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Mechanism of the Reverse Water Gas Shift Reaction over Cu/ZnO Catalyst[1]

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The reverse water gas shift reaction (RWGS) and the reaction with CO_2 alone were carried out over a Cu/ZnO catalyst. The surface of the catalyst was characterized by N_2O titration, XPS, and FT-IR spectroscopy. CO_2 dissociated to give CO and the surface oxygen species. Surface Cu(I) oxide was formed by the reaction with CO_2. The oxygen species were hydrogenated to H_2O and the surface Cu(I) oxide was reduced to metallic Cu. It is suggested that the RWGS reaction proceeds through surface oxidation and reduction with CO_2 and H_2, and the dissociation of CO_2 is the rate determining step. © 1992 Academic Press, Inc.

INTRODUCTION

The water gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is mostly used for the adjustment of the CO/H_2 ratio in the product gas from the steam reforming of hydrocarbons (*1*). Cu/ZnO catalysts are used for the commercial process of the WGS reaction at relatively low temperatures. These catalysts are also highly effective for the reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). Although numerous studies have been carried out on the WGS and RWGS reactions (*2–17*), the mechanisms of these reactions over Cu-based catalysts are still controversial. Two different mechanisms have been proposed for the reactions. One is a surface formate decomposition mechanism (*2–4, 6, 7, 9, 10*) and the other is a surface redox mechanism (*5, 11–13, 15–17*). It was recently reported that CO was produced from CO_2 alone over unsupported Cu powder (*12, 15*), and that no CO was produced from the surface formate species in the course of the temperature programmed desorption over Cu(110), Cu/SiO_2, and unsupported Cu powder (*18–20*). These results suggest that no formate participates in the title reaction.

In the present work, the mechanism of the RWGS reaction was studied over a Cu/ZnO catalyst by use of the temperature programmed desorption method, oxidation with CO_2, N_2O titration, diffuse reflectance FT-IR spectroscopy, and X-ray photoelectron spectroscopy. We show that the surface redox mechanism is involved in the title reaction.

EXPERIMENTAL

Cu/ZnO catalyst (Cu/Zn = 3/7 mole ratio) was prepared by coprecipitation of a solution of copper and zinc nitrates with sodium carbonate, according to the method adopted by Herman *et al.* (*21*) and Okamoto *et al.* (*22*). The precipitate was filtered out, dried at 373 K overnight, and calcined in air at 623 K for 4 h. The catalyst thus prepared was reduced in a reactor or in an IR cell on the following schedule: the reduction temperature was first raised from 483 K to 523 K stepwise by 10 K/h in a stream containing 3 vol.% of H_2 and then finally kept at 523 K for 1 h in a pure H_2 stream. The BET surface area of the reduced catalyst was 28 m^2/g.

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For comparison with the Cu/ZnO catalyst, unsupported Cu, Cu/SiO_2, and ZnO catalysts were also used for the experiments.

The RWGS reactions and the oxidation with CO_2 were carried out in a flow reactor at atmospheric pressure. The weight of the catalyst used was 2 g and the total flow rate was kept at 100 cm^3/min. Helium was used as a diluent. The effluent from the reactor was analyzed by gas chromatography.

Temperature programmed desorption (referred to as TPD) was carried out over 1 g of the catalyst in a He flow at a total flow rate of 200 cm^3/min. The heating rate was always kept at 5 K/min.

FT-IR spectra of adsorbed species were obtained in a He stream at room temperature with an infrared spectrophtometer (Japan Spectroscopy Co. FT-IR-5M) to which a diffuse reflectance instrument (Japan Spectroscopy Co. DR-500H) was attached. The structure of the IR cell was similar to one developed previously by one of the authors (*23*).

XPS spectra were measured on an ESCALAB-Mk2 (V.G. Scientific) with Mg*Kα* radiation. A sample of the catalyst was pressed on a Ni holder coated with gold and was then placed in a reaction chamber from which the catalyst could be transferred to the analysis chamber without exposure to air. The Zn($2P_{3/2}$) peak at 1021.7 eV was used as a reference.

