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Research Article

Operating Conditions and Composition Effect on the Hydrogenation of Carbon Dioxide Performed over $CuO/ZnO/Al_2O_3$ Catalysts

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Abstract

A series of catalysts constituted of mixed copper and zinc oxides supported on alumina were prepared by co-precipitation method. The cooper content was in the 10-90 wt.% range. Their catalytic behavior in the hydrogenation of carbon dioxide to methanol was investigated at high pressure (up to 75 bars). The catalysts were characterized by elemental analysis, N_2-adsorption, N_2O-chemisorptions, and X-ray diffraction (XRD). The catalysts showed a clear activity in the hydrogenation reaction that could be correlated to the surface area of the metallic copper and to the reaction pressure. The $CuO/ZnO/Al_2O_3$ catalyst with a Cu/Zn/Al weight ratio of 60/30/10, exhibits the highest carbon dioxide conversion and methanol selectivity. Finally, a mechanism pathway has been proposed on copper active sites of (Cu^0/Cu^I) oxidation state.

Keywords: carbon dioxide; hydrogenation; methanol; $CuO/ZnO/Al_2O_3$ catalysts

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1. Introduction

Methanol is an important intermediate in the petrochemical industry used in the production of a variety of products, including gasoline and alternative raw materials for the production of olefin such as ethylene and propylene [1]. The increasing demand for methanol has drawn considerable attention in enhancing its production. Currently, methanol is industrially produced starting from $CO/CO_2/H_2$ mixture over $CuO/ZnO/Al_2O_3$ catalysts operating at 50-100 bars, and 220-300 °C [2]. If the $CuO/ZnO/Al_2O_3$ catalyst exhibits high activity in the methanol synthesis from syngas, its catalytic activity in the hydrogenation of pure CO_2 results very poor [3-5]. In order to improve the catalytic performance for methanol synthesis from H_2/CO_2, it is important to synthesize and develop new catalysts with a higher activity in the carbon dioxide hydrogenation reaction. Moreover, being CO_2 one of the most common greenhouse gases, to develop new and efficient industrial routes for its valorization is extremely interesting from the economic and environmental point of view.

Therefore, numerous investigations and great efforts have been done in preparing ameliorate catalysts for the hydrogenation of carbon dioxide [6-11]. Most researchers consider that the CuO/ZnO system is responsible for the activity of the copper phase [12,13]. For this reason, the majority of the modified catalysts still con-

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tain Cu-Zn oxides as main constituents, and others components can be added in order to modify the catalytic properties.

In this optic, CuO/ZnO catalysts have been modified by addition of different metals oxides such as PdO, CeO_2, ZrO_2, Ga_2O_3, Al_2O_3, Cr_2O_3 and V_2O_5 [14-32]. It was found that the support or promoters act only on the Cu dispersion to increase the specific activity. Copper oxide alone is not very active in methanol production, but, when mixed with ZnO, a combined oxide is formed, and the synergic-activity end up in improved catalytic performances, if compared to those of the separate oxides. Consequently, many studies have been focused on the identification of the structure and the nature of the active sites of the catalyst surface. It was suggested that the predominant active site for methanol synthesis were Cu-Zn pair [33,34], Cu^+ ions [35,36], Cu^0-Cu^+ [37,38], or metallic copper [39,40].

The aim of the present research is to study of the influence of CuO/ZnO weight ratios, surface property, and reaction pressure on the activity of $CuO/ZnO/Al_2O_3$ catalyst in the synthesis of methanol starting from CO_2/H_2. The listed parameters play indeed an important role in driving the catalytic performance of such mixed oxides catalyst.

2. Materials and Methods

2.1 Catalysts Preparation

All the chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. A series of $CuO/ZnO/Al_2O_3$ catalysts with 10 wt.% of Al_2O_3 and different CuO/ZnO weight ratios were prepared by co-precipitation method on 10 wt% alumina [41]. The copper and zinc nitrate precursors $Cu(NO_3)_2.2.5H_2O$ (98% purity) and $Zn(NO_3)_2.6H_2O$ (99% purity) were dissolved in deionized water and sodium carbonate Na_2CO_3 (99.5% purity) was used as precipitating agent. Prior to precipitation, the estimated 10 wt.% of alumina, Al_2O_3 (98% purity) was added to the solution and the slurry was stirred and kept at 85 °C. The addition of sodium carbonate increased the pH to 7, allowing the co-precipitation of Cu and Zn hydroxides on the alumina surface. Then, the obtained solid material was aged during 2 h under intensive stirring. In the next step, sodium and nitrate ions were thoroughly removed by washing the solid with redistilled water (6 times) until the total elimination of Na^+ and NO_3^- ions. Analysis of the filtrate by electrical conductivity confirmed this result.

To avoid agglomeration of the CuO and ZnO particles in the CuO-ZnO solid solution, the dried precipitate was calcined in air at 350 °C for 12 h. Several studies have shown that when the calcination temperature exceeded 350 °C, specific area and catalytic activity decreased. After calcination, all catalysts were characterized by IR spectroscopy (Table 1), only O-H stretching and metallic carbonates vibration band were observed.

Table 1. Infra-red absorption bands of catalysts

Catalysts	Adsorption bands (cm^{-1})	Assignment
C_1	1385 (s)	Metallic carbonates
	1497 - 1631 (l)	Metallic carbonates
	3442 (l)	H_2O (O-H)
C_2	1385 (s)	Metallic carbonates
	1631 (l)	Metallic carbonates
	3442 (l)	Eau
C_3	1385 (s)	Metallic carbonates
	1497 - 1631 (l)	Metallic carbonates
	3442 (l)	O-H (H_2O)
C_4	1385 (s)	Metallic carbonates
	3442 (l)	O-H (H_2O)
C_5	1385 (s)	Metallic carbonates
	1631 (l)	Metallic carbonates
	3442 (l)	O-H (H_2O)

- S : Strong
- l : Low intensity

2.2 Catalysts Characterization

X-ray patterns were collected on PANATICAL MPD X'Pert Pro diffractometer operating with Cu-Kα radiation (Kα = 0.15418 nm) and equipped with an X' Accelerator. The real-time multiple strip pattern was collected at 295 K in the 5°-70° 2θ range with a step of 0.017° 2θ and a time /step of 220 sec; the total collecting time was about 2h.

