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Study on the mechanism of CO formation in reverse water gas shift reaction over Cu/SiO_2 catalyst by pulse reaction, TPD and TPR

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The mechanism of reverse water gas shift reaction over Cu catalyst was studied by pulse reaction with QMS monitoring, temperature programmed desorption (TPD) and temperature programmed reduction (TPR) of Cu/SiO_2 catalyst. The reduced and/or oxidized copper offered low catalytic activity for the dissociation of CO_2 to CO in the pulse reaction study with 1 ml volume of He/CO_2, but the rate of CO formation was significantly enhanced with H_2 participating in the reaction. The TPD spectra of CO_2 obtained by feeding H_2/CO_2 over copper at 773 K provided strong evidence of the formation of formate at high temperature. The formate derived from the association of H_2 and CO_2 is proposed to be the key intermediate for CO production. The formate dissociation mechanism is the major reaction route for CO production.

KEY WORDS: reverse water gas shift; temperature programmed desorption; Cu/SiO_2; formate mechanism.

1. Introduction

Synthesis gas, H_2 and CO, can be used in methanol synthesis to produce long-chain hydrocarbons *via* the Fischer–Tropsch reaction. The water gas shift (WGS) and reverse water gas shift (RWGS) reactions are mostly used in combination with steam reforming of hydrocarbons to adjust the H_2/CO ratio in the products [1,2]. Copper-based catalysts have been applied in the commercial process of WGS reaction and are also effective for the RWGS reaction [3,4]. On the other hand, the increase in carbon dioxide concentration will influence the equilibrium condition of weather and environment on earth. Conversion of CO_2 to CO by catalytic reactions has been recognized as a promising process for CO_2 utilization [5]. Currently, the CAMERE process has been developed to produce methanol [6,7]. CO_2 and H_2 are converted to CO and H_2O by the RWGS reaction, then the mixed gas of $H_2/CO/CO_2$ is used to synthesize methanol. A proper feed ratio of $H_2/CO/CO_2$ has been mentioned to enhance methanol synthesis [8]. The CAMERE process can provide the advantages of low cost in equipment and operation for methanol production [6].

The mechanism of the reverse water gas shift reaction has been discussed over Cu-based catalysts, but it has still been controversial [9–14]. Two models, redox and formate decomposition mechanisms, were proposed to explain the mechanism of CO formation in the RWGS reaction. 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 oxidized Cu catalyst has to be faster than the oxidation process [9–11]. Hydrogen was proposed to be only a reducing reagent without direct participation in the formation of intermediates in the RWGS reaction. However, the redox mechanism described above cannot be used to completely explain the reaction behavior from our experimental results [15]. The other model, the formate decomposition mechanism, suggested that CO could be formed from decomposition of formate intermediate, derived from the association of hydrogen with CO_2 [13,16]. It was reported that CO production rate increased with the concentration of formate species in Cu.

The goal of this paper is to study the mechanism of CO formation in the RWGS reaction in more detail. The RWGS reaction over Cu/SiO_2 catalyst was studied by pulse reactions with QMS monitoring and temperature programmed desorption (TPD). Both pulse reactions of CO_2 alone and an H_2/CO_2 mixture were used to compare the difference in catalytic activity. The TPD spectra of H_2/CO_2 adsorption at high temperature were compared with formic acid adsorbed on copper. Our experimental results will be used to examine the redox and formate decomposition pathways and provide a reasonable reaction mechanism.

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2. Experimental

The 10 wt% Cu/SiO_2 was prepared by impregnating Cab-O-Sil M-5 SiO_2 with an aqueous solution of $Cu(NO_3)_2$. The catalyst was dried at 353 K before pretreatment. The catalyst was calcined in air and reduced in pure H_2 at 773 K for 5 h, respectively, before reaction.

