

## Effect of pressure on the mechanisms of the CO<sub>2</sub>/H<sub>2</sub> reaction on a CO-precipitated CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst

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**Abstract** The influence of working pressure on the mechanisms of the CO<sub>2</sub>/H<sub>2</sub> reaction on a co-precipitated CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst have been studied at 230 °C and in the pressure range of 1–75 bar. In the CO<sub>2</sub> hydrogenation using CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, the products were found to be CO, methanol and water almost exclusively. Only a trace of methane formation was observed. Methanol and carbon monoxide are competitively formed. The former is produced directly from CO<sub>2</sub> whatever the pressure whereas carbon monoxide stems either from CO<sub>2</sub> directly at high pressure or both methanol decomposition and CO<sub>2</sub> directly at low pressure.

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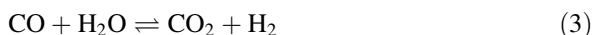
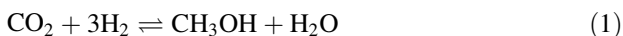
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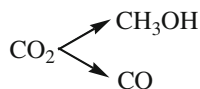
## Introduction

Carbon dioxide is accumulating more and more in the atmosphere and seems to participate to the so-called green-house effect. So the reduction of this waste is of great interest. The simplest way to utilize carbon dioxide is its hydrogenation into valuable compounds such as methanol, generally on copper based catalysts. The synthesis of methanol from CO/CO<sub>2</sub>/H<sub>2</sub> mixtures using CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts is currently attracting much interest due to its economical importance [1–7]. As this reaction produces methanol and carbon monoxide competitively, the role of each oxide in the mechanism of methanol formation (reactions 1 and 2) is still a matter of debate [8–11] since the reaction of conversion (reaction 3) also occurs: (1), hydrogenation of carbon dioxide, (2) the hydrogenation of carbon monoxide (3) water–gas shift reaction.



According to Klier [8, 9] (CuO/ZnO = 30/70, 250 °C, 75 bar), carbon monoxide is the principal source of methanol production (reaction 1). However, Schack et al. [10] suggested that carbon monoxide hydrogenation is the main route to methanol at typical industrial conditions while carbon dioxide is the main route under lower temperatures and pressures. According to Chinchén et al. [11] (industrial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> = 60/30/10 catalyst, 250 °C, 50 bar), methanol is directly formed from carbon dioxide. Using isotopic labeling to determine the main reaction that occurs in the methanol synthesis under the typical industrial conditions of 250 °C and 5.2 MPa, Chinchén et al. [12] found that the methanol produced had the same <sup>14</sup>C as that of carbon dioxide used in the feed gas. Therefore, this points out that methanol is directly produced from carbon dioxide immediately whereas carbon monoxide is first converted to carbon dioxide via the reverse water gas shift reaction and carbon dioxide remains the principal source of methanol. A study by Lee et al. [13] asserted that carbon dioxide hydrogenation to methanol is the dominant reaction. On the other hand, the results reported by Liu et al. [14] (CuO/ZnO = 30/70, 220 °C, 17 bar) indicate that methanol originates from the hydrogenation of both of the two carbon oxides.

Due to these conflicting results, the synthesis of methanol from the hydrogenation of CO<sub>2</sub> on the same catalysts has also received attention [15–19]. Indeed, this reaction competitively produces methanol and carbon monoxide and thus, due to the occurrence of the above reactions (1–3), the problem of carbon source of methanol is also posed. Rosovskii et al. [20] (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> SNM1 industrial catalyst, 250 °C, 50 bar) as well as Bardet et al. [21] (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> academic catalyst, 250 °C, 1 bar) concluded that the products are formed by parallel reactions (Reaction 1):



### Reaction 1

In the earliest work of Ipatieff (CuO/Al<sub>2</sub>O<sub>3</sub> catalyst, 300 °C/400 bar) [18], it is proposed that methanol is produced by the intermediary of carbon monoxide through a successive reaction path (Reaction 2):

However, the results obtained on the CuO/MgO and CuO/ZrO<sub>2</sub> catalysts at 20 °C/1 bar [19] as well as those achieved on CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts at 230 °C/1 bar [22] contradictorily show that a second type of successive reactions occurs in the CO<sub>2</sub>/H<sub>2</sub> in which methanol is the primary product (Reaction 3):

The above reported results about the synthesis of methanol in both the CO/CO<sub>2</sub>/H<sub>2</sub> and the CO<sub>2</sub>/H<sub>2</sub> reactions let us think that the different proposed mechanisms may be related to different solids and, even, to different operating conditions. The present work deals with the influence of pressure on the kinetics of the CO<sub>2</sub>/H<sub>2</sub> reaction on a co-precipitated CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. The method of investigation is the variation of the relative selectivity  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  as a function of the contact time [19, 20].

