Article

Cu-Mo$_2$C/MCM-41: An Efficient Catalyst for the Selective Synthesis of Methanol from CO$_2$

Xiaoran Liu, Yingquan Song, Wenhao Geng, Henan Li, Linfei Xiao and Wei Wu *

International Joint Research Center of Catalytic Technology, Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province; School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, China; liuxiaoranhljuhg@tom.com (X.L.); songyingquanhljuhg@tom.com (Y.S.); gengwenhaohljuhg@tom.com (W.G.); lihenanhljuhg@tom.com (H.L.); xiaolf@hlju.edu.cn (L.X.)

* Correspondence: wuwei@hlju.edu.cn; Tel./Fax: +86-451-8660-9227

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Abstract: Supported molybdenum carbide (γMo$_2$C/M41) and Cu-promoted molybdenum carbide, using a mechanical mixing and co-impregnation method (xCu$_y$Mo$_2$C/M41-M and xCu$_y$Mo$_2$C/M41-I) on a mesoporous molecular sieve MCM-41, were prepared by temperature-programmed carburization method in a CO/H$_2$ atmosphere at 1073 K, and their catalytic performances were tested for CO$_2$ hydrogenation to form methanol. Both catalysts, which were promoted by Cu, exhibited higher catalytic activity. In comparison to 20Cu20Mo$_2$C/M41-M, the 20Cu20Mo$_2$C/M41-I catalyst exhibited a stronger synergistic effect between Cu and Mo$_2$C on the catalyst surface, which resulted in a higher selectivity for methanol in the CO$_2$ hydrogenation reaction. Under the optimal reaction conditions, the highest selectivity (63%) for methanol was obtained at a CO$_2$ conversion of 8.8% over the 20Cu20Mo$_2$C/M41-I catalyst.

Keywords: CO$_2$ hydrogenation; Cu-promoted Mo$_2$C; supported catalyst; methanol synthesis

1. Introduction

Due to increasing CO$_2$ emissions every year, human life and the environment have been greatly affected by global warming and climate changes [1,2]. The chemical utilization of CO$_2$, which is the cheapest and most abundant C1 resource, has become an important global challenge [3–5]. Catalytic hydrogenation of CO$_2$ can produce various types of valuable chemicals and has been recently identified as one of the most promising processes for the utilization of CO$_2$ [6]. Among these processes, the synthesis of methanol from CO$_2$ is important because methanol can be used as a starting feedstock for chemical industries as well as an alternative to fossil fuels [7–10].

Over the past decades, significant efforts have been devoted to developing effective catalysts for CO$_2$ hydrogenation to form methanol. These studies primarily focused on modifying and improving the Cu/Zn-based catalyst by introducing suitable promoters or supports (e.g., Au [11], TiO$_2$ [12], Ga$_2$O$_3$ [13,14], MgO [15], and CeO$_2$ [16]). In recent years, researchers found that the addition of an appropriate amount of ZrO$_2$ could enhance the copper dispersion and the surface basicity [17,18], and a high selectivity for methanol was obtained over the CuO/ZrO/ZrO$_2$ catalyst, while the conversion of CO$_2$ was limited [19]. In addition, some studies reported that the noble metal Pd could be used as an active component in catalysts for CO$_2$ hydrogenation to produce higher catalytic activity and methanol selectivity [20–22]. However, because both Cu/Zn-based and noble metal Pd catalysts have poor resistance to sulfur poisoning, their requirements for the purity of the feed gas are very high. Moreover, the wide industrial application of noble metal Pd catalyst is also limited due to its high cost.
Due to their unique tolerance of sulfur and potential alternatives to noble metals, transition metal carbides have attracted considerable attention in catalytic applications since the 1970s [23,24]. Molybdenum carbide exhibits catalytic properties similar to those of Pt or Pd catalysts, and this catalyst has been applied in various chemical reactions, such as the isomerization of n-heptane [25], steam reforming of methanol [26], dry reforming of methane [27], CO hydrogenation [28–30], and CO\textsubscript{2} hydrogenation [31–33]. Recently, researchers have demonstrated that a higher catalytic activity was obtained when another metal, which acted as a promoter, was introduced into the transition metal carbides, because the metal promoter results in the preferential formation of admetal-C bonds with significant electronic perturbations in the admetal [34]. Rodriguez et al. systematically studied the conversion of CO\textsubscript{2} into methanol catalyzed by α-MoC\textsubscript{1−x}, β-Mo\textsubscript{2}C, Cu/β-Mo\textsubscript{2}C, Ni/β-Mo\textsubscript{2}C, and Co/β-Mo\textsubscript{2}C surfaces and found that Cu/β-Mo\textsubscript{2}C exhibited preferable catalytic activity for the selective synthesis of methanol [31,35]. Recently, they proposed a new route for methanol production over Cu/β-Mo\textsubscript{2}C catalysts by means of a combined experimental and theoretical study [36]. In this case, the Cu particles were effective sites for hydrogen dissociation and enhanced the hydrogen surface coverage [37]. However, the effects of the loading amount of Mo\textsubscript{2}C and Cu, as well as the degree of interaction between Cu and Mo\textsubscript{2}C on the catalytic performance for CO\textsubscript{2} hydrogenation, have not been previously investigated.