The copper and zinc content were determined using an AAS 6800 spectrometer (Shimadzu). The specific surface areas of the alumina support and the obtained catalyst were measured by nitrogen adsorption at -196 °C by applying the BET method and using a Quantachrome apparatus. The metallic copper surface area was measured by the decomposition of N_2O at 90 °C [42-44] on the surface of metallic copper by the following reaction:

$$2Cu_{(s)} + N_2O_{(g)} \rightarrow N_{2(g)} + Cu_2O_{(s)} \quad (1)$$

The pulse titration technique was employed and a thermal conductivity detector (TCD) was used to detect the amount of N_2O consumed.

2.3 Catalytic Tests

The catalytic tests have been performed in a continuous tubular flow fixed-bed microreactor at different reaction pressures and at constant temperature of 230 °C for all catalysts. For the most active catalyst (C4) further investigations at different temperature (in the 170-270 °C range) have been performed. Prior to reaction, the catalyst (0.5 g) was reduced in H_2 flow (1.3 $L.h^{-1}$). The reduction program consisted in an increment of the temperature from room temperature to 350 °C at 10 $°C.min^{-1}$ and of a plateau to 350 °C for 8 h. After the reduction step, the reactor was fed with the reaction mixture: CO_2/H_2 = 1/3. The total flow rate was in the 0.3-3.6 $L.h^{-1}$ range and the tested operating pressures were: 1, 20, 35, 50, and 75 bar, respectively. The reaction mixture and products were analyzed on line by using gas chromatographs equipped with TCD and FID detectors and Carbosieve and Porapak Q columns, respectively. The products, detected in the stream flow exiting form the reactor during CO_2 hydrogenation on $CuO/ZnO/Al_2O_3$ catalysts, were almost exclusively constituted of methanol and carbon monoxide. Only traces of methane could be observed. Methanol and carbon monoxide selectivity and CO_2 conversion were calculated using the following equations:

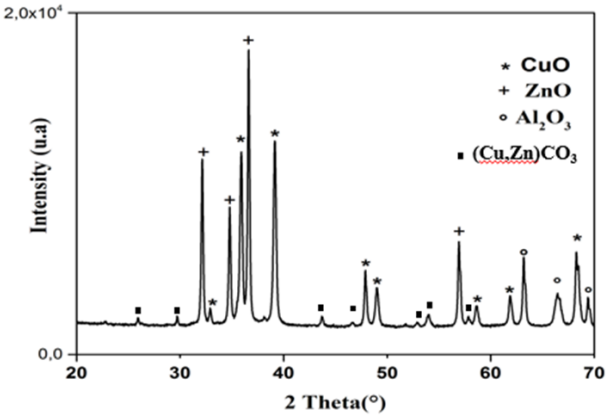

Figure 1. XRD pattern of $CuO/ZnO/Al_2O_3$ catalyst after calcination

$$CO_2\ conversion\ (\%) = \frac{S_{CO_2\ in} - S_{CO_2\ out}}{S_{CO_2\ in}} \times 100 \quad (2)$$

$$CH_3OH\ selectivity\ (\%) = \frac{S_{CH_3OH\ out}}{CO_2\ conversion} \times 100 \quad (3)$$

$$CO\ selectivity\ (\%) = \frac{S_{CO\ out}}{CO_2\ conversion} \times 100 \quad (4)$$

3. Results and Discussion

3.1 Textural properties of $CuO/ZnO/Al_2O_3$ catalysts

3.1.1 N_2 adsorption-desorption

The BET surface area of the $CuO/ZnO/Al_2O_3$ catalysts with different Cu/Zn theoretical and experimental weight ratios are summarized in Table 2. The surface area significantly decreases when increasing the Cu/Zn ratio. The increase of Cu/Zn ratio should be responsible for the decrease of surface area. The growth of crystal grain or agglomeration of particles with the increase of Cu/Zn ratio should be responsible for the decrease of surface area. At the opposite, the metallic copper surface area increased with the Cu/Zn ratio, suggesting that the Cu-containing phase is mainly distributed on the surface of the composite.

3.1.2 XRD analysis

The XRD patterns of the calcined $CuO-ZnO/Al_2O_3$ samples with different Cu/Zn weight ratios are constituted of mixtures of CuO, ZnO and Al_2O_3 (Figure 1). The Bragg angles 2θ peaks of 32.5, 35.5, 38.7, 48.7, 58.3, 61.5, 65.8, and 66.2° [45-46] was attributed to

Table 2. Textural properties and catalytic performance of different $CuO/ZnO/Al_2O_3$ catalysts

Catalyst	Theoretical Cu/Zn/Al (at %)	Experimental Cu/Zn (at %)	S_{Cu} (m^2/g)	S_{BET} (m^2/g)	X_{CO2} (%)	S_{CO} (%)	S_{CH3OH} (%)
C1	10/80/10	8.70/81.30	1.12	59	6.0	98.4	1.6
C2	40/50/10	39.85/49.71	2.52	42	7.5	97.9	2.1
C3	50/40/10	48.69/38.37	3.56	33	9.0	96.5	3.5
C4	60/30/10	59.15/28.14	4.45	21	11.4	94.7	5.3
C5	70/20/10	69.34/18.66	5.60	14	13.0	97.8	2.2

Reaction conditions P = 1 bar, T_R = 230 °C, CO_2/H_2 = 1/3 (molar ratio); X_{CO2}: CO_2 conversion; S: Selectivity

CuO and consistent with the characteristic peaks of ZnO at of 31.7, 34.1, 36.2, and 56.9° [46], and those of alumina at 2θ of 66.5 and 68.2° 2θ [47]. Increasing of Cu/Zn ratio, the diffraction peaks of CuO become stronger and sharper, while the peaks attributed to ZnO have the opposite variation trend. The small peaks at 2θ: 29.1, 44.3, and 54.8 are attributed to the undecomposed metallic carbonates, such as: $CuCO_3$ and/or $ZnCO_3$.