## Experimental

### Catalyst preparation

The catalyst was prepared by co-precipitating a solution of copper and zinc nitrates with sodium carbonate at 80 °C. At pH = 7, 10% Al<sub>2</sub>O<sub>3</sub> was added to the co-precipitate. The resulting Cu/Zn/Al suspension was centrifuged and the obtained precipitate was dried at 110 °C and calcined for 3.5 h under air at 350 °C after a 100 °C h<sup>-1</sup> heating rate treatment. The copper, zinc and aluminum contents of the calcined solid were 21.7, 50.0 and 4.1% respectively. The detected impurities were as follows (ppm): Mg(<80), Ca(<80), Na(<90), Fe(<90).

### Catalyst characterization

The surface area of the oxidized precursor was 29.4 m<sup>2</sup> g<sup>-1</sup>. Its XRD spectra show well defined bands of expected phases: CuO, ZnO and  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, whereas the presence of no decomposed carbonates phases is observed by IR spectroscopy. The copper surface area was 2.0 m<sup>2</sup> g<sup>-1</sup> and has been determined by N<sub>2</sub>O decomposition using a pulse technique as described by Evans [23].



### Reaction 2



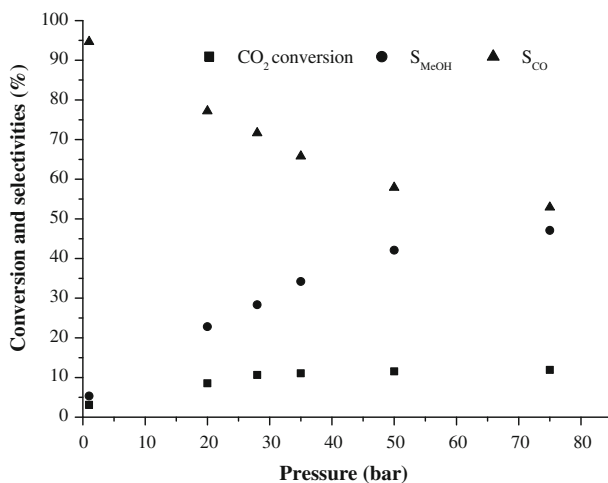
### Reaction 3

## Kinetic study

The catalyst testing was carried out in a stainless steel reactor (Sotalem RDP). The sample (0.2 g) was reduced in flowing  $\text{H}_2$  ( $1.3 \text{ L h}^{-1}$ ) by heating at  $20 \text{ }^\circ\text{C min}^{-1}$  to  $300 \text{ }^\circ\text{C}$  and holding at this temperature for 16 h. The temperature was then lowered to the reaction temperature ( $230 \text{ }^\circ\text{C}$ ) and the reactor was fed with the reaction mixture:  $\text{CO}_2/\text{H}_2 = 1/3$ . The total flow rate was in the range  $0.3\text{--}3.6 \text{ L h}^{-1}$  and the operating pressures were 1, 20, 28, 35, 50, and 75 bar. Reactants and products were analyzed on line using TCD and FID chromatographs equipped with Carbosieve and porapak Q columns. The results are expressed as a function of the reciprocal of the flow-rate  $1/d$  ( $\text{h L}^{-1}$ ).