Usually, transition metal carbides are prepared using alkanes, alkene, and alkyne as carbon sources, but excess polymeric carbon from the pyrolysis of the carbonaceous gases at relatively low temperatures can deposit on the surface of the resultant carbide. To solve this problem, one strategy was to introduce H\textsubscript{2} into carburizing gas, which made it possible for deposited carbon species to be converted into gas hydrocarbon by hydrogenation [38,39]. In this study, a series of supported yMo\textsubscript{2}C/M41 and Cu-promoted yMo\textsubscript{2}C/M41 catalysts were prepared using the mixture of CO and H\textsubscript{2} as a carburizing gas, which can be derived from coal and heavy oil via steam reforming and applied to CO\textsubscript{2} hydrogenation to methanol. In particular, the effects of the degree of interaction between Cu and Mo\textsubscript{2}C on the surface of the catalysts, which were prepared using different methods, on the catalytic performance were investigated. In addition, the relationship between the catalytic performance and the surface property was studied.  

2. Results and Discussion

2.1. Catalyst Characterization

2.1.1. X-Ray Diffraction (XRD)

The XRD patterns of the yMo\textsubscript{2}C/M41 samples with different Mo\textsubscript{2}C loadings are shown in Figure 1. Several peaks that were located at 2θ = 34.4°, 38.0°, 39.4°, 52.1°, 61.5°, 69.5°, and 74.6° were assigned to the β-Mo\textsubscript{2}C phase with a hexagonal closest packed (hcp) crystal structure, and the peak located at 2θ = 15°−30° was attributed to the MCM-41 molecular sieve phase. However, for the 10Mo\textsubscript{2}C/M41 sample, the characteristic diffraction peaks corresponding to β-Mo\textsubscript{2}C were not observed, which may be due to the high dispersion of the Mo\textsubscript{2}C particles on the support. In addition, the intensity of the diffraction peaks corresponding to β-Mo\textsubscript{2}C became more intense as the Mo\textsubscript{2}C loading increased, which indicated that the crystallite size or crystallinity of β-Mo\textsubscript{2}C increased.
To improve the catalytic performance of 20Mo2C/M41, a series of xCu20Mo2C/M41-I catalysts with different Cu loadings (12%, 20% and 28%) were prepared using the co-impregnation method, and the XRD patterns are shown in Figure 2. Except for several characteristic diffraction peaks corresponding to β-Mo2C phase, the peaks located at 2θ = 43.4°, 50.5°, and 74.2° were ascribed to Cu°. In addition, the peak located at 2θ = 36.7° corresponded to α-MoC1–x. These results indicated that the Cu promoter had a substantial effect on the crystal phase of molybdenum carbide [26,40]. As the Cu loading increased, the intensity of the diffraction peak corresponding to the Cu° phase increased (Figure 2), which indicated that the crystallite size of Cu increased. This result is in agreement with the average crystallite size of Cu° in xCu20Mo2C/M41-I (Table 1).

