurred, this effect being more pronounced for the Cs/Mo\(_2\)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 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\(_x\)C\(_y\), and/or to reduce Mo oxide layers [24,25]. Then, for Cu/Cs/Mo\(_2\)C and Cs/Mo\(_2\)C, 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\(_2\)C.
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/Mo_xC and Cs/Mo_xC 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 Mt year\(^{-1}\) [28]. Therefore, Cu/ZnO/Al\(_2\)O\(_3\) series still attract numerous attention [29]. As shown in Table 1, the CO\(_2\) conversion and methanol selectivity towards Cu/ZnO/Al\(_2\)O\(_3\) highly depend on the temperatures. The CO\(_2\) conversion and CH\(_3\)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 the methanol synthesis field, such as Cu/Mg/Al [30], Cu/ZnO/ZrO\(_2\) [31,32]. For comparison’s sake, the performances of other Mo\(_x\)C related catalysts have also been listed in Table 1 [15,33]. 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 [31].

### Table 1. Performance of catalysts towards methanol synthesis.

| Catalysts          | Reaction Condition | CO\(_2\) Conversion (%) | Methanol Selectivity (%) | Ref      |
|--------------------|--------------------|--------------------------|--------------------------|----------|
| \(\beta\)-Mo\(_x\)C| P (bar) T (°C)     | H\(_2\)CO\(_2\) GHSV     |                          |          |
| Cu/Mo\(_x\)C       | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 3.25% 5% 3% 4%           |          |
| Cu/Mo\(_x\)C       | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 60% 70% 50% 55%          |          |
| Cu/Cs/Mo\(_x\)C    | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 3.25% 5% 3% 4%           |          |
| Cu/Cs/Mo\(_x\)C    | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 60% 70% 50% 55%          |          |
| Mo\(_x\)C          | 20 bar 250 °C      | 5/l 75 mL min\(^{-1}\)g\(^{-1}\) | 2.5% 2.2% 1.7% 1.4%      | [15]     |
| Mo\(_x\)C          | 20 bar 250 °C      | 5/l 75 mL min\(^{-1}\)g\(^{-1}\) | 3% 11% 4% 5%             |          |
| Cu/Mg/Al           | 20 bar 200 °C      | 2.8/l 2000 h\(^{-1}\)     | 3% 30% 12% 1%            | [30]     |
| Cu/ZnO/Al\(_2\)O\(_3\)| 20 bar 200 °C | 3/l 2000 h\(^{-1}\)     | 5.19% 13.4% 13% 67%    | [29]     |
| Cu/ZnO/Al\(_2\)O\(_3\)| 20 bar 200 °C | 3/l 2000 h\(^{-1}\)     | 5.19% 13.4% 13% 67%    | [29]     |
| Cu/ZnO/Al\(_2\)O\(_3\)| 20 bar 200 °C | 3/l 2000 h\(^{-1}\)     | 5.19% 13.4% 13% 67%    | [29]     |
| Cu/Mo\(_x\)C       | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 3.25% 5% 3% 4%           |          |
| Cu/Mo\(_x\)C       | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 60% 70% 50% 55%          |          |
| Cu/Cs/Mo\(_x\)C    | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 3.25% 5% 3% 4%           |          |
| Cu/Cs/Mo\(_x\)C    | 20 bar 150 °C      | 3/l 120 mL min\(^{-1}\)g\(^{-1}\) | 60% 70% 50% 55%          |          |

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 \(\beta\)-Mo\(_x\)C catalyst was obtained through TPC procedure using \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\) 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:

\[ X_{CO_2} = \frac{\sum_{i} n_i \times moli}{\sum_{i} n_i \times mol_i + molCO_2 - un} \times 100 \]  

(4)

\[ S_i = \frac{n_i \times mol_i}{\sum_{i} n_i \times mol_i} \times 100 \]  

(5)