RESULTS AND DISCUSSION

When a CO_2–H_2 mixture (CO_2/H_2 = 1/9) was fed over the catalyst at 438 K, CO was produced together with CH_3OH and H_2O. Figure 1 shows the outlet partial pressures of CO and CH_3OH against time. The outlet partial pressures of CH_3OH and CO vary with time in very different manners. CO is rapidly formed and then decreases to a steady value within a few minutes. By contrast, CH_3OH increases slowly in a monotonic manner. A steady state value is obtained after 2–3 h. On the other hand, when a CO–H_2 mixture was fed over the catalyst, no CH_3OH was detected in the effluent. These findings strongly suggest that the RWGS reaction and CH_3OH synthesis ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) proceed through parallel pathways.

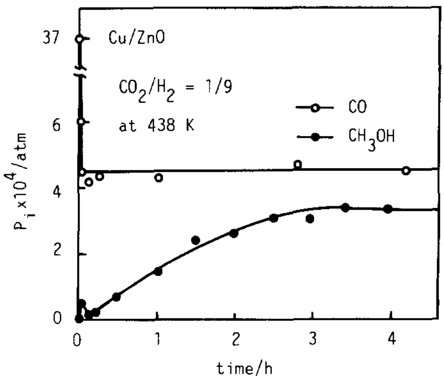


FIG. 1. Variation of the outlet partial pressure of CO and CH_3OH with time.

FT-IR spectra revealed that two types of formate species were formed on the catalyst along with the methoxide species in the course of the CO_2–H_2 reaction. The one formate species (referred to as formate I) gave absorptions at 2850, 1615, and 1350 cm^{-1}, the other (referred to as formate II) at 2975, 2880, 2740, 1580, 1350, and 1368 cm^{-1}. The methoxide species gave absorptions at 2935, 2825, and 1060 cm^{-1}. TPD runs showed that the formate I species decomposed rapidly to CO_2 and H_2 under the present reaction conditions whereas formate(II) and methoxide remained unchanged. As observed on unsupported Cu and Cu/SiO_2 catalysts (*20*), no CO was formed by decomposition of formate(I).

When a CO_2–He mixture (CO_2/He = 1/9) was fed over the catalyst at 438 K, only CO was formed. This suggests that the catalyst was oxidized by CO_2. Figure 2 illustrates the outlet partial pressure of CO against time. The formation of CO is initially rapid and then decreases with time. When the catalyst treated with CO_2 is exposed to a H_2 stream, only H_2O is detected in the effluent (Fig. 3). Figure 4 illustrates the total amount of H_2O formed against that of CO formed in the

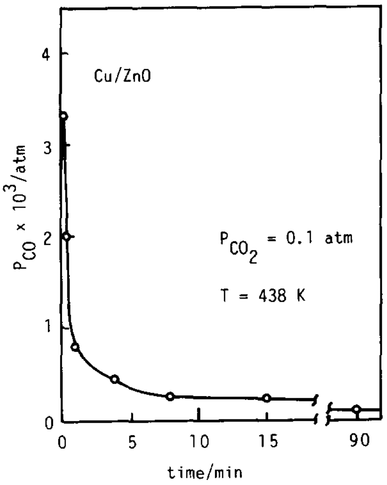


FIG. 2. CO formation from CO_2 over Cu/ZnO catalyst.

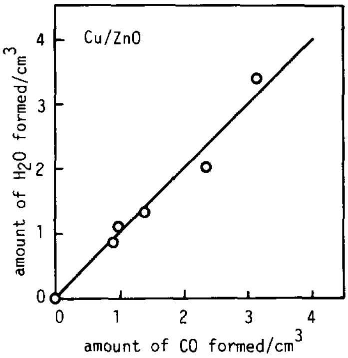


FIG. 4. Correlation between the amount of CO formed by CO_2 dissociation and that of H_2O formed by hydrogenation of the surface oxygen species.

CO_2 stream. The amount of H_2O formed is practically the same as that of CO previously formed. This indicates that all of the oxygen species formed from CO_2 are reduced to H_2O with H_2 and that the surface oxidation and reduction with CO_2 and H_2 occurs over Cu/ZnO.

In