![X-ray diffraction (XRD) patterns](image1)

**Figure 1.** X-ray diffraction (XRD) patterns of the yMo2C/M41 samples.

![X-ray diffraction (XRD) patterns](image2)

**Figure 2.** XRD patterns of the xCu20Mo2C/M41-I samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average Cu Crystallite Size (nm) ¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Cu20Mo2C/M41-I</td>
<td>10.2</td>
</tr>
<tr>
<td>20Cu20Mo2C/M41-I</td>
<td>24.4</td>
</tr>
<tr>
<td>28Cu20Mo2C/M41-I</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Table 1. The average Cu crystallite size of the xCu20Mo2C/M41-I samples.

¹ calculated by the Scherrer formula.

2.1.2. N2 Adsorption–Desorption

The N2 adsorption–desorption isotherms measured at 77.36 K allowed the textural properties of samples yMo2C/M41 to be assessed, and the results are shown in Figure 3 and Table 2. All the samples
exhibited type IV isotherms as defined by the International Union of Pure and Applied Chemistry (IUPAC) classification with type H1 hysteresis loop at P/P₀ = 0.4–1.0. These results indicated that the mesoporous structure of MCM-41 was not destroyed when the catalysts were carbonized. However, the Brunauer-Emmett-Teller (BET) surface area and pore volume of the yMo₂C/M₄₁ samples decreased as the Mo₂C loading increased (Table 2), which suggests that a portion of the pores in MCM-41 was blocked by Mo₂C.

![Figure 3. N₂ adsorption and desorption isotherms of the yMo₂C/M₄₁ samples.](image)

**Table 2.** N₂ adsorption data of the yMo₂C/M₄₁ samples. BET: Brunauer–Emmett–Teller.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₄₁</td>
<td>1083</td>
<td>0.945</td>
</tr>
<tr>
<td>10Mo₂C/M₄₁</td>
<td>413</td>
<td>0.280</td>
</tr>
<tr>
<td>20Mo₂C/M₄₁</td>
<td>282</td>
<td>0.235</td>
</tr>
<tr>
<td>30Mo₂C/M₄₁</td>
<td>248</td>
<td>0.203</td>
</tr>
<tr>
<td>40Mo₂C/M₄₁</td>
<td>221</td>
<td>0.156</td>
</tr>
</tbody>
</table>

2.1.3. X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) analysis was carried out to elucidate the surface properties of the catalysts. The Cu and Mo surface contents for xCu20Mo₂C/M₄₁-I are listed in Table 3. As shown in Table 3, as the Cu loading increased from 12% to 20%, the surface Cu atom content increased. When the Cu loading was 20%, the surface Cu atom content was the highest (i.e., 43.8%). However, as the Cu loading continues to 28%, the surface Cu content decreased to 35.2% because Cu atoms agglomerated, leading to the formation of larger Cu particles that reduced the Cu content exposed on the surface of the catalyst. This result is consistent with the calculated average Cu crystallite size listed in Table 1.

**Table 3.** Surface Cu and Mo atom content of the xCu20Mo₂C/M₄₁-I samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu Atom Content (mol %)</th>
<th>Mo Atom Content (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Cu20Mo₂C/M₄₁-I</td>
<td>35.7</td>
<td>64.3</td>
</tr>
<tr>
<td>20Cu20Mo₂C/M₄₁-I</td>
<td>43.8</td>
<td>56.2</td>
</tr>
<tr>
<td>28Cu20Mo₂C/M₄₁-I</td>
<td>35.2</td>
<td>64.8</td>
</tr>
</tbody>
</table>