3.2 Catalytic Properties of $CuO/ZnO/Al_2O_3$ Catalyst

3.2.1 Relation between catalytic performance and S_{Cu}

The results of the CO_2 hydrogenation over the various $CuO/ZnO/Al_2O_3$ catalysts are given in Table 2. The selectivity to methanol increased with the metallic copper surface area for the samples containing 10-60% of copper, while it decreased when the copper content exceeded 60%, although the metallic copper surface area was even higher, a result that is consistent with other reports [45,48,49]. This can be explained by the positive synergetic effect obtained by the contact between copper and zinc oxides. On the other hand, the conversion of CO_2 continuously increased by increasing the Cu/Zn weight ratios, while the selectivity to CO decreased with the Cu/Zn weight ratios augmentation, for the catalysts containing from 10 to 60% of copper content, but increased when the copper content exceeded 60% [48]. The effect of metallic cooper surface area on the CO_2 conversion at 230 °C is shown in Figure 2. With increasing the Cu/Zn weight ratios, the metallic cooper surface area increased and the CO_2 conversion was linearly enhanced. This indicated that the CO_2 conversion is directly proportional to the surface area of metallic copper. These results confirm that there must be some other factors affecting the catalytic performance during the synthesis of methanol from CO_2/H_2. Apparently, Cu^0 atoms are the active sites in the dissociation of CO_2 to CO and Cu-O-Cu species [50-53]. The dissociation reaction is the follows:

$$CO_{2\,(g)} + 2Cu^0 \leftrightarrow CO_{\,(g)} + \text{Cu-O-Cu} \qquad (5)$$

The presence of surface oxygen (Cu-O-Cu) enhances both the adsorption of CO_2 and of H_2. The new created Cu-O-Cu active site enhances both the adsorption of CO_2 and the formation of monodentate carbonate (Cu-O-CO-O-Cu) species that, after hydrogenation, lead to the formation of monodentate formate (Cu-O-CH=O), which is the key intermediate in methanol production. The $CuO/ZnO/Al_2O_3$ catalyst with a Cu/Zn/Al weight ratio of 60/30/10 exhibited the highest selectivity (5.34 %) to methanol at 230 °C.

3.2.2 Temperature effect

Table 3, illustrates the effects of temperature on CO_2 hydrogenation reaction at atmospheric pressure and stoichiometric feed ratio (H_2/CO_2 = 3).The product stream mostly contains CO and methanol at reaction temperature in the range between 170 and 270 °C. Moreover, by increasing the temperature, the CO_2 conversion and carbon monoxide selectivity was enhanced, while the methanol selectivity decreased simultaneously. At constant reaction pressure, a lower temperature leads to

Table 3. Effect of temperature on the C4 catalyst performance

T (°C)	CO_2 conversion (%)	CO selectivity (%)	CH_3OH selectivity (%)
170	2.60	84.00	16.00
190	5.00	90.86	9.14
210	7.16	93.72	7.28
230	11.4	94.66	5.34
250	16.4	95.87	4.13
280	19.0	96.90	3.10

Reaction conditions flow = 2 $L.h^{-1}$, P = 1 bar, CO_2/H_2 = 1/3 (molar ratio)

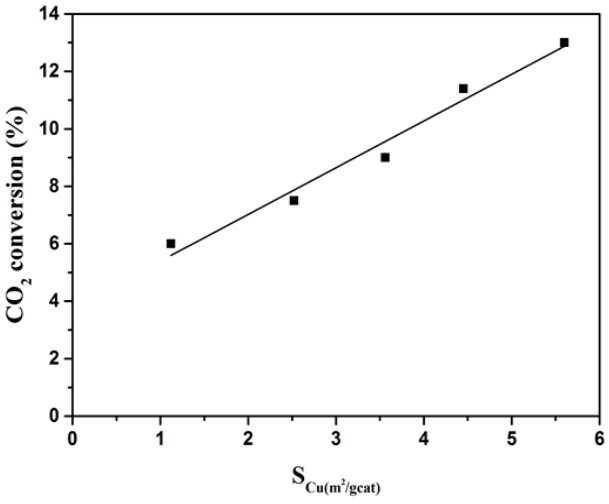

Figure 2. Correlation between the metallic copper surface area and the CO_2 conversion at 230 °C, P =1 bar

higher methanol selectivity. This result suggests that the formate, which is the main route for methanol synthesis is unstable at high temperature and decompose to CO and H_2O through the reverse water gas shift (RWGS) reaction.

The effect of flow-rate variation was also tested at 0.6, 1, 1.4, 2, and 3.6 L/h, and 230 °C. The data for the selectivity ratios during 10 hours on-stream with the C4 catalyst are reported in Figure 3. By increasing the flow-rate, the CO_2 conversion and CO selectivity decreased, while the methanol selectivity considerably increased. A high flow-rate is favorable to methanol formation, whereas the CO formation is enhanced at low flow-rate.

