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Mechanism of CO formation in reverse water–gas shift reaction over Cu/Al_2O_3 catalyst

Ching-Shiun Chen, Wu-Hsun Cheng * and Shou-Shiun Lin

Department of Chemical and Materials Engineering, Chang Gung University, Tao-Yuan 333, Taiwan, ROC

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The mechanism of the reverse water–gas shift reaction over a Cu catalyst was studied by CO_2 hydrogenation, temperature-programmed reduction of the Cu catalyst and pulse reaction with QMS monitoring. In comparison with the reaction of CO_2 alone, hydrogen can significantly promote the CO formation in the RWGS reaction. The formate derived from association of H_2 and CO_2 is proposed to be the key intermediate for CO production. Formate dissociation mechanism is the major reaction route for CO production. Cu(I) species were formed from the oxidation of Cu^0 associated with CO_2 dissociation.

Keywords: reverse water–gas shift, temperature-programmed reduction, copper catalysts, formate mechanism

1. Introduction

Carbon dioxide, mostly generated from combustion, is the most important greenhouse gas, which causes global warming. The increase of carbon dioxide concentration will strongly influence the equilibrium condition of weather and environment on earth. It has been important to reduce the release of CO_2 and recycle CO_2. Conversion of CO_2 to CO by catalytic hydrogenation has been recognized as one of the most promising processes for CO_2 utilization. In industry, synthesis gas, H_2 and CO, can be used to produce long-chain hydrocarbons via the Fischer–Tropsch reaction [1,2]. The reverse water–gas shift reaction is one of the available methods for production of CO.

The mechanisms of the water–gas shift (WGS) and reverse water–gas shift (RWGS) reactions over Cu-based catalysts have been discussed, but they are still controversial [3–14]. Two models, the redox and formate decomposition mechanisms, were proposed to explain the mechanism of CO formation in the RWGS reaction. For the redox mechanism, the concept of the oxidation and reduction cycle was suggested. CO_2 oxidized Cu^0 and generated CO. H_2 reduced Cu(I) to Cu^0 and formed H_2O [3–5]. CO can be produced from CO_2 alone over Cu powder or Cu/ZnO catalyst. The reactant, H_2, plays a role of reducing reagent for reduction of Cu_2O. In the other model, the formate decomposition mechanism, it was suggested that CO could be formed from decomposition of a formate intermediate derived from hydrogen associated with CO_2 [10,12]. It has been reported that CO production rate increased with the concentration of formate species on Cu.

The purpose of this paper is to study the pathway of CO formation in the RWGS reaction in more detail. The mechanism of the RWGS reaction was studied on a Cu/Al_2O_3 catalyst by using CO_2 hydrogenation, temperature-programmed reduction of the Cu catalyst and pulse reaction with QMS monitoring. Both feeds of CO_2 alone and H_2/CO_2 mixture were used to compare the difference in catalytic activity and TPR profiles of the catalyst for post-reaction. Our experimental results will be used to examine the redox and formate decomposition pathways and provide a reasonable reaction mechanism.

2. Experimental

A 10 wt% Cu/Al_2O_3 catalyst was prepared by impregnating Al_2O_3 with an aqueous solution of $Cu(NO_3)_2{\cdot}2.5H_2O$. The catalyst was dried at 80 °C and calcined in flowing air at 250 °C for 5 h before reduction treatment.

Carbon dioxide hydrogenation was carried out in a fixed-bed reactor at atmospheric pressure. Samples of 1 g Cu/Al_2O_3 were reduced in flowing H_2 at 500 °C for 5 h. The products were analyzed by gas chromatography with a 6 ft Porapak-T column and a thermal conductivity detector.

The pulse reaction of CO_2 was performed in a fixed-bed reactor connected with a quadrupole mass spectrometer. A sample of 1 ml CO_2 was fed by a sampling valve into a He or H_2 stream at 60 ml/min, then passed over the catalyst bed at 773 K. The spectra were collected with a VG smart IQ + 300D mass spectrometer. The CO and CO_2 in the pulse reaction were admitted into the mass vacuum chamber with He or H_2 through a leak valve at a pressure of about 5×10^{-7} Torr. The base pressure in the chamber was typically 2×10^{-9} Torr.

Temperature-programmed reduction of catalysts were performed at atmospheric pressure in a conventional flow system. A sample of 0.6 g catalyst was placed in a U-shaped tube reactor and heated in 5% H_2/N_2 mixed gas

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* To whom correspondence should be addressed.

stream flowing at 30 ml/min at a heating rate of 10 °C/min from 25 to 400 °C.