In addition, the valence distribution of molybdenum on the catalyst surface was affected by the Cu loading. The Mo 3d XPS spectra of the 20Mo₂C/M₄₁ and xCu20Mo₂C/M₄₁-I samples are shown in Figure 4. As shown in Figure 4, the doublet peaks, which were assigned to Mo 3d₅/₂ and
Mo 3d$_{3/2}$, exhibited a splitting of ~3.13 eV, and the ratio of Mo 3d$_{5/2}$ to Mo 3d$_{3/2}$ was 3:2. The XPS results suggested the presence of four molybdenum species as follows: the Mo 3d$_{5/2}$ binding energy of 228.8–229.0 eV corresponded to Mo$^{VI}$ species involved in Mo–C bonding and the Mo 3d$_{5/2}$ binding energies of 229.6–229.8, 232.1–232.2, and 233.3–233.4 eV corresponded to Mo$^{IV}$ (MoO$_2$), Mo$^\delta$ (MoO$_x$C$_y$), and Mo$^{VI}$ (MoO$_3$), respectively, in which the $\delta$ was an intermediate oxidation state between 4 and 6 ($4 < \delta < 6$) [26,41]. By curve fitting the Mo 3d profiles, the ratio of the surface Mo$^{IV}$ and Mo$^\delta$ species to the total molybdenum species (i.e., (Mo$^{IV}$ + Mo$^\delta$)/Mo$_{total}$) was obtained and summarized in Table 4. When Cu was introduced to 20Mo$_2$C/M41 using the co-impregnation method, the (Mo$^{IV}$ + Mo$^\delta$)/Mo$_{total}$ ratio increased, and the ratio reached the highest value for the 20Cu20Mo$_2$C/M41-I sample (Table 4). This result is similar to that reported by Liu where (Mo$^{IV}$ + Mo$^\delta$)/Mo$_{total}$ increased when the Ca promoter was introduced into the Mo$_2$C system [29].

![Figure 4. X-ray photoelectron spectroscopy (XPS) spectra of 20Mo$_2$C/M41 and xCu20Mo$_2$C/M41-I.](image)

Table 4. Mo 3d$_{5/2}$ binding energies and (Mo$^{IV}$ + Mo$^\delta$)/Mo$_{total}$ ratios of 20Mo$_2$C/M41 and xCu20Mo$_2$C/M41-I.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mo 3d$_{5/2}$ (eV)</th>
<th>(Mo$^{IV}$ + Mo$^\delta$)/Mo$_{total}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo$^{IV}$</td>
<td>Mo$^\delta$</td>
</tr>
<tr>
<td>20Mo$_2$C/M41</td>
<td>228.8</td>
<td>229.8</td>
</tr>
<tr>
<td>12Cu20Mo$_2$C/M41-I</td>
<td>228.8</td>
<td>229.7</td>
</tr>
<tr>
<td>20Cu20Mo$_2$C/M41-I</td>
<td>229.0</td>
<td>229.7</td>
</tr>
<tr>
<td>28Cu20Mo$_2$C/M41-I</td>
<td>228.9</td>
<td>229.6</td>
</tr>
</tbody>
</table>

2.2. Catalytic Performance for the Hydrogenation of CO$_2$

2.2.1. Catalytic Performance of the yMo$_2$C/M41 Samples

The catalytic performances of the yMo$_2$C/M41 samples were studied for the hydrogenation of CO$_2$ at 493 K under a pressure of 3.0 MPa and GHSV of 3600 mL/(h·g), and the results are shown in
The conversion of CO₂ increased from ~6% to ~8% as the Mo₂C loading increased from 10% to 30%, which was due to a higher density of active sites on the catalyst surface. In this process, H₂ was activated by the forming C–H between the surface of Mo₂C and the adsorbed H₂ [41]; at the same time, CO₂ was activated by the forming C–C bond between the surface of Mo₂C and the adsorbed CO₂ by a net carbide→CO₂ charge transfer [33]. As the Mo₂C loading increased, a decrease in the selectivity of CH₄ was observed. However, the selectivity to CO increased. When the loading of Mo₂C was 10% and 20%, the selectivity for CH₃OH was higher, and a selectivity of 28% for CH₃OH was observed over the 20Mo₂C/M41 catalyst when the reaction was carried out for 14 h. However, the selectivity for CH₃OH decreased when the Mo₂C loading exceeded 30%, and more CO was produced. During the hydrogenation of CO₂, CO and CH₃OH were produced by two competitive pathways. The HOCO intermediate was formed firstly on the Mo₂C surface. The cleavage of one C–O bond of the HOCO intermediate results in its decomposition to CO. However, the HOCO intermediate can transform into the HCOO intermediate, which can undergo stepwise hydrogenation to CH₃OH [34,42]. Therefore, based on the effect of the Mo₂C loading amount on CO₂ conversion and CH₃OH selectivity, the optimal Mo₂C loading was 20%.