The effects of the reaction pressure, on the activity and selectivity has been studied over the most active catalyst C4 ($CuO/ZnO/Al_2O_3$: 60/30/10) at the reaction temperature of 230 °C (Table 4). The conversion of carbon dioxide and methanol selectivity increased with the total pressure, while the carbon monoxide selectivity decreased by increasing the total pressures. At 75 bar, the methanol selectivity reached the maximum value. Such a behavior may be due to the decomposition of the formate species that is much lower at high pressure. Consequently, CO formation can be minimized increasing the pressure. The CO/CH_3OH selectivity ratios expressed as function of the pressure show the same trend that observed as a function of the flow-rate, Figure 4. Finally, high pressure and high flow-rate are favorable to methanol production, while they present the opposite effect on the CO formation.

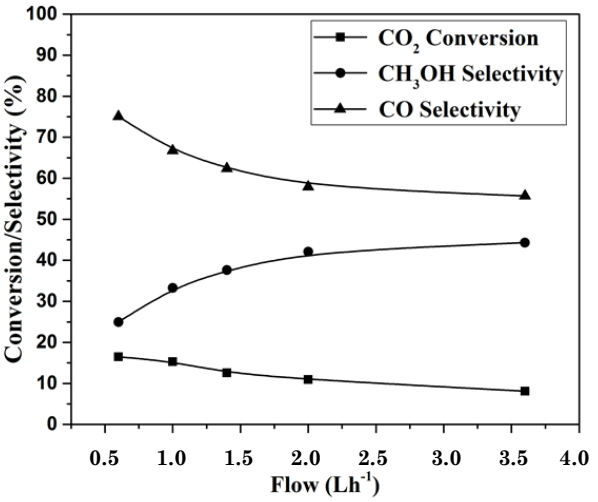

Figure 3. The effect of flow-rate on the Conversion/selectivity ratios at 230 °C, P=50 bar

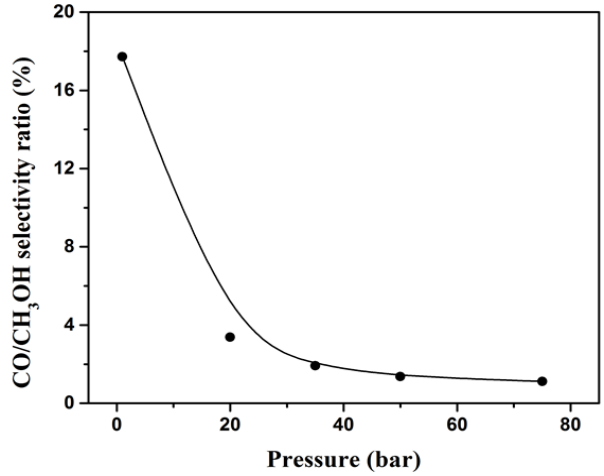

Figure 4. Influence of the pressure on the CO/CH_3OH selectivity ratios at 230 °C

3.3 Kinetics and Mechanism of Carbon Dioxide Hydrogenation

3.3.1 The activation energy

Overall, apparent activation energy can be determined from the effect of temperature on the rate for the CO_2 hydrogenation reaction, with constant composition and pressure.

An Arrhenius type plot of *ln (rate)* is obtained from CO_2 conversion to methanol with the reaction temperature 170, 190, 210, 230, 250 and 270 °C (Figure 5). The activation energy, obtained from the slope of the straight line, for fine powdered catalyst $CuO/ZnO/Al_2O_3$ (Cu/Zn/Al weight ratio of 60/30/10), corresponds to 38 kJ/mol for the methanol synthesis from CO_2 hydrogenation. The activation energy is lower than that on copper Cu (110 plane) (67 kJ/mol) and on polycrystalline Cu (77 kJ/mol) [53-54].

Table 4. Effect of pressure on the C4 catalyst performance

Pressure (bar)	CO_2 Conversion (%)	CO Selectivity (%)	CH_3OH Selectivity (%)
01	11.4	94.7	05.3
20	17.5	77.2	22.8
35	19.0	65.8	34.2
50	21.4	57.9	42.1
75	23.0	52.9	47.1

Reaction conditions flow = 2 $L.h^{-1}$, T_R= 230 °C, CO_2/H_2 = 1/3 (molar ratio)

3.3.2 Carbon dioxide hydrogenation mechanism

The $CuO/ZnO/Al_2O_3$ catalytic system have been widely used in industry in the synthesis of methanol from syngas and then widely studied in the hydrogenation reaction of pure CO_2 to methanol. In the literature the debate remains still open on the methanol synthesis mechanism and on the nature of catalytic active sites involved. Two types of reaction pathways have been identified in the literature for the hydrogenation of CO_2 to methanol. The first consists in the direct hydrogenation of CO_2 to methanol. The second pathway suggests that CO_2 is firstly converted to CO (through the RWGS reaction), then to methanol. Several active sites configurations have been proposed, some authors, proposed that Cu^+ is the site active in methanol synthesis, for others the active species are constituted of Cu^0 or of a mixture of Cu^+ and Cu^0. It is often reported that methanol formation occurs preferentially on Cu^+ centers [35,36], however, it seems that methanol formation is activated only in presence of Cu^0 [37,40].