## Results and discussion

The hydrogenation of carbon dioxide over supported copper catalysts produces both carbon monoxide and methanol, and the influence of pressure on the activity and selectivity of the reaction was examined. The catalyst activity was tested at 1, 20, 28, 35, 50, 75 bar,  $230 \text{ }^\circ\text{C}$ , and a flow-rate of  $2 \text{ L h}^{-1}$ . Data for the conversion of  $\text{CO}_2$  and selectivities of methanol and CO during 16 h on-stream with the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst are given in Fig. 1. When the  $\text{CO}_2/\text{H}_2$  mixture was fed over the catalyst, methanol was produced together with carbon monoxide and water. The catalyst was stable after about 3 h on stream and so the results refer to a steady state situation. With an increase in the pressure, the  $\text{CO}_2$  conversion and methanol selectivity increased, and the CO selectivity decreased considerably. At  $230 \text{ }^\circ\text{C}$  and a flow-rate of  $2 \text{ L h}^{-1}$ , the  $\text{CO}_2$  conversion increases from 3.1 to 11.9% when the total pressure is raised from 1 bar to 75 bar. In the same range of pressure, the



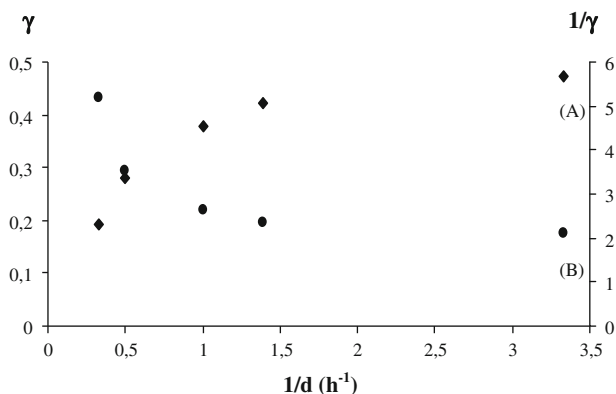
**Fig. 1** Variation of  $\text{CO}_2$  conversion,  $S_{\text{CH}_3\text{OH}}$  and  $S_{\text{CO}}$  as a function of pressure at  $230 \text{ }^\circ\text{C}$  for the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst

methanol selectivity increased from 5.3 to 47.1% and carbon monoxide selectivity decreased from 94.66 to 52.9%.

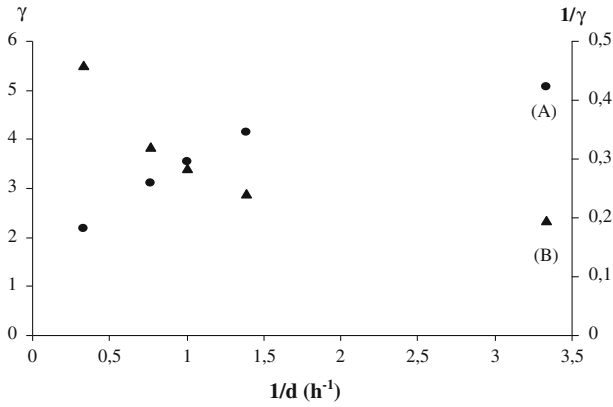
Through Fig. 1, carbon monoxide is predominant at low pressure, unlike methanol, which is favored at high pressure. This result shows that carbon dioxide is transformed into carbon monoxide at low pressure via the reverse water gas shift reaction (RWGS: reaction 4) occurring simultaneously with methanol formation over the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, or could be formed from methanol decomposition, whereas at high pressure CO<sub>2</sub> is converted to methanol. Generally, in the methanol synthesis (reaction 1) from CO<sub>2</sub> hydrogenation, the reverse water gas shift (RWGS: reaction 4) also occurs simultaneously. Therefore, reactions 1 and 4 make the total reaction system of methanol synthesis.