\( n_i \): 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 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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References
1. Galadima, A.; Muraza, O. Catalytic thermal conversion of CO₂ into fuels: Perspective and challenge. Renew. Sustain. Energy Rev. 2019, 115, 109333–109353. [CrossRef]
2. Scotti, N.; Bossola, F.; Zaccheria, F.; Ravasio, N. Copper–Zirconia Catalysts: Powerful Multifunctional Catalytic Tools to Approach Sustainable Processes. Catalysts 2020, 10, 168. [CrossRef]
3. Din, I.U.; Shaharun, M.S.; Alotaibi, M.A.; Alharthi, A.I.; Naeem, A. Recent developments on heterogeneous catalytic CO₂ reduction to methanol. J. CO₂ Util. 2019, 34, 20–33. [CrossRef]
4. Chan-Thaw, C.E.; Villa, A. Metal Carbides for Biomass Valorization. Appl. Sci. 2018, 8, 259. [CrossRef]
5. Hwu, H.H.; Chen, J.G. Surface Chemistry of Transition Metal Carbides. Chem. Rev. 2005, 105, 185–212. [CrossRef]
6. Chen, Y.; Choi, S.; Thompson, L.T. Low temperature CO₂ hydrogenation to alcohols and hydrocarbons over Mo₂C supported metal catalysts. J. Catal. 2016, 343, 147–156. [CrossRef]
7. Pérez, S.P.; Ramirez, P.J.; Gutierrez, R.A.; Rodriguez, J.A. The Conversion of CO2 to Methanol on orthorhombic β-Mo2C and Cu/β-Mo2C Catalysts: Mechanism for Admetal Induced Change in the Selectivity and Activity. *Catal. Sci. Technol.* 2016, 6, 6766–6777. [CrossRef]

8. Nie, X.; Li, W.; Jiang, X.; Guo, X.; Son, C. Recent advances in catalytic CO2 hydrogenation to alcohols and hydrocarbons. In *Advances in Catalysis*, 1st ed.; Song, C., Ed.; Elsevier: Philadelphia, PA, USA, 2019; Volume 65, pp. 121–231.

9. Porosoff, M.D.; Baldwin, J.W.; Peng, X.; Mpourmpakis, G.; Willauer, H.D. Potassium-Promoted Molybdenum Carbide as a Highly Active and Selective Catalyst for CO2 Conversion to CO. *ChemSusChem* 2017, 10, 2408–2415. [CrossRef]

10. Dongil, A.B. Recent progress on transition metal nitrides nanoparticles as heterogeneous catalysts. *Nanomaterials* 2019, 9, 1111. [CrossRef]

11. Liao, W.; Liu, P. Methanol Synthesis from CO2 Hydrogenation over a Potassium-Promoted CuxO/Cu(111) (x ≤ 2) Model Surface: Rationalizing the Potential of Potassium in Catalysis. *ACS Catal.* 2020, 20, [CrossRef]

12. Pastor-Pérez, L.; Baibars, F.; Le Saché, E.; Arellano-García, H.; Gu, S.; Reina, T.R. CO2 valorisation via Reverse Water-Gas Shift reaction using advanced Cs doped Fe-Cu/Al2O3 catalysts. *J. CO2 Util.* 2017, 21, 423–428. [CrossRef]

13. Perez, L.P.; Saha, M.; Le Saché, E.; Reina, T.R. Improving Fe/Al2O3 Catalysts for the Reverse Water-Gas Shift Reaction: On the Effect of Cs as Activity/Selectivity Promoter. *Catalysts* 2018, 8, 608. [CrossRef]

14. Zhang, Q.; Pastor-Pérez, L.; Jin, W.; Gu, S.; Reina, T.R. Understanding the promoter effect of Cu and Cs over highly effective β-Mo2C catalysts for the reverse water-gas shift reaction. *Appl. Catal. B Environ.* 2019, 244, 889–898. [CrossRef]

15. Hamdan, M.A.; Nassereddine, A.; Checa, R.; Jahjah, M.; Pinel, C.; Piccolo, L.; Perret, N. Supported Molybdenum Carbide and Nitride Catalysts for Carbon Dioxide Hydrogenation. *Front. Chem.* 2020, 9, 452–464. [CrossRef]

16. Posada-Pérez, S.; Ramirez, P.J.; Evans, J.; Viñes, F.; Liu, P.; Illas, F.; Rodriguez, J.A. Highly Active Au/#-MoC and Cu/#-MoC Catalysts for the Conversion of CO2: The Metal/C Ratio as a Key Factor Defining Activity, Selectivity, and Stability. *J. Am. Chem. Soc.* 2016, 138, 8269–8278. [CrossRef] [PubMed]

17. Dubois, J.L.; Sayama, K.; Arakawa, H. CO2 Hydrogenation over Carbide Catalysts. *Chem. Lett.* 1992, 21, 5–8. [CrossRef]

18. Vidal, A.B.; Feria, L.; Evans, J.; Takahashi, Y.; Liu, P.; Nakamura, K.; Illas, F.; Rodriguez, J.A. CO2 Activation and Methanol Synthesis on Novel Au/TiC and Cu/TiC Catalysts. *J. Phys. Chem. Lett.* 2012, 3, 2275–2280. [CrossRef]