Generally, methanol synthesis by CO_2 hydrogenation over CuO/ZnO based catalysts implicates three competitive reactions. The first reaction is the direct synthesis of methanol from CO_2:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (6)$$

The second one is the inter-conversion between carbon dioxide and carbon monoxide (RWGS reaction):

$$CO_{2\,(g)} + H_2 \rightarrow CO_{\,(g)} + H_2O \quad (7)$$

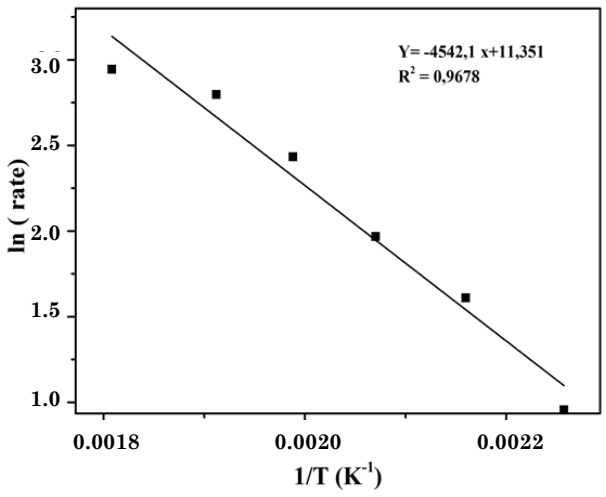

Figure 5. Arrhenius plot of CO_2 conversion with the reaction conditions: flow = 2 $L.h^{-1}$, P = 1 bar, CO_2/H_2 = 1/3 (molar ratio).

The third one is the synthesis of methanol from CO:

$$CO + 2H_2 \rightarrow CH_3OH \quad (8)$$

By subtracting the reaction in Equation (7) from the reaction in Equation (6) results in:

$$[CO]/[CH_3OH] = k/P^2_{H2} \quad (9)$$

The $[CO]/[CH_3OH]$ selectivity ratio is inversely proportional to the total pressure as displayed in Figure 4, for the reaction performed at 230 °C. It is clear that at low pressure, the carbon monoxide is the main product, while, at high pressure, CO is transformed to methanol, demonstrating that carbon monoxide and methanol are produced from CO_2 by parallel reactions.

This mechanism is also supported by the fact that methanol forms very fast if the pressure is high. Moreover, the increasing of the flow-rate also enhances methanol formation. When the CO_2/H_2 mixture was feed over the $CuO/ZnO/Al_2O_3$ catalysts, CH_3OH was produced together with CO and H_2O. The methanol synthesis reaction, $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$, takes place in parallel to the reverse water gas shift reaction, $CO_2 + H_2 \leftrightarrow CO + H_2O$. The impact of pressure, flow-rate and temperature on the products formation suggests that CH_3OH and CO are produced through parallel pathways. By increasing the pressure, the CH_3OH selectivity increased, while the CO selectivity decreased. The same trend was observed by varying the feedstock flow-rate. At the contrary, by increasing the reaction temperature, the methanol selectivity decreased and the carbon monoxide selectivity increased. These observations suggest that methanol and carbon monoxide are directly formed starting from the surface formate (O-CH=O) species that is formed via hydrogenation of CO_2.

The proposed mechanism for carbon dioxide hydrogenation at high pressure suggests that the reaction between formate (HCOO) and hydrogen brings to the formation of dioxomethylene (H_2COO). The dioxomethylene formation reaction may strongly compete with the decomposition reaction of formate to CO. Hence, high pressures favor the methanol selectivity, as confirmed by the results reported in Table 3. Pressure has a very strong influence on the production of methanol, probably due to the increasing of moles that characterize the involved reactions and that consequently shifts the equilibrium towards the condensation reaction.

Previous works suggested that over copper based catalysts, the hydrogenation of carbon dioxide to methanol proceeds via the formation of the formate surface intermediate [53,56-58]. This reaction is usually considered the rate-determining step. The idea was previously reported by Fujita and co-workers [59] whose used IR spectroscopy to study the chemisorption of CO_2/H_2 on a CuO/ZnO-based catalyst. The reaction intermediates observed on the catalyst surface were carbonate (CO_3^{2-}), formate ($HCOO^-$), dioxomethylene (H_2COO), formaldehyde (CH_2O), methoxy (CH_3O^-) species and the final product, CH_3OH. The adsorbed species detected on the catalyst (carbonates, formates and methoxy) are also in agreement with a similar study reported by Bailey *et al*. [60].

Chinchen *et al*. [61] proposed that the surface atomic oxygen O* (Cu-O-Cu) (**a**) plays an important role during the methanol synthesis by promoting the adsorption of CO_2, and by participating in the hydrogenation step. Based on the observations just reported, a tentative mechanism is schematized in Figure 6, for the methanol synthesis from CO_2/H_2 over a CuO/ZnO containing catalyst. At the first, the carbonate adsorption species (b) are produced by exposing the CuO/ZnO catalyst surface to CO_2/H_2. Then the hydrogenation to formate ($HCOO^-$) (c), followed by the formation of dioxomethylene (H_2COO) (f) and of methoxy (CH_3O^-) species (g) take place to bring to the final product, methanol (CH_3OH) (Sequence B). The CO is produced by decomposition of the monodentate and bidentate formate. In the same way than that of the formate decomposition, the decomposition of surface hydroxyl species leads to water formation (sequence A).