![Figure 5](image-url) Figure 5. Catalytic performance of γMo₂C/M41 in CO₂ hydrogenation. (a) CO₂ conversion; (b) CH₄ selectivity; (c) CO selectivity; (d) CH₃OH selectivity. Reaction conditions: catalyst 0.5 g, temperature 493 K, pressure 3.0 MPa (H₂:CO₂ = 3:1), GHSV 3600 mL/(h·g).

2.2.2. Catalytic Performance for the Cu-Promoted 20Mo₂C/M41 Catalyst

Due to the high capability of the Cu promoter to absorb and activate H₂ [37], which are beneficial to CO₂ hydrogenation, a series of Cu-promoted 20Mo₂C/M41 catalysts were prepared using the mechanical mixing method (M) and the co-impregnation method (l) (i.e. 20Cu20Mo₂C/M41-M and 20Cu20Mo₂C/M41-I, respectively), and their catalytic performances were evaluated for CO₂ hydrogenation to synthesize CH₃OH. As shown in Figure 6, both 20Cu/M41 and 20Mo₂C/M41 catalysts exhibited low CO₂ conversion and methanol selectivity. However, the CO₂ conversion and CH₃OH selectivity increased over the 20Cu20Mo₂C/M41-M catalyst (mechanical mixing 20Cu/M41 and 20Mo₂C/M41). When 20Cu20Mo₂C/M41-I prepared by co-impregnation method was employed...
as the catalyst, its catalytic performance further improved. Furthermore, regardless of the method used to introduce the Cu promoter to 20Mo2C/M41 catalytic system, the CO2 conversion and CH3OH selectivity increased, and the selectivity to CH4 and CO decreased. This indicated that there was a synergetic effect between Cu and Mo2C in the hydrogenation of CO2 when the Cu-promoted supported molybdenum carbide was used as a catalyst. In the hydrogenation of CO2, the adsorption and activation of hydrogen primarily occurred on Cu sites; in addition, the adsorption and activation of CO2 occurred over Mo2C sites in the Cu–Mo2C/M41 system (Scheme 1). In particular, the CO2 molecule was attached to the Mo2C surface, and a C–C bond was formed between the surface and the adsorbate by a net carbide→CO2 charge transfer. Simultaneously, some bonding interactions were generated between the O atoms of CO2 and nearby Mo atoms [33]. Then, the activated hydrogen was transported from the Cu surface to the Mo2C surface sites via spillover followed by hydrogenation of the adsorbed CO2 to form the HOCO intermediate. The HOCO intermediate decomposed to CO due to cleavage of the C–O bond. If the C–O bond of CO cracked continually, C was produced, which was hydrogenated to yield CH4. However, the HOCO intermediate was isomerized to the HCOO intermediate, which underwent stepwise hydrogenation to CH3OH [34,42]. In combination with the experimental results shown in Figure 6, the introduction of Cu in 20Cu20Mo2C/M41 increased the concentration of Mo6+ and Mo5+ cations, which may be favorable for the isomerization of HOCO to HCOO, leading to an increase in the CH3OH selectivity.

Figure 6. Catalytic performance of 20Cu20Mo2C/M41 with different introducing method of Cu promoter in CO2 hydrogenation. (a) CO2 conversion; (b) CH4 selectivity; (c) CO selectivity; (d) CH3OH selectivity. Reaction conditions: catalyst 0.5 g, temperature 493 K, pressure 3.0 MPa (H2:CO2 = 3:1), GHSV 3600 mL/(h·g).
were also studied, and the results are shown in Figure 7. When the Cu loading increased to 20%, the results were found in the literature [29].

To explain this result, the mechanism of CO2 hydrogenation over Cu–Mo2C/M41 catalysts was proposed (Scheme 1). The key step in this mechanism is the isomerization of HOCO to HCOO on the Cu surface, which is promoted by the Cu atom content exposed on the catalyst surface. This isomerization favors the hydrogenation of CO2 to CH4 and H2O. Moreover, the CH3OH selectivity significantly increased, which is consistent with previous reports [43].