3. Results

Figure 1 shows the results of CO production versus time in the CO_2 dissociation and RWGS reaction over the Cu/Al_2O_3 catalyst at 773 K. Pure CO_2 at 200 ml/min was fed over the freshly reduced Cu/Al_2O_3 catalyst to produce CO (figure 1(a)). Initially, CO is rapidly formed, but its production rate decreases dramatically with time to almost zero within 20 min. CO was formed from CO_2 dissociation. The decay of catalytic activity is due to oxygen adatoms from CO_2 dissociation associated with the formation of Cu_2O from Cu. After CO_2 dissociation over Cu/Al_2O_3 for 1 h at 773 K, the Cu catalyst without reduction treatment was exposed to a $H_2/CO_2 = 1/9$ stream (figure 1(b)). In comparison with the CO formation in figure 1(a), figure 1(b) reveals an initial rate for CO production about three times that from CO_2 alone. The curve of figure 1(b) appears to reach steady state after 20 min with about 20% decaying of catalytic activity. The same H_2/CO_2 stream with 1/9 ratio was also passed over the freshly reduced Cu/Al_2O_3 catalyst (figure 1(c)). The initial rate of CO production slightly increased compared to that of figure 1(b). The tendency of CO production with time in figure 1(c) is almost the same as that in figure 1(b) after 10 min.

The TPR profiles of oxidized copper catalysts undergoing different treatments are shown in figure 2. Figure 2(a) is the TPR profile of the CuO/Al_2O_3 catalyst treated by air at 523 K for 5 h without reduction treatment. The typical single peak of hydrogen consumption appears at about 523 K, indicating a one-stage reduction mechanism. After the reduced catalyst was oxidized by CO_2 alone for 1 h at 773 K, the reduction peak appeared at 423 K, as shown in figure 2(b). The peak at 423 K belongs to reduction of Cu(I) species. For further investigation of oxidation state of Cu under RWGS reaction, reduced Cu catalysts were in oxidized by CO_2 for 1 h at 773 K, and then exposed to H_2/CO_2 with 1/9 ratio for 1 and 60 min at 773 K, respectively. Figure 2 (c) and (d) shows TPR profiles of the catalysts. In figure 2(c), two kinds of peaks appear at 447 and 488 K. In comparison with figure 2(b), the peak of Cu_2O reduction shifted to higher temperature. A shoulder peak appearing at 488 K is assigned to the reduction of CuO species. In figure 2(d), the TPR profile reveals two peaks at 467 and 490 K. The amount of CuO increased with reaction time. On the other hand, the amount of Cu_2O decreased. Obviously, the reduced Cu catalyst can be easily oxidized to Cu_2O by CO_2, but the H_2/CO_2 mixture did not reduce Cu_2O to Cu during reaction. In contrast, the H_2/CO_2 mixture further oxidized Cu_2O to CuO. Figure 2(e) shows the TPR profile of the reduced Cu catalyst treated by H_2/CO_2 with 1/9 ratio at 500 °C for 1 h. A single peak at 467 K was found. This peak belonging to reduction of Cu_2O indicates that the H_2/CO_2 mixture can oxidize Cu^0 to Cu^+ during reaction.

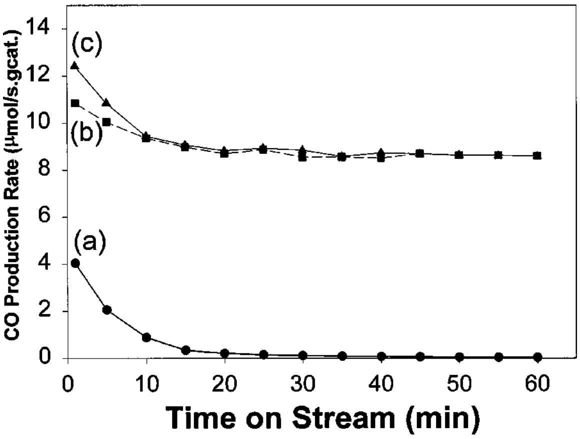

Figure 1. The dependence of CO production on time for CO_2 or H_2/CO_2 with 1/9 ratio reaction over Cu/Al_2O_3 at 773 K: (a) 200 ml/min CO_2 was passed through freshly reduced Cu/Al_2O_3 catalyst for 1 h; (b) following step (a), 200 ml/min H_2/CO_2 was fed over the catalyst without any further treatment; (c) 200 ml/min H_2/CO_2 was passed over freshly reduced Cu/Al_2O_3 catalyst.