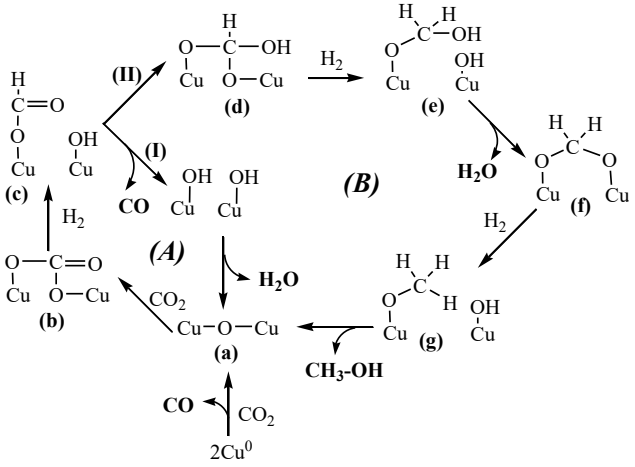

Figure 6. Reaction pathway of CO_2 hydrogenation over Cu (I) centers

4. Conclusions

Methanol synthesis over $CuO/ZnO/Al_2O_3$ catalysts occurs via CO_2 hydrogenation on the partially oxidized copper surface (Cu^0/Cu^I). CO_2 conversion and methanol selectivity strongly depend on the catalyst composition, pressure, reaction temperature and flow rate. High pressure and high flow-rate enhance the methanol formation. Besides a high reaction temperature favors the carbon monoxide production. The present results show the great influence of the catalyst composition and operating pressure on the kinetic and catalytic performances of $CuO/ZnO/Al_2O_3$ catalysts in the CO_2/H_2 reaction. Methanol is directly produced from CO_2 whatever the pressure, while carbon monoxide can be produce by the decomposition of the formate at low pressure or directly from CO_2 reduction.

References

[1] Vora, B.V., Marker, T.L., Barge, P.T., Nilsen, H.R., Kvisle, S., Fuglerud, T. (1997). Economic Route for Natural Gas Conversion to Ethylene and Propylene. *Stud. In. Surf. Sci. Catal.,* 107: 87-98.

[2] Behrens, M. (2014). Heterogeneous Catalysis of CO_2 Conversion to Methanol on Copper Surfaces. *Angew. Chem. Int. Ed.*, 53: 12022-12024.

[3] Inui, T., Hara, H., Takeguchi, T., Kim, J. (1997). Structure and function of Cu-based composite catalysts for highly effective synthesis of methanol by hydrogenation of CO_2 and CO. *Catal. Today.*, 36: 25-32.

[4] Ma, Y., Sun, Q., Wu, D., Fan, W., Zhang, Y., Deng, J. (1998). A practical approach for the preparation of high activity $Cu/ZnO/ZrO_2$ catalyst for methanol synthesis from CO_2 hydrogenation. *Appl. Catal. A.*, 171: 45-55.

[5] Arena, F., Barbera, K., Italiano, G., Bonura, G., Spadaro, L., Frusteri, F. (2007). Synthesis, characterization and activity pattern of $Cu–ZnO/ZrO_2$ catalysts in the hydrogenation of carbon dioxide to methanol. *J. Catal.*, 249: 185-194.

[6] Koppel, R.A., Baiker, A. (1992). Copper/zirconia catalysts for the synthesis of methanol from carbon dioxide: Influence of preparation variables on structural and catalytic properties of catalysts. *Appl. Catal.*, 84: 77-102.

[7] Satio, M., Fujitani, T., Takeuchi, M. (1996). Development of copper/zinc oxide-based multicomponent catalysts for methanol synthesis from carbon dioxide and hydrogen. *Appl. Catal.*, 138: 311-318.

[8] Brown, J.A., Homs, N., Bell, A.T. (1990). Hydrogenation of CO_2 and CO_2/CO mixtures over copper-containing catalysts. *J. Catal.*, 124: 73-85.

[9] Lee, J.S., Moon, K.I., Lee, S.H., Lee, S.Y., Kim, Y.G. (1995). Modified Cu/ZnO/Al_2O_3 catalysts for methanol synthesis from CO_2/H_2 and CO/H_2. *Catal. Lett.*, 34: 93-99.

[10] Frohlich, C., Koppel, R.A., Baiker, A., Kilo, M., Wokaun, A. (1993). Hydrogenation of carbon dioxide over silver promoted copper/zirconia catalysts. *Appl. Catal.*, 106: 275-293.

[11] Deng, J.F., Sun, Q., Zhang, Y.L., Wu, D., Chen, S.Y. (1996). A novel process for preparation of a Cu/ZnO/Al_2O_3 ultrafine catalyst for methanol synthesis from CO_2 + H_2: comparison of various preparation methods. *Appl. Catal.*, 139: 75-85.

[12] Waugh, K.C. (2012). Methanol synthesis, *Catal. Lett.*, 142: 1153-1166.

[13] Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., Zander, S., Girgsdies, F., Kurr, P., Kniep, B.L., Tovar, M., Fischer, R.W., Nørskov, J.K., Schlögl, R. (2012). The active site of methanol synthesis over Cu/ZnO/Al_2O_3 industrial catalysts. *Sci.*, 336: 893-897.

[14] Fujitani, T., Saito, M., Kanai, Y., Takeuchi, M., Moria, K., Watanabe, T., Kawai, M., Kakumoto, T. (1993). Methanol synthesis from CO_2 and H_2 over Cu/ZnO/Ga_2O_3 catalyst. *Chem. Lett.*, 22: 1079-1080.

[15] Fornero, E.L., Sanguineti, P.B., Chiavassa, D.L., Bonivardi, A.L. (2013). Performance of ternary Cu–Ga_2O_3–ZrO_2 catalysts in the synthesis of methanol using CO_2-rich gas mixtures. *Catal. Today.*, 213: 163-170.

[16] Ladera, R., Perez-Alonso, F.J. (2013). Catalytic valorization of CO_2 via methanol synthesis with Ga-promoted Cu–ZnO–ZrO_2 catalysts. *Appl. Catal. B. Envir.*, 142: 241-248.

[17] Słoczyński, J., Grabowski, R., Olszewski, P., Kozłowska, A., Stoch, J., Lachowska, M., Skrzypek, J. (2006). Effect of metal oxide additives on the activity and stability of Cu/ZnO/ZrO_2 catalysts in the synthesis of methanol from CO_2 and H_2. *Appl. Catal. A. General.*, 310: 127-137.