These results indicate that a higher CH3OH selectivity can be achieved when the co-impregnation method was used to introduce Cu into the 20Mo2C/M41-catalytic system. Therefore, the effects of Cu loading on the catalytic performance of the xCu20Mo2C/M41-I catalysts in CO2 hydrogenation were also studied, and the results are shown in Figure 7. When the Cu loading increased to 20%, the highest content of Cu was observed on the catalyst surface (Table 3), and the loaded Cu was beneficial for the activation of H2 and had a substantial positive effect on the conversion of CO2. The highest CO2 conversion was 11.4%; however, the conversion of CO2 decreased when the Cu loading was 28% because the size of the Cu particles increased. In addition, the Cu atom content exposed on the surface of the catalyst decreased (Tables 1 and 3). When Cu was introduced to the catalyst system as a promoter, the selectivity of the catalysts for CH4 and CO decreased, and the CH3OH selectivity increased. This result may be due to the promotion of the isomerization of HOCO to HCOO when 20Mo2C/M41 was modified by Cu. The highest selectivity (63%) for methanol was obtained at a CO2 conversion of 8.8% over the 20Cu20Mo2C/M41-I catalyst because the highest amount of MoIV and Moδ species was detected on the catalyst surface, which favored the synthesis of methanol. The same results were found in the literature [29].

Figure 7. Cont.
performance over 110 h, and the results are presented in Figure 8. It can be seen that the stable catalytic reaction was carried out for 110 h, the selectivity for methanol and the conversion of CO remained stable, which exhibited an excellent stability in CO₂ hydrogenation.

2.2.3. The Stability of the 20Cu20Mo₂C/M41-I Catalyst

In order to study the stability of the 20Cu20Mo₂C/M41-I catalyst, we investigated its catalytic performance over 110 h, and the results are presented in Figure 8. It can be seen that the stable catalytic performance was given when the 20Cu20Mo₂C/M41-I catalyst was used for more than 10 h. When the reaction was carried out for 110 h, the selectivity for methanol and the conversion of CO₂ remained stable, which exhibited an excellent stability in CO₂ hydrogenation.

**Figure 7.** Catalytic performance of xCu20Mo₂C/M41-I in CO₂ hydrogenation. (a) CO₂ conversion; (b) CH₄ selectivity; (c) CO selectivity; (d) CH₃OH selectivity. Reaction conditions: catalyst 0.5 g, temperature 493 K, pressure 3.0 MPa (H₂:CO₂ = 3:1), GHSV 3600 mL/(h·g).

**Figure 8.** Catalytic performance of 20Cu20Mo₂C/M41-I in CO₂ hydrogenation. (a) CO₂ conversion; (b) CH₄ selectivity; (c) CO selectivity; (d) CH₃OH selectivity. Reaction conditions: catalyst 0.5 g, temperature 493 K, pressure 3.0 MPa (H₂:CO₂ = 3:1), GHSV 3600 mL/(h·g).
3. Experimental Section

3.1. Catalyst Preparation

The catalysts were prepared by incipient wetness co-impregnation onto MCM-41 (purchased from Nankai University Catalyst Co., Ltd. Tianjin, China) with an aqueous solution consisting of (NH4)6Mo7O24·4H2O and Cu(NO3)2·3H2O. Then, the catalysts were dried overnight at 373 K, followed by calcination at 923 K for 3 h to afford supported molybdenum oxide and copper oxide. Carburization of the catalysts was accomplished using a temperature-programmed reaction. Specifically, this step was performed in a quartz tube reactor by heating at a rate of 10 K min⁻¹ from room temperature to 573 K and then at a rate of 1 K min⁻¹ from 573 to 1073 K in 20% CO/H2 mixture, and the temperature was maintained at 1073 K for 4 h. The catalysts were subsequently cooled to room temperature in H2, followed by passivation in a stream of 1% O2/N2 mixture at room temperature for 2 h prior to exposure to air. These catalysts are referred to as xCu₂Mo₂C/M41-I, where x and y represent the mass percentages of Cu and Mo₂C, respectively, and I refers to the co-impregnation method. In addition, xCu₂Mo₂C/M41-M was prepared by mechanical mixing and grinding xCu/M41 and yMo₂C/M41, where M refers to the mechanical mixing method.