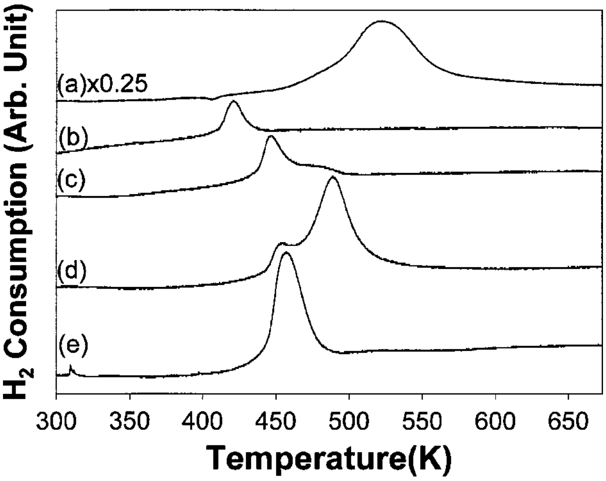

Figure 2. TPR profiles of oxidized copper catalysts by different treatments: (a) CuO catalyst without reduction treatment; (b) reduced Cu/Al_2O_3 catalyst was oxidized by 200 ml/min CO_2 alone at 773 K for 1 h; (c) after step (b) the catalyst was exposed to 200 ml/min H_2/CO_2 at 773 K for 1 min; (d) after step (b) the catalyst was exposed to 200 ml/min H_2/CO_2 at 773 K for 60 min; (e) the freshly reduced Cu/Al_2O_3 catalyst was exposed to 200 ml/min H_2/CO_2 at 773 K for 60 min.

Figure 3(a) illustrates the dependence of initial rate of CO formation on the mole fraction of H_2 in the H_2/CO_2 feed. With increasing H_2 concentration, CO production rate passes over a volcano showing the maximum value at $H_2/CO_2 = 1$. In comparison with CO produced by CO_2 alone, it is clear that H_2 can significantly enhance the formation of CO from CO_2. A small amount of methane was formed at high mole fraction, as shown in figure 3(b). No methane was found below a hydrogen mole fraction of 0.5.

Figure 4 shows the conversion of CO_2 in the pulse reaction by sampling 1 ml CO_2 in He or H_2 stream. Figure 4(a) shows low CO_2 conversion in He stream in four times of CO_2 sampling. The partial oxidation by N_2O gas can be used to determine the surface area of

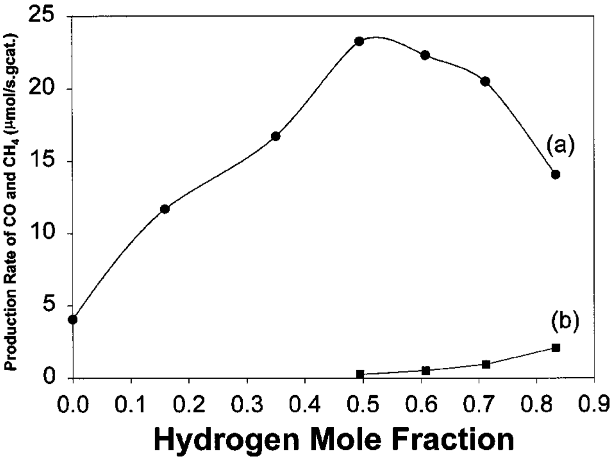

Figure 3. The dependence of initial CO and CH_4 production rate on hydrogen concentration in a H_2/CO_2 mixture flowing at 200 ml/min over a Cu/Al_2O_3 catalyst at 773 K: (a) CO production rate; (b) CH_4 production rate. The mole fractions of H_2 and CO_2 in the feed are defined to be $X(H_2) = [H_2]/([H_2] + [CO_2])$ and $X(CO_2) = 1 - X(H_2)$, respectively.

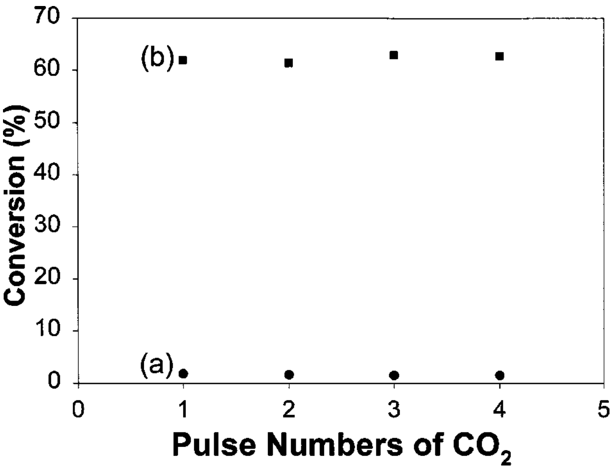

Figure 4. The conversion of CO_2 to CO at 773 K over a Cu/Al_2O_3 catalyst with 1 ml pulse feed in (a) He and (b) H_2 stream at 60 ml/min.