19. Xu, W.; Ramirez, P.J.; Stacchiola, D.; Rodriguez, J.A. Synthesis of α-MoC1-x and β-MoC2 Catalysts for CO2 Hydrogenation by Thermal Carburation of Mo-oxide in Hydrocarbon and Hydrogen Mixtures. *Catal. Lett.* 2014, 144, 1–7. [CrossRef]

20. Tominaga, H.; Nagai, M. Density functional study of carbon dioxide hydrogenation on molybdenum carbide and metal. *Appl. Catal. A Gen.* 2005, 282, 5–13. [CrossRef]

21. Posada-Pérez, S.; Viñes, F.; Ramirez, P.J.; Vidal, A.B.; Rodriguez, J.A.; Illas, F. The bending machine: CO2 activation and hydrogenation on δ-MoC(001) and β-Mo2C(001) surfaces. *Phys. Chem. Chem. Phys.* 2014, 16, 14912–14921. [CrossRef]

22. Schaidle, J.A.; Schweitzer, N.M.; Ajenifujah, O.T.; Thompson, L.T. On the preparation of molybdenum carbide-supported metal catalysts. *J. Catal.* 2012, 289, 210–217. [CrossRef]

23. Wyvratt, B.M.; Gaudet, J.R.; Thompson, L.T. Effects of passivation on synthesis, structure and composition of molybdenum carbide supported platinum water-gas shift catalysts. *J. Catal.* 2015, 330, 280–287. [CrossRef]

24. Rozanov, V.V.; Krylov, O.V. Hydrogen spillover in heterogeneous catalysis. *Russ. Chem. Rev.* 1997, 66, 107–119. [CrossRef]

25. Srinivas, S.; Rao, P.K. Direct Observation of Hydrogen Spillover on Carbon-Supported Platinum and Its Influence on the Hydrogenation of Benzene. *J. Catal.* 1994, 148, 470–477. [CrossRef]

26. Morse, J.R.; Juneau, M.; Baldwin, J.W.; Porosoff, M.D.; Willauer, H.D. Alkali promoted tungsten carbide as a selective catalyst for the reverse water gas shift reaction. *J. CO2 Util.* 2020, 35, 38–46. [CrossRef]

27. Yang, X.; Su, X.; Chen, X.; Duan, H.; Liang, B.; Liu, Q.; Liu, X.; Ren, Y.; Huang, Y.; Zhang, T. Promotion effects of potassium on the activity and selectivity of Pt/zeolite catalysts for reverse water gas shift reaction. *Appl. Catal. B Environ.* 2017, 216, 95–105. [CrossRef]
28. Behrens, M.; Studt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-pedersen, F.; Zander, S.; Grgies, F.; Kurr, P.; Kniep, B.; et al. The Active Site of Methanol Synthesis over Cu/ZnO/Al2O3 Industrial Catalysts. *Science* 2012, 759, 893–898. [CrossRef]

29. Sun, J.T.; Metcalfe, I.S.; Sahibzada, M. Deactivation of Cu/ZnO/Al2O3 methanol synthesis catalyst by sintering. *Ind. Eng. Chem. Res.* 1999, 38, 3868–3872. [CrossRef]

30. Dasireddy, V.D.B.C.; Štefančič, N.S.; Likozar, B. Correlation between synthesis pH, structure and Cu/MgO/Al2O3 heterogeneous catalyst activity and selectivity in CO2 hydrogenation to methanol. *J. CO2 Util.* 2018, 28, 189–199. [CrossRef]

31. Marcos, F.C.F.; Lin, L.; Betancourt, L.E.; Senanayake, S.D.; Rodriguez, J.A.; Assaf, J.M.; Giudici, R.; Assaf, E.M. Insights into the methanol synthesis mechanism via CO2 hydrogenation over Cu-ZnO-ZrO2 catalysts: Effects of surfactant/Cu-Zn-Zr molar ratio. *J. CO2 Util.* 2020, 41, 101215. [CrossRef]

32. Blanco, A.A.G.; Furlong, O.J.; Stacchiola, D.J.; Sapag, K.; Nazzarro, M.S. Porous MoxCy/SiO2 Material for CO2 Hydrogenation. *Top. Catal.* 2019, 62, 1026–1034. [CrossRef]

33. Mureddu, M.; Ferrara, F.; Pettinau, A. Highly efficient CuO/ZnO/ZrO2 @ SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO2. *Appl. Catal. B Environ.* 2019, 258. [CrossRef]

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