TPD spectra were collected with a quadruple mass spectrometer (VG smart IQ^+ 300D). The heating rate of TPD was 15 °C/min. Desorbed molecules were admitted into a vacuum chamber with He carrier through a leak valve at a pressure of about 3×10^{-7} torr. The based pressure in the chamber was typically 2×10^{-9} torr. He/CO_2 and H_2/CO_2 streams were fed over catalysts for the adsorption study. Pulse reaction was also performed in the TPD system. Samples of 1 ml CO_2 or H_2/CO_2 were fed by a sampling valve into an He stream at 100 ml/min, and passed over the catalyst bed containing 0.15 g catalysts. The molar ratio of H_2 to CO_2 was 1 in the H_2/CO_2 feed in this paper. Formic acid was dosed onto catalysts by injecting formic acid into the flowing He at 100 ml/min through a port located at the upstream of the reactor. A 1 μl syringe was used to perform the injections for liquid formic acid. This injection port is similar to that used in gas chromatography and was heated to 373 K to prevent the condensation of the sample. The CO_2 from formic acid decomposition was monitored at 44 amu by QMS. The mass spectrum has been corrected by subtracting the contribution of the fragments of formic acid.

Temperature programmed reduction of catalysts was performed at atmospheric pressure in a conventional flow system. A sample of 0.06 g catalyst was placed in a U-shaped tube reactor and heated in a 5% H_2/N_2 mixed gas stream, flowing at 30 ml/min at a heating rate of 10 °C/min from 300 K to 673 K. The surface area of copper catalyst can be determined by using TPR of Cu oxidized by N_2O [17]. The Cu/SiO_2 catalyst used in this study had 55 m^2/g Cu surface area.

3. Results

Figure 1 shows the pulse reactions of CO_2 converted to CO, which were performed by sampling 1 ml gas onto 0.05g Cu/SiO_2 at 773 K in 100 ml/min He stream. Figure 1(a) shows the specific activity of the dissociation reaction of 1 ml He/CO_2 (1 : 1) on reduced Cu/SiO_2. The catalytic activity was low for each pulse. CO production only slightly decreased with pulse numbers due to oxidation of Cu/SiO_2. The used catalyst of figure 1(a) was reduced by H_2 for 30 min at 773 K after He/CO_2 reactions; then this catalyst was used to react immediately with 1 ml H_2/CO_2 as figure 1(b) showed. CO production significantly increased more than three times by adding H_2. The same measurements of figure 1(a) and (b) were repeated on the 0.05 g oxidized Cu/SiO_2, which was obtained by passing pure CO_2 (100 ml/min) through reduced Cu/SiO_2 for 1 h at 773 K. The pulse reactions of 1 ml CO_2 of figure 1(c) reveal very low CO production approaching zero conversion. Obviously, the CO formation rate from CO_2 dissociation was strongly inhibited by the oxidized Cu surface. Nevertheless, CO production was boosted by the H_2/CO_2 mixture, even if these pulse reactions were performed on a strongly oxidized Cu surface.

Figure 2 shows the TPD spectra for CO_2 as a function of CO_2 exposure on 0.15 g reduced 10% Cu/SiO_2. The single CO_2 peak at 320 K was independent of coverage on the Cu/SiO_2 catalyst. Many papers have reported the