Cu catalysts [15]. The amount of surface atoms of the Cu catalyst was calculated to be 4.53×10^{20} atoms/g-cat. The $O_{(ad)}$/surface Cu was calculated to be only about 10% after the dissociation of 4 ml CO_2 by four pulses over Cu. When the same reaction was carried out in H_2 stream, CO_2 conversion was significantly increased due to the presence of H_2. This is taken as further evidence that the major role of hydrogen is not a reducing reagent for the reduction of Cu_2O. Instead, it largely participated in the reaction to form CO *via* some intermediates.

4. Discussion

The redox mechanism for the RWGS reaction has been simply modeled by the following scheme:

$$CO_2 + 2Cu \rightarrow Cu_2O + CO$$
$$H_2 + Cu_2O \rightarrow Cu^0 + H_2O$$

It indicates that Cu^0 atoms provide active sites to dissociate CO_2, while the reduction of the oxidized Cu catalyst has to be faster than the oxidation process [3–5]. Hydrogen is proposed to be a reducing reagent without direct participation for formation of intermediates in the RWGS reaction. However the redox mechanism described above cannot be completely used to explain the reaction behavior from our experimental results. Indeed, CO_2 dissociation may take place on the Cu^0 surface to form CO and Cu_2O as evidenced in figures 1 and 2, but it is not the sole source of CO for the RWGS reaction. In figure 1, although the catalytic activity of Cu decayed significantly in CO_2, the CO yield could be largely increased by adding a small amount of hydrogen, even if Cu(I) was not reduced to Cu^0 by hydrogen during reaction. The TPR profile of the Cu catalyst in figure 2 has demonstrated that Cu(I) and Cu(II) may exist under H_2/CO_2 stream and provide high catalytic activity. Surprisingly, the activity of the Cu catalyst oxidized by CO_2 is very close to that of the reduced Cu catalyst in a H_2/CO_2 stream with 1/9 feed ratio. The pulse reaction of CO_2 to CO provides strong evidence for the promotion effect of hydrogen in the RWGS reaction. Figure 4(a) shows very low CO_2 conversion. Due to low $O_{(a)}$ coverage, residual oxygen atoms from 4 ml CO_2 dissociation did not decrease the catalytic activity of Cu after four times pulse reaction in He. On the other hand, H_2 stream dramatically increased CO production from 1 ml CO_2 feed.

For CO_2 dissociation, as figures 1 and 2 show, the reaction has to take place on Cu^0 active sites, while the formation of Cu_2O will inhibit the reaction rate due to disappearance of Cu^0 sites. In figure 1(a), the amount of Cu(I) species from the catalyst oxidized by CO_2 for 1 h was calculated to be about 36% of surface copper atoms. When RWGS reaction takes place on the Cu_2O catalyst, this oxidized catalyst was not completely reduced by hydrogen in contrast to previous papers [3–5]. Therefore, the high reaction activity over Cu_2O in figure 1(b) should mostly come from hydrogen promotion. By comparing figure 1 (b) and (c), the difference of initial catalytic activity between oxidized catalyst and freshly reduced catalyst is proposed to be due to CO_2 dissociation on the reduced catalyst. CO_2 dissociation may be inhibited in the case of figure 1(b) because oxidized Cu was not reduced by hydrogen. Iwasawa reported the similar results that hydrogen promotes the rate of RWGS reaction over ZnO [10]. Formate species was suggested to be the reaction intermediate. The decomposition rate of formate was promoted eight to ten times by hydrogen. Bell also indicated the coexistence of the mechanisms of redox and formate for potassium-promoted Cu/SiO_2 catalysts [16]. Hydrogenation of CO_2 was carried out on polycrystalline Cu and Cu(110) indicating that the copper surface was covered by almost a full monolayer of formate after reaction [9,17]. On the other hand, the catalyst of Cu/SiO_2 promoted with ZrO_2 was also used to study the mechanisms of methanol synthesis and RWGS reactions. Parallel pathways for CO formation and methanol synthesis were suggested. Formate species was the main common intermediate that results in CO formation by decomposition and/or methanol synthesis by hydrogenation [18]. The bicarbonate species formed from adsorbed CO_2 were converted to formate species due to the presence of hydrogen. It was interesting that the rate of RWGS reaction was decreased with ZrO_2 content, but copper surface area was not influenced by ZrO_2 addition. Considering the results described above, if the model of redox mechanism dominates in CO formation, the rate should strongly depend on surface area of copper. However, the phenomenon was not present [18]. Obviously, a redox mechanism cannot completely explain all phenomena for RWGS.