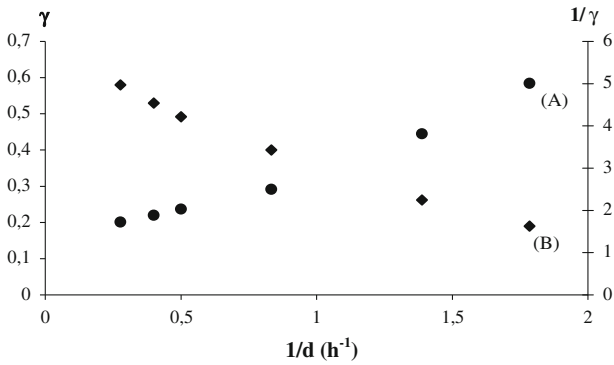
The literature suggests two possible reaction pathways for CH<sub>3</sub>OH synthesis from CO<sub>2</sub> and H<sub>2</sub> over the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst: (i) Formate route, where the reaction proceeds through the formation of formate (HCOO), dioxomethylene (H<sub>2</sub>COO), formaldehyde (CH<sub>2</sub>O), methoxy (CH<sub>3</sub>O) and the final product, CH<sub>3</sub>OH [24–26]. This species was commonly detected in experiments [26, 27]. (ii) The pathway involves the reverse water–gas–shift (RWGS, reaction 4) reaction, where CO<sub>2</sub> is first converted to CO which is then hydrogenated to form methanol (reaction 2). In Order to obtain more insight into the real route to methanol in the CO<sub>2</sub>/H<sub>2</sub> reaction, we studied the variation of the ratio  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$ , or its reciprocal  $1/\gamma$ , as a function of the contact time  $1/d$ . In effect, depending upon involved reaction paths, as the contact time tends to zero,  $\gamma$  should tend towards a finite value for the parallel reactions (Reaction 1), towards zero for the first type of successive reactions (Reaction 2) or towards infinity for the second type of successive reactions (Reaction 3). The obtained results show a great influence of the pressure on the reaction mechanisms. Indeed, as illustrated in Figs. 2, 3, 4 and 5 for the experiments carried out at P = 20, 28, 35 and 75 bar, the behavior of the ratio  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  as a function of the contact time depends strongly on the working pressure.



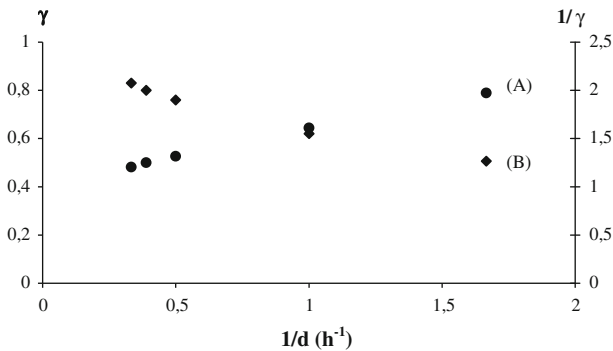
**Fig. 2** Variation of the ratio **a**  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  and **b**  $1/\gamma = [\text{CO}]/[\text{CH}_3\text{OH}]$  as a function of contact time  $1/d$  at 20 bar and 230 °C for the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>



**Fig. 3** Variation of the ratio **a**  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  and **b**  $1/\gamma = [\text{CO}]/[\text{CH}_3\text{OH}]$  as a function of contact time  $1/d$  at 28 bar and 230 °C for the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$



**Fig. 4** Variation of the ratio **a**  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  and **b**  $1/\gamma = [\text{CO}]/[\text{CH}_3\text{OH}]$  as a function of contact time  $1/d$  at 35 bar and 230 °C for the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$



**Fig. 5** Variation of the ratio **a**  $\gamma = [\text{CH}_3\text{OH}]/[\text{CO}]$  and **b**  $1/\gamma = [\text{CO}]/[\text{CH}_3\text{OH}]$  as a function of contact time  $1/d$  at 75 bar and 230 °C for the  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$

Two domains of pressure are to be noted:

- (i) Up to 28 bar,  $\gamma$  increases sharply as  $1/d$  tends towards zero (Figs. 2 and 3, curve A) whereas  $1/\gamma$  tends towards zero (Figs. 2 and 3, curve B). This implies a reaction mechanism of the type represented in Reaction 3.
- (ii) From 35 bar,  $\gamma$  tends towards a finite value as  $1/d$  tends towards zero (Figs. 4 and 5, curve A) whereas  $1/\gamma$  tends towards a finite value also (Figs. 4 and 5, curve B).

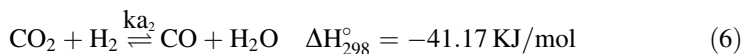
Thus, it appears that carbon dioxide is the immediate precursor of methanol in the  $\text{CO}_2/\text{H}_2$  reaction whatever the working pressure.