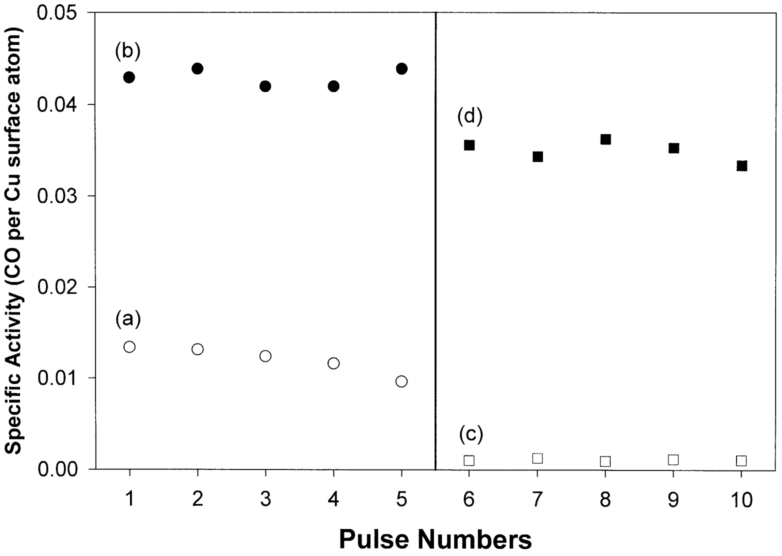

Figure 1. The conversion of CO_2 to CO at 773 K over a reduced and oxidized Cu/SiO_2 catalyst with 1 ml pulse of He/CO_2 and H_2/CO_2 with 1 : 1 ratio feed in helium at 100 ml/min. (a) 1 ml pulse of He/CO_2 on reduced catalyst, (b) 1 ml pulse of H_2/CO_2 on reduced catalyst, (c) 1 ml pulse of He/CO_2 on oxidized catalyst, (d) 1 ml pulse of H_2/CO_2 on oxidized catalyst.

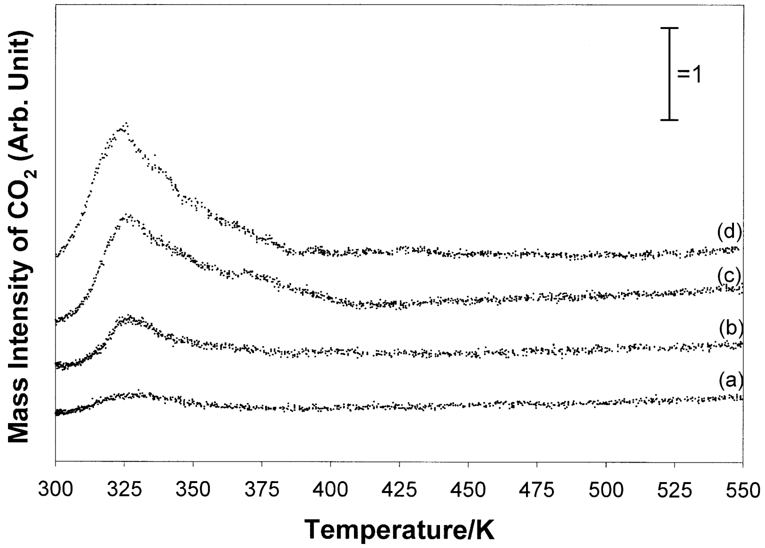

Figure 2. TPD spectra of CO_2 from He/CO_2 fed over 10% Cu/SiO_2 with 1 : 1 ratio and 100 ml/min flow rate at 300 K for (a) 1 min, (b) 10 min, (c) 30 min, (d) 60 min.

temperature of CO_2 desorption from the Cu surface could be less than room temperature. Nevertheless, Bönicke *et al.* studied CO_2 TPD on stepped (332) copper surface, and showed a desorption peak of CO_2 at 376 K [18]. We think the peak of CO_2 at 320 K in this study may depend on CO_2 absorbed on steps and/or kink sites on Cu particles.

Figure 3 displays TPD spectra of CO_2, obtained by exposing Cu/SiO_2 to an H_2/CO_2 stream with 1 : 1 ratio and 100 ml/min at 773 K. The H_2/CO_2 stream was fed over 0.15 g Cu/SiO_2 for the desired dosing time. 100 ml/min of helium stream then purged the residual gas in the reactor and cooled it quickly to room temperature. Compared to figure 2, the peak maximums of CO_2 were surprisingly shifted to high temperature and formed a wide desorption band. On the other hand, the amount of CO_2 desorption was also increased with dosing time.

Figure 4 shows the TPD spectra of CO_2 for the same H_2/CO_2 exposure over Cu/SiO_2 at 773 K (figure 4(a)) and 473 K (figure 4(b)), respectively. After the H_2/CO_2 exposure, the treatment by He-stream purging was identical to that of figure 3 as described above. Figure 4(b) presents a similar CO_2 desorption profile as figure 4(a), implying the same adsorbed species generated at both temperatures. The desorbed band of figure 4(b) was slightly increased in intensity compared to figure 4(a). The desorptions of CO_2 in figure 3 and figure 4 may be considered to be from formate produced by the H_2/CO_2 mixture. The formate synthesis by hydrogenation of CO_2 has been studied on Cu/SiO_2 and Cu single crystal in some papers, showing that the desorbed maximums of CO_2 were in the range of 400–473 K [19–21].