3.2. Characterization

Powder XRD patterns of the prepared samples were recorded on a Bruker D8 Advance diffractometer using Cu Kα (λ = 1.5404 Å) irradiation at 40 kV and 40 mA with a Lynx eye detector in the range of 2θ = 5°–80°. The N2 adsorption–desorption characterization of the samples was performed using an Autosorb-1-MP apparatus (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to the adsorption measurements, the catalysts were degassed under vacuum for nearly 12 h at 573 K. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The pore volumes were estimated from the desorption branch of the N2 adsorption-desorption isotherms by applying the Barrett-Joyner-Halenda (BJH) method. The XPS analyses were performed using a Surface Science Instruments spectrometer (ESCALAB 250) (Waltham, MA, USA) with focused Al Kα radiation (1486.6 eV).

3.3. Catalytic Test

The performances of the catalysts for CO2 hydrogenation were investigated under pressurized conditions with a high-pressure fixed bed reactor system. A 0.5-g portion of the catalyst was placed in the reactor along with inert quartz sands above and below the catalyst. All the catalysts were reduced in a flow of hydrogen at 673 K for 1 h prior to the reaction. When the temperature was cooled from 673 K to 493 K, the feed gas (i.e., CO2/H2/Ar (H2:CO2 volume ratio was 3:1)) flowed into the system at a pressure of 3.0 MPa and GHSV of 3600 mL/(h·g). All the products were produced in the gaseous state and analyzed using a gas chromatograph (GC). Ar, CO and CO2 were analyzed using a GC equipped with a thermal conductivity detector (TCD) and a column consisting of activated charcoal. CH4 and CH3OH were analyzed using another GC equipped with a flame ionization detector (FID). Ar was used as the internal standard for the GC/TCD analyses. It was important to note that only trace amounts of C2H6, C3H8, and CH3OCH3 were detected in the products, and their content was ignored.

4. Conclusions

In summary, the catalytic performance of yMo₂C/M41 for the hydrogenation of CO₂ to methanol can be tuned by loading the appropriate amount of Mo₂C. Among these catalysts, the 20Mo₂C/M41 catalyst exhibited excellent catalytic performance. When Cu was introduced to 20Mo₂C/M41 by the mechanical mixing method (M) and co-impregnation method (I), the catalytic performance improved to different extents. In the Cu–Mo₂C/M41 catalytic system, a synergistic effect was observed between Cu and Mo₂C on the catalyst surface. Therefore, the adsorption and activation of hydrogen primarily occurred on Cu sites, and the adsorption of CO₂ occurred over Mo₂C sites.
In addition, the introduction of Cu increased the concentration of Mo\textsuperscript{IV} and Mo\textsuperscript{δ} cations, which may be beneficial to the isomerization of HOCO to HCOO, leading to an increase in CH\textsubscript{3}OH selectivity. In comparison to 20Cu20Mo\textsubscript{2}C/M41-M, the 20Cu20Mo\textsubscript{2}C/M41-I catalyst exhibited significantly increased CH\textsubscript{3}OH selectivity because the Cu promoter was highly dispersed on the surface of the catalyst. In addition, enhanced interactions existed between Cu and Mo\textsubscript{2}C active sites. The valence distribution of molybdenum on the catalyst surface was affected by loaded Cu introduced by the co-impregnation method. When the Cu loading amount was 20%, the surface Cu atom content was the highest with the largest amount of Mo\textsuperscript{IV} and Mo\textsuperscript{δ} species, and the highest selectivity (63%) for methanol was obtained at a CO\textsubscript{2} conversion of 8.8% and excellent stability during 110 h was observed over it.

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Author Contributions: Xiaoran Liu, Yingquan Song, Wenhao Geng, and Henan Li performed the experiment. Wei Wu and Linfei Xiao analyzed and discussed the experimental results. Xiaoran Liu wrote the paper.

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

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