### Thermodynamic equilibrium

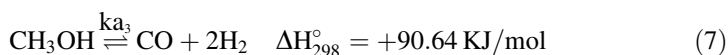
At higher pressures, methanol selectivities from carbon dioxide increased with increasing pressure over  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst. This tendency can be explained by the thermodynamic equilibrium for the related reaction. In particular, methanol synthesis over Cu-based catalysts proceeds exclusively via  $\text{CO}_2$  hydrogenation and can be described by a reaction network involving the synthesis of methanol (5):



Simultaneously with methanol synthesis, the reverse water–gas shift reaction (RWGS) takes place depending on the reaction conditions (6):



The possible secondary reaction is (7):



Methane is the most thermodynamically favored product, and is generally undesirable economically (8):



The equilibrium constants,  $k_{a1}$ , and  $k_{a2}$  for reactions 1 and 2, were calculated from well-known thermodynamic relations and expressed in the following forms literature [28, 29]:

$$k_{a1} = k_{a2} \exp \left[ 22.225 + \frac{9143.6}{T} - 7.492 \ln T + 4.076 \times 10^{-3} T - 7.161 \times 10^{-8} T^2 \right]$$

where  $k_{a1}$  is in  $\text{atm}^{-2}$ , and

$$k_{a2} = \exp \left[ 13.148 + \frac{5693}{T} - 1.07 \ln T + 5.44 \times 10^{-4} T - 1.125 \times 10^{-7} T^2 + \frac{49170}{T^2} \right]$$

The  $k_a$  is a function of temperature only, while  $K_\phi$  is a function of both temperature and pressure. This P, T dependence of  $K_\phi$  is taken from Klier [8] in the following form,

$$K_{\phi 1} = (1 - A_1 P)(1 - A_2 P)$$

$$K_{\phi 2} = 1/(1 - A_2 P)$$

$$K_{\phi 3} = K_{\phi 2}/K_{\phi 1} = 1/(1 - A_1 P)$$

where  $A_1 = 1.95 \times 10^{-4} \exp\left(\frac{1703}{T}\right)$  and  $A_2 = 4.24 \times 10^{-4} \exp\left(\frac{1107}{T}\right)$

The corresponding equilibrium equations are:

$$K_{P1} = \frac{(P_{\text{CH}_3\text{OH}})(P_{\text{H}_2\text{O}})}{(P_{\text{CO}_2})(P_{\text{H}_2})^3} \quad (9)$$

$$K_{P2} = \frac{(P_{\text{CO}})(P_{\text{H}_2\text{O}})}{(P_{\text{CO}_2})(P_{\text{H}_2})^3} \quad (10)$$

$$K_{P3} = \frac{(P_{\text{CO}})(P_{\text{H}_2})^2}{(P_{\text{CH}_3\text{OH}})} \quad (11)$$

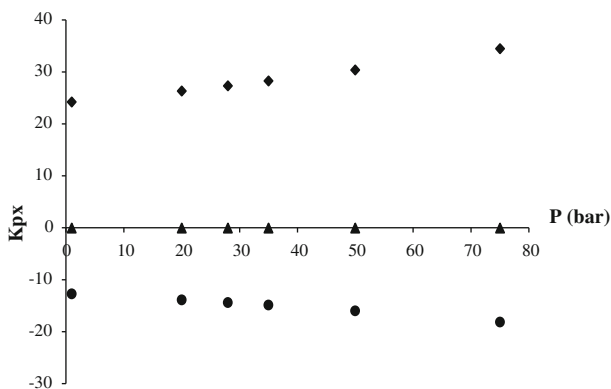
Here, Eq. 7 represents a linear combination of Eqs. 5 and 6, and thus the thermodynamic evaluation depends on the analysis of Eqs. 5 and 6, although Eq. 7 can shed light on the CO/CH<sub>3</sub>OH distribution [ $k_{p3} = k_{p2}/k_{p1}$ ], where

$$k_{p1} = ka_1/k_{\phi 1}; \quad k_{\phi 1} = \phi_{\text{CH}_3\text{OH}} \phi_{\text{H}_2\text{O}} / \phi_{\text{CO}_2} \phi_{\text{H}_2}^3$$

$$k_{p2} = ka_2/k_{\phi 1}; \quad k_{\phi 2} = \phi_{\text{CO}} \phi_{\text{H}_2\text{O}} / \phi_{\text{CO}_2} \phi_{\text{H}_2}$$

$$k_{p3} = k_{p2}/k_{p1}; \quad k_{\phi 3} = k_{\phi 2}/k_{\phi 1} = \phi_{\text{CO}} \phi_{\text{H}_2} / \phi_{\text{CH}_3\text{OH}}$$