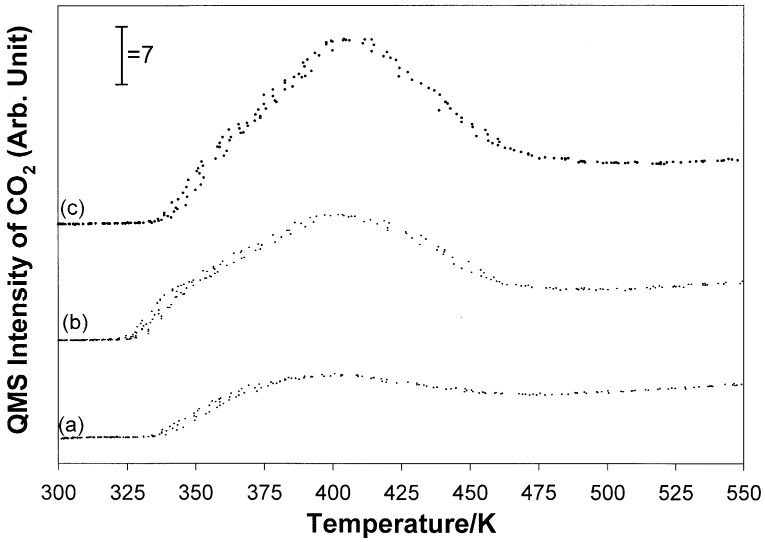

Figure 3. TPD spectra of CO_2 from H_2/CO_2 fed over 10% Cu/SiO_2 with 1 : 1 ratio and 100 ml/min flow rate at 773 K for (a) 5 min, (b) 15 min, (c) 30 min.

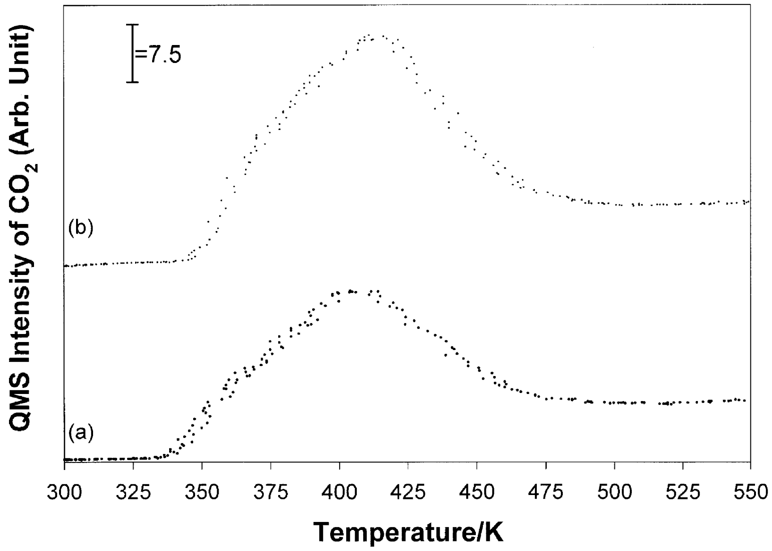

Figure 4. TPD spectra of CO_2 from H_2/CO_2 fed over 10% Cu/SiO_2 with 1 : 1 ratio and 100 ml/min flow rate for 30 min at (a) 773 K, (b) 473 K.

Formic acid was used as a source of formate for adsorption on Cu/SiO_2 to confirm the desorbed CO_2 from formate dissociation in figure 3 and figure 4. Figure 5 shows the TPD spectra of CO_2 from formic acid. At 0.1 μl and 0.5 μl formic acid dosing, three desorption peaks of CO_2 at 360, 385 and 430 K were found during temperature-programmed decomposition. These peaks correspond well with the CO_2 peaks in figure 3 and figure 4.