Based on our experimental results, we deduce that CO formation strongly depends on hydrogen participation. The role of hydrogen may be associated with adsorbed CO_2 to form intermediates for the RWGS reaction. Formate species is reasonably proposed to be the dominant intermediate to form CO *via* a decomposition process. On the other hand, TPR profiles provide strong evidence for formation of Cu(I) species that come from reduced Cu catalyst treated by CO_2 and/or H_2–CO_2. The number of atoms in copper surfaces can be determined by using TPR of Cu oxidized by N_2O [15]. The extent of Cu oxidized by CO_2 and/or H_2–CO_2 mixture was estimated to be about 0.36–0.4 monolayer. Therefore, Cu^0 and Cu^+ atoms were proposed to coexist in the catalyst surface. Cu catalyst with a small amount of Cu^+ species has been reported to enhance the rate of methanol synthesis [19]. Methanol synthesis and RGWS reaction have been demonstrated to be competitively parallel pathways over Cu catalyst. The roles of Cu^0 and Cu^+ are possibly to dissociate H_2 and stabilize formate species, respectively [19]. The effect of Cu^0 and Cu^+ described above can also be used to explain CO formation in the RWGS reaction.

5. Conclusion

The experimental results indicate that CO is largely formed from a key intermediate. The key intermediate is reasonably proposed to be the formate species from association of H atoms and CO_2. Based on the results of the RWGS reaction, hydrogen participation is the important factor for CO formation from CO_2. CO production can be significantly enhanced by hydrogen over Cu catalyst. TPR profiles show that Cu_2O is formed during RWGS reaction and/or CO_2 dissociation due to oxygen adatoms reacting with Cu^0.

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References

[1] T. Riedel, M. Claeys, H. Schulz, G. Schaub, S.S. Nam, K.W. Jun, M.J. Choi, G. Kishan and K.W. Lee, Appl. Catal. 186 (1999) 201.
[2] S.S. Nam, H. Kim, G. Kishan, M.J. Choi and K.W. Lee, Appl. Catal. 179 (1999) 155.
[3] K.H. Ernst, C.T. Campbell and G. Moretti, J. Catal. 134 (1992) 66.
[4] S.I. Fujita, M. Usui and N. Takezawa, J. Catal. 134 (1992) 220.
[5] M.J.L. Ginés, A.J. Marchi and C.R. Apesteguía, Appl. Catal. 154 (1997) 155.
[6] M.S. Spencer, Catal. Lett. 32 (1995) 9.
[7] J. Nakamura, J.M. Campbell and C.T. Campbell, J. Chem. Soc. Faraday Trans. 86 (1990) 2725.
[8] E. Iglesia and M. Boudart, J. Catal. 81 (1983) 214.
[9] J. Yoshihara, S.C. Parker, A. Schafer and C.T. Campbell, Catal. Lett. 31 (1995) 313.
[10] T. Shido and Y. Iwasawa, J. Catal. 140 (1993) 575.
[11] C.T. Campbell and K.A. Daube, J. Catal. 104 (1987) 109.
[12] Q. Sun, C.W. Liu, W. Pan, Q.M. Zhu and J.F. Deng, Appl. Catal. 171 (1998) 301.
[13] T. Salmi and R. Hakkarainen, Appl. Catal. 49 (1989) 285.
[14] D.C. Grenoble, M.M. Estadt and D.F. Ollis, J. Catal. 67 (1981) 90.
[15] C.J.G. van der Grift, A.F.H. Wielers, B.P.J. Joghi, J.V. Beijnum, M.E. Boer, M.V. Helder and J.W. Geus, J. Catal. 131 (1991) 178.
[16] D.B. Clarke and A.T. Bell, J. Catal. 154 (1995) 314.
[17] J. Yoshihara and C.T. Campbell, J. Catal. 161 (1996) 776.
[18] I.A. Fisher, H.C. Woo and A.T. Bell, Catal. Lett. 44 (1997) 11.
[19] J. Nakamura, I. Nakamura, T. Uchijima, Y. Kanai, T. Watanabe, M. Saito and T. Fujitani, Catal. Lett. 31 (1995) 325.