Fig. 6 shows the experimental and equilibrium constants in carbon dioxide hydrogenation as a function of reaction pressure over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. This figure clearly shows that equilibrium constants of methanol production from carbon dioxide (5) increased with increasing pressure (Fig. 6a), where CO production by reverse water–gas shift reaction (6) decreased with increasing pressure owing to the equilibrium (Fig. 6b). Under such conditions, CO<sub>2</sub> becomes a reactant of reaction 1 and a product in reaction 2. Hence the CO equilibrium constant becomes a negative



**Fig. 6** Experimental and equilibrium constants in CO<sub>2</sub> hydrogenation as a function of pressure. **a** CO<sub>2</sub> + 3H<sub>2</sub> ↔ CH<sub>3</sub>OH + H<sub>2</sub>O, **b** CO<sub>2</sub> + H<sub>2</sub> ↔ CO + H<sub>2</sub>O, **c** CH<sub>3</sub>OH ↔ CO + 2H<sub>2</sub>



value, which means that some CO is converted into CO<sub>2</sub>. Under such a condition, methanol decomposition to carbon monoxide (7) should also be in equilibrium (Fig. 6c). High temperature favors the endothermic reactions 6 and 7, whereas a high pressure favors reaction 5. Moreover, the methanol equilibrium constant is always higher, while the equilibrium constant of CO shows the opposite trend.

At a pressure of 75 bar, methanol selectivity reached 47%. This tendency can be explained by Le Chatelier's principle as the methanol synthesis reaction 5 proceeds under a volume contraction. Higher methanol selectivities are therefore obtained at higher pressures (Fig. 1).

The reaction between CO<sub>2</sub> and H<sub>2</sub> is exothermic. Reaction 5 is of interest for the methanol production from CO<sub>2</sub>. Reaction 6 is competitive with this for the CO<sub>2</sub> conversion and it produces undesired CO, reducing the overall effectiveness of the process. Therefore, it is important to study the conversion of CO<sub>2</sub> and the methanol/CO selectivity. The selectivity of methanol/CO increases as the pressure increases, which shows that the impact of competitive reaction 6 is very insignificant.

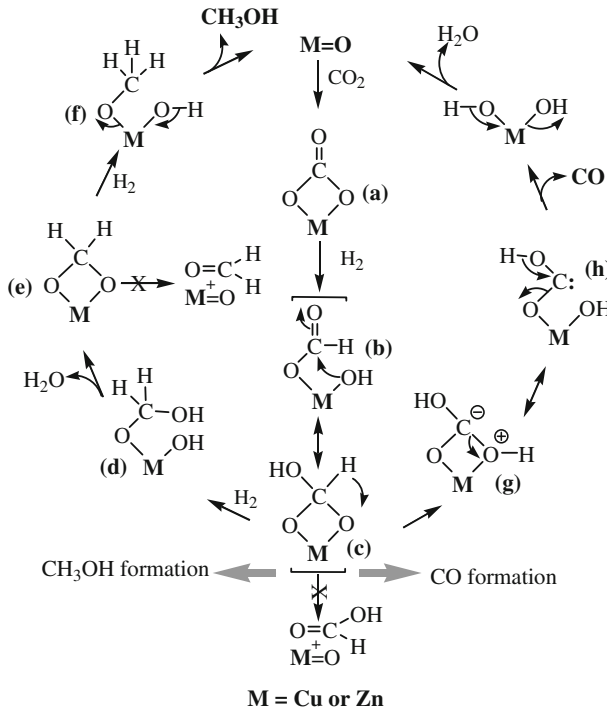
Methanol selectivity increases with the pressure and decreases with the temperature. Thus, CO<sub>2</sub> produces mainly CO at low pressures and high temperature. It should be noticed that carbon dioxide can be hydrogenated at lower temperatures than carbon monoxide, which suggests that methanol can be formed directly from carbon dioxide at least in the lower temperature range. Methanol formation from carbon dioxide is always accompanied by carbon monoxide production. However, recent mechanistic studies of carbon dioxide hydrogenation over copper catalysts indicate that carbon dioxide is the main carbon source of methanol even from a carbon dioxide and carbon monoxide mixture [30, 31]. The experimental data were in fairly good agreement with the proposed mechanism.

### Mechanism and pathway of CO<sub>2</sub> hydrogenation

The formation of methanol can be described by an adsorption–desorption mechanism. Previous studies on CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> [32–34] suggest that the formate and carbonate unidentate or bidentate species [35, 36] were formed when the Cu-based catalyst was exposed to CO<sub>2</sub>/H<sub>2</sub> or CO/CO<sub>2</sub>/H<sub>2</sub> at low temperatures, and carbonate species were transformed to stable formate species by hydrogenation which are then reduced to methoxy [37] and further hydrogenated to methanol. On the other hand, Fujitani et al. [38], who worked on the Pd/Ga<sub>2</sub>O<sub>3</sub> catalyst, reported that surface formate and methoxy species were observed during CO and CO<sub>2</sub> hydrogenation. In contrast, the reaction pathway was clearly different between CO and CO<sub>2</sub> hydrogenation over the Pd/ZrO<sub>2</sub> catalyst. That is, surface formaldehyde and methoxy species were observed as intermediates during CO hydrogenation, while surface formate and methoxy species were detected during CO<sub>2</sub> hydrogenation.

The intermediates of CO<sub>2</sub> hydrogenation were carbonate (CO<sub>3</sub>) formate (HCOO), carboxylate (HCOOH), methylenebisoxo (H<sub>2</sub>COO) and methoxy (H<sub>3</sub>C–O) species. This species was commonly detected in experiments [35–38].

Based on the observations noted above and in our experimental results, two mechanisms have been suggested to explain the formation of methanol and carbon



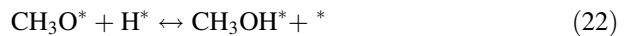
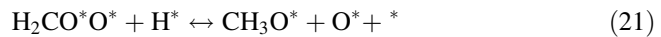
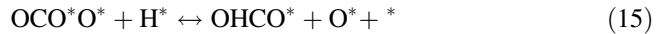
**Fig. 7** Possible reaction pathways for CO<sub>2</sub> hydrogenation on M=O oxide

monoxide over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. In the first mechanism (Fig. 7), adsorbed CO<sub>2</sub> reacts on the surface M=O oxide with dissociatively adsorbed hydrogen in a series of hydrogenation steps to give methanol. Thus, the results suggest that adsorbed species were formed on single metal, M site.

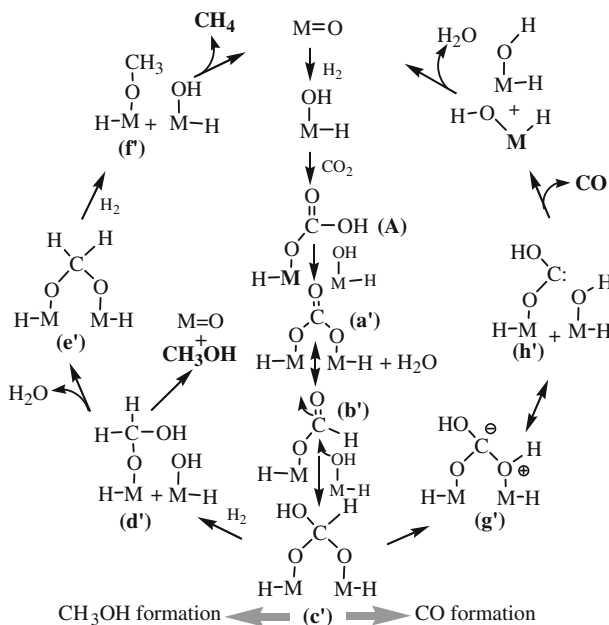
In this scheme, methanol synthesis proceeds by prior formation of the carbonate (bidentate chelating) (a) adsorption species on the metal oxide, followed by hydrogenation of carbonate to the formate unidentate (b). The formate monodentate (b) species is stable only at low temperatures (<200 °C) and is converted to the stable adsorbed bidentate chelating formic acid (c) through the reaction of C=O group of formate (c) with OH groups adjacent [39]. The H(HO)COO (c) species is transformed easily to other intermediate such as H<sub>2</sub>(OH)C–O (d) in the presence of hydrogen. The dehydration of H<sub>2</sub>(OH)C–O (d) intermediate would give H<sub>2</sub>COO(e), which reacts with H<sub>2</sub> to produce methoxy H<sub>3</sub>C–O (f) and methanol [40].