4. Discussion

For the redox mechanism, CO formation is proposed to be strongly dependent on the reactions of CO_2 dissociation and 2H with O to produce H_2O. The dissociative adsorption probability for H_2 is several orders of magnitude larger than that for CO_2 [9]. Ernst *et al.* studied the RWGS reaction on Cu(110) and indicated that oxygen coverage should be below 1% of a monolayer of copper surface atoms, since the dissociative adsorption rate of H_2 is several orders of magnitude faster than H_2O production [9]. By the redox model, the reaction has to take place on Cu^0 active sites. Figure 6 shows the TPR profiles of H_2/CO_2 with 1:1 ratio and 40 ml/min flow rate fed over Cu/SiO_2 at 873 K for 1 h, 60 h, and 96 h, respectively. Figure 6(a) shows the typical reduction peaks of Cu_2O at 453 K. The reduction temperature and peak area increase with reaction time. Figure 6(c) presents the reduction peak at 490 K. The reduction peaks of Cu_2O and CuO are typically positioned at 453 and 523 K, respectively. Therefore, the reduction peak of figure 6(c) at 490 K might imply that part of the Cu_2O could be further

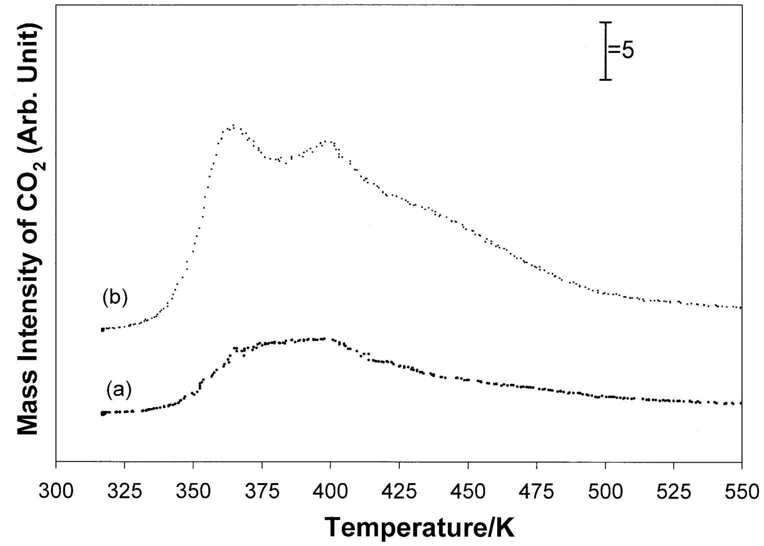

Figure 5. TPD spectra of CO_2 from formic acid dosing over 10% Cu/SiO_2, (a) 0.1 μl, (b) 0.5 μl.

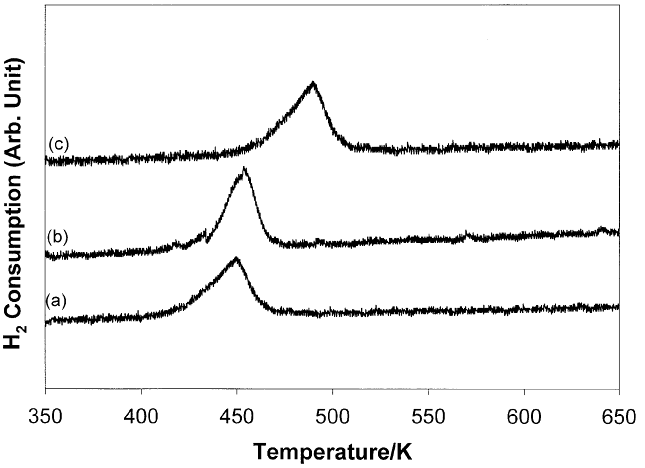

Figure 6. TPR profiles of 10% Cu/SiO_2 catalysts after exposure to H_2/CO_2 with 1 : 1 ratio and 40 ml/min over catalysts at 873 K for (a) 1 h, (b) 60 h, (c) 96 h.

oxidized to CuO after the long reaction time. A similar result has been found in our previous paper, showing that copper can be oxidized in the process of the RWGS reaction [15]. Although H_2 provides a highly dissociative adsorption rate on copper as some papers described, the results of TPR show that H_2 in H_2/CO_2 feed also did not immediately reduce oxidized copper during the RWGS reaction. It indicates that most of the H_2 may be consumed for the other reaction pathway, not for the reduction of Cu_2O.