[18] Toyir, J., Ramoirez, P., de la Piscina, P.R., Fierro, J.L.G., Homs, N. (2001). Catalytic performance for CO_2 conversion to methanol of gallium-promoted copper-based catalysts: influence of metallic precursors. *Appl. Catal. B. Envi.*, 34: 255-266.

[19] Arena, F., Mezzatesta, G., Zafarana, G., Trunfio, G., Frusteri, F., Spadaro, L. (2013). How oxide carriers control the catalytic functionality of the Cu-ZnO system in the hydrogenation of CO_2 to methanol. *Catal. Today.*, 210: 39-46.

[20] Bonura, G., Arena, F., Mezzatesta, G., Cannilla, C., Spadaro, L., Frusteri, F. (2011). Role of the ceria promoter and carrier on the functionality of Cu-based catalysts in the CO_2-to-methanol hydrogenation reaction. *Catal. Today.*, 171: 251-256.

[21] Pokrovski, K.A., Bell, A. (2006). Effect of dopants on the activity of Cu/$M_{0.3}Zr_{0.7}O_2$ (M= Ce, Mn, and Pr) for CO hydrogenation to methanol. *J. Catal.*, 244: 43-51.

[22] Melian-Cabrera, I., Lopez Granados, M., Terreros, P., Fierro, J.L.G. (1998). CO_2 hydrogenation over Pd-modified methanol synthesis catalysts. *Catal. Today.*, 45: 251-256.

[23] Zhang, L., Zhang, Y., Chen, S. (2012). Effect of promoter SiO_2, TiO_2 or SiO_2-TiO_2 on the performance of CuO-ZnO-Al_2O_3 catalyst for methanol synthesis from CO_2 hydrogenation. *Appl. Catal. A. General.*, 415: 118-123.

[24] Guo, X., Mao, D., Lu, G., Wang, S., Wu, G. (2011). The influence of La doping on the catalytic behavior of Cu/ZrO_2 for methanol synthesis from CO_2 hydrogenation. *J. Mol. Catal. A Chem.*, 345: 60-68.

[25] Fujitani, T., Saito, M., Kanai, Y., Kakumoto, T., Watanabe, T., Nakamura, J., Uchijima, T. (1994). The role of metal oxides in promoting a copper catalyst for methanol synthesis. *Catal. Lett.,* 25: 271-276.

[26] Toyir, J., de la Piscina, P.R., Fierron, J.L.G., Homs, N. (2001). Highly effective conversion of CO_2 to methanol over supported and promoted copper-based catalysts: influence of support and promoter. *Appl. Catal.*, 29: 207-215.

[27] Inui, T., Takeguch, T. (1991). Effective conversion of carbon dioxide and hydrogen to hydrocarbons. *Catal. Today.*, 10: 95-106.

[28] Cai, W., de la Piscina, P.R., Toyir, J., Homs, N. (2015). CO_2 hydrogenation to methanol over CuZnGa catalysts prepared using microwave-assisted methods. *Catal. Today.*, 242: 193-199.

[29] Fujimoto, K., Yu, Y. (1993). CO hydrogenation to methanol. New Aspects of Spillover Effect in Catalysis: For Development of Highly Active Catalysts. *Studies in Surface Science and Catalysis*, 77: 369-393.

[30] Sahibzada, M., Chadwick, D., Metcalfe, I.S. (1996). Hydrogenation of carbon dioxide to methanol over palladium-promoted Cu/ZnO/Al_2O_3 catalysts. *Catal. Today.*, 29: 367-372.

[31] Gotti, A., Prins, R. (1998). Basic metal oxides as co-catalysts in the conversion of synthesis

gas to methanol on supported palladium catalysts. *J. Catal.*, 175: 302-311.

[32] Melian-Cabrera, I., Granados, M.L., Terreros, P., Fierro, J.L.G. (1998). CO_2 hydrogenation over Pd-modified methanol synthesis catalysts. *Catal. Today.*, 45: 251-256.

[33] Klier, K. (1982). Methanol synthesis. *Adv. Catal.*, 31: 243-313.

[34] Nonneman, L.E.Y., Ponet, V. (1990). On the problem of the activity in methanol synthesis of supported, unpromoted copper catalysts. *Catal. Lett.*, 7: 213-217.

[35] Herman, R.G., Klier, K., Simmons, G., Finn, B.P., Bulko, J.W., Kobylinski, T.P. (1979). Catalytic synthesis of methanol from CO H_2: I. Phase composition, electronic properties, and activities of the Cu/ZnO/M_2O_3 catalysts. *J. Catal.*, 56: 407-429.

[36] Kau, L., Hodgson, K.O., Solomon, E.I. (1989). X-ray absorption edge and EXAFS study of the copper sites in zinc oxide methanol synthesis catalysts. *J. Am. Chem. Soc.*, 111: 7103-7109.

[37] Okamoto, Y., Fukino, K., Imanaka, T., Teranishi, S. (1983). Surface characterization of copper(II) oxide-zinc oxide methanol-synthesis catalysts by x-ray photoelectron spectroscopy. 1. Precursor and calcined catalysts. *J. Phys. Chem.*, 87: 3740-3747.

[38] Chinchen, G.C., Waugh, K.C., Whan, D.A. (1986). The activity and state of the copper surface in methanol synthesis catalysts. *Appl. Catal.*, 25: 101-107.

[39] Denise, B., Sneeden, R.P.A., Beguin, B., Cherifi, O. (1987). Supported copper catalysts in the synthesis of methanol: N_2O-titrations. *Appl. Catal.*, 30: 353-363.

[40] Chinchen, G.C., Hay, C.M., Vandervell, H.D., Waugh, K.C. (1987). The measurement of copper surface areas by reactive frontal chromatography. *J. Catal.*,103: 79-86.