The intermediates H(HO)COO (c) and H<sub>2</sub>COO (e) are formic acid and formaldehyde in the adsorbed state respectively over M=O oxide. Formic acid and formaldehyde are not observed under our reaction conditions, we suggest that these compounds are adsorbed strongly on the surface of catalyst and transformed easily to other intermediates such as methylenebisoxo H<sub>2</sub>COO (e) and methoxy H<sub>3</sub>C–O (f) respectively in the presence of hydrogen.

$\text{CH}_3\text{OH}$  formation requires several steps through the formate pathway leading to the various adsorbed species [41] as follows:



In the second mechanism (Fig. 8), the first step is the insertion of  $\text{CO}_2$  into a surface OH group with formation of surface bicarbonate (A). The  $\text{HOCOO}$  (A) intermediate can react with the surface hydroxyl group leading to the bidentate

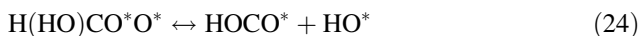


**Fig. 8** Possible reaction pathways for  $\text{CO}_2$  hydrogenation on MH-OH

carbonate (a') and H<sub>2</sub>O. This is followed by further hydrogenation steps to give a surface H<sub>2</sub>(HO)CO (d') species, from which methanol is formed. That adsorbed bidentate species was formed on the catalyst surface (Fig. 8) between two M sites.

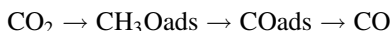
Both CH<sub>3</sub>OH and CO are produced dominantly via the formate pathway as shown in Figs. 7 and 8. From the formate pathway, the formation of CO probably passes through the intermediate hydroxycarbene HO–C–Oads (h) which can dissociate into CO and H<sub>2</sub>O via dehydration [42].

This clearly shows that the H(OH)COO (c) intermediate transfers hydrogen from carbon to a neighboring adsorbed oxygen atom, which inserts in the M–O–C bond leading to the formation of a stable carbanion (g) and transformed into adsorbed hydroxyl group and hydroxycarbene HO–C–O (h) [43] which is responsible for CO formation as shown in following pathway:



It appears that the adsorbed formic acid H(OH)COO (c) is the key intermediate in this reaction. It is responsible for both methanol and carbon monoxide formation. At low pressure, it is transformed predominantly into CO, while at high pressure it is transformed mainly into CH<sub>3</sub>OH.

On the other hand, at low pressure CO seems to stem from the decomposition of methanol re-adsorbed as a methoxy species on a different site:



Whereas at high pressure, it appears to be produced directly from CO<sub>2</sub>, in good agreement with thermodynamics which does not favor the decomposition of methanol into carbon monoxide.

## Conclusion

The effect of pressure on CO<sub>2</sub> hydrogenation into methanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst has been investigated.

Our results show a great influence of the operating pressure on the kinetics of the CO<sub>2</sub>/H<sub>2</sub> reaction on CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. The selectivity of methanol increases with the increase of pressure, suggesting that methanol is the primary product and is formed directly from CO<sub>2</sub>.

CO<sub>2</sub> hydrogenation to methanol over M=O centers shows a consecutive pathway at low pressure (<35 bar) and parallel pathway at high pressure (>35 bar).

Both CH<sub>3</sub>OH and CO are produced dominantly via the formate pathway, and the CO formation proceeds through a hydroxycarbene intermediate.

The thermodynamic analysis shows that the reaction of methanol formation from CO<sub>2</sub> is favored at high pressure rather than the reverse water–gas shift reaction (RWGS).

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