Figure 1 displays the comparison of CO formation by pulse reactions in H_2/CO_2 and He/CO_2 with 1 ml volume, and shows that the pulse reaction of CO_2 to CO provides strong evidence for the promotion effect of hydrogen in the RWGS reaction. The CO formation rate at the second pulse of He/CO_2 was very close to that of the first pulse (figure 1(a)). It indicates no significant deactivation of the catalyst by the formation of adsorbed oxygen in a single pulse. The drastic enhancement of CO formation in the H_2/CO_2 experiment (figure 1(b)) cannot be explained simply by the removal of adsorbed oxygen with H_2. The oxidized Cu/SiO_2 was characterized for the surface state of Cu by a TPR measurement. The peak area of TPR of oxidized Cu was found to be about 2.1 times that of a monolayer Cu_2O on Cu/SiO_2. The monolayer Cu_2O was made by N_2O (30 ml/min) reaction on reduced Cu/SiO_2 at 80 °C for 4 min. On the other hand, the reduction temperature of oxidized Cu/SiO_2 was also elevated to 483 K from typical Cu_2O reduction at 453 K. These phenomena show that the surface of Cu/SiO_2 catalyst has been oxidized completely to CuO by CO_2 at 773 K. The oxidized Cu/SiO_2 offers low catalytic activity for He/CO_2, implying that the strongly oxidized Cu catalyst cannot offer enough Cu^0 atoms to convert CO_2 to CO. Nevertheless, CO production was still markedly enhanced by H_2 on the oxidized surface. In our previous paper, a copper surface with 36% Cu^+ species made by CO_2 oxidation was observed to have higher catalytic activity for the RWGS reaction than the dissociation of CO_2 to CO on reduced copper [15].

On the basis of these descriptions, the redox mechanism may not be a suitable model to interpret completely the behavior of the RWGS reaction. Figure 3 and figure 4 are the TPD spectra of post-reaction from Cu/SiO_2, which provide extremely different CO_2 desorption behavior from that of CO_2 adsorbed on reduced copper as figure 2 shows. The TPD peaks of post-reaction exhibit higher desorption temperature and higher peak area of CO_2 in comparison with CO_2 adsorption on Cu/SiO_2. The TPD spectra of CO_2 in figure 4(a) could be attributed to the result of formate decomposition. Considering methanol synthesis by CO_2 hydrogenation, the operation temperature has been widely used at a temperature of 473–573 K and the formate species was proposed to be the important intermediate. Some papers also reported that formate species could be synthesized by H_2/CO_2 feed at 530 K [19]. Figure 4(b) reveals similar TPD spectra as figure 4(a). This implies that its CO_2 also derived from formate decomposition. Figure 5 reveals typical formate decomposition peaks for CO_2 that almost match the TPD peaks of post-reaction of figure 3 and figure 4. These results demonstrate that residual species on Cu/SiO_2 after the RWGS reaction under high temperature can be proposed to associate with formate species adsorbed on the copper surface.

Based on these results, we reasonably deduce the key intermediate of the RWGS reaction to be formate species. 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 the reaction [19,22]. The formate decomposition mechanism dominates the reaction pathway on copper. The bicarbonate species formed from adsorbed CO_2 were converted to the formate species due to the presence of hydrogen. Clarke and Bell studied the IR spectra of H_2 and CO_2 coadsorption on Cu/SiO_2 [23], showing that the adsorbed species, bidentate and CO were observed immediately on the copper surface and the surface concentrations of both species increased with temperature. The formate species was the main common intermediate that results in CO formation by decomposition and/or methanol synthesis by hydrogenation [24].

5. Conclusions

Formate decomposition is suggested to be the main reaction pathway for CO formation in the RWGS reaction. The reduced and/or oxidized copper offers low catalytic activity for the dissociation of CO_2 to CO in the pulse reaction study with 1 ml volume of He/CO_2, but the rate of CO formation is significantly reduced if H_2 is also present in the feed. The TPD spectra of CO_2 obtained by H_2/CO_2, fed over copper at 773 K, have given strong evidence to demonstrate the formation of formate at high temperature.

Acknowledgments

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