[41] Li, D., Xu, S., Cai, Y., Chen, C., Zhan, Y., Jiang, L. (2017). Characterization and Catalytic Performance of Cu/ZnO/Al_2O_3 Water–Gas Shift Catalysts Derived from Cu–Zn–Al Layered Double Hydroxides. *Ind. Eng. Chem. Res.*, 56: 3175-3183.

[42] Evans, J.W., Wainwright, M.S., Bridgewater, A.J., Young, D.J. (1983). On the determination of copper surface area by reaction with nitrous oxide. *Appl. Catal.*, 7: 75-83.

[43] Meli´an-Cabrera, I., L´opez-ranados, M., Fierro, J.L.G. (2002). Reverse topotactic transformation of a Cu–Zn–Al catalyst during wet Pd impregnation: relevance for the performance in methanol synthesis from CO_2/H_2 mixtures. *J. Catal.*, 210: 273-284.

[44] Ernsta, K.H., Campbell, C.T., Moretti, G. (1992). Kinetics of the reverse water-gas shift reaction over Cu (110). *J. Catal.*, 134: 66-74.

[45] Witoon, T., Permsirivanich, T., Donphai, W., Jaree, A., Chareonpanich, M. (2013). CO_2 hydrogenation to methanol over Cu/ZnO nanocatalysts prepared via a chitosan-assisted co-precipitation method. *Fuel. Proc. Tech.*, 116: 72-78.

[46] Habibi, M.H., Karimi, B. (2014). Preparation of nanostructure CuO/ZnO mixed oxide by sol–gel thermal decomposition of a $CuCO_3$ and $ZnCO_3$: TG, DTG, XRD, FESEM, and DRS investigations. *J. Ind. Eng. Chem*., 20: 925-229.

[47] Lei, H., Hou, Z., Xie, J. (2016). Hydrogenation of CO_2 to CH_3OH over CuO/ZnO/Al_2O_3 catalysts prepared via a solvent-free routine, *Fuel*., 164: 191-198.

[48] Dong, X., Li, F., Zhao, N., Tan, Y., Wang, J., Xiao, F. (2017). CO_2 hydrogenation to methanol over Cu/Zn/Al/Zr catalysts prepared by liquid reduction. *Chin. J. Catal.*, 38: 717-725.

[49] Li, L., Mao, D., Yu, J., Guo, X. (2015). Highly selective hydrogenation of CO_2 to methanol over CuO–ZnO–ZrO_2 catalysts prepared by a surfactant-assisted co-precipitation method. *J. Power. Sources*., 279: 394-404.

[50] Gao, P., Li, F., Xiao, F., Zhao, N., Sun, N., Wei, W., Sun. Y. (2012). Preparation and activity of Cu/Zn/Al/Zr catalysts via hydrotalcite-containing precursors for methanol synthesis from CO_2 hydrogenation. *Catal. Sci. Technol.*, 2: 1447-1454.

[51] Fujita, S.I., Usui, M.,Takezawa, N. (1992). Mechanism of the reverse water gas shift reaction over Cu/ZnO catalyst. *J. Catal*., 134: 220-225.

[52] Gine's, M.J.L., Marchi, A.J., Apesteguı´a, C.R. (1997). Kinetic study of the reverse water-gas shift reaction over CuO/ZnO/Al_2O_3 catalysts, *Catal. A.*, 154: 155-171.

[53] Schilke, T.C., Fisher, I.A., Bell, A.T. (1999). In Situ Infrared Study of Methanol Synthesis from CO_2/H_2 on Titania and Zirconia Promoted Cu/SiO_2, *J. Catal.*, 184: 144-156.

[54] Yoshihara, J., Campbell, C.T. (1996). Methanol Synthesis and Reverse Water–Gas Shift Kinetics over Cu(110) Model Catalysts: Structural Sensitivity. *J. Catal.*, 161: 776-782.

[55] Yoshihara, J., Parker, S.C., Schafer, A., Campbell, C.T. (1995). Methanol synthesis and reverse water-gas shift kinetics over clean polycrystalline copper. *Catal. Lett.*, 31: 313-324.

[56] Jung, K.D., Bell., A.T. (2000). Role of hydrogen spillover in methanol synthesis over Cu/ZrO_2. *J. Catal.*, 193: 207-223.

[57] Chiavassa, D.L., Collins, S.E., Bonivardi, A.L., Baltanas, M.A. (2009). Methanol synthesis from CO_2/H_2 using Ga_2O_3-Pd/silica catalysts: kinetic modeling. *Chem. Eng. J.*, 150: 204-212.

[58] Lim, H.W., Park, M.J., Kang, S.H., Chae, H.J., Bae, J.W., Jun, K.W. (2009). Modeling of the kinetics for methanol synthesis using $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst: influence of carbon dioxide during hydrogenation. *Ind. Eng. Chem. Res.*, 48: 10448-10455.

[59] Fujita, S., Usui, M., Ito, H.,Takezawa, N. (1995). Mechanisms of methanol synthesis from carbon dioxide and from carbon monoxide at atmospheric pressure over Cu/ZnO. *J. Catal.*,157: 403-413.

[60] Bailey, S., Froment, G.F., Snoeck, J.W., Waugh, K.C. (1995). A drifts study of the morphology and surface adsorbate composition of an operating methanol synthesis catalys. *Catal. Lett.*, 30: 99-111.

[61] Chinchen, M.S., Spencer, K.C., Waugh-Whan, D.A. (1987). Promotion of methanol synthesis and the water-gas shift reactions by adsorbed oxygen on supported copper catalysts. *J. Chem. Soc., Faraday Trans. 1.*, 83: 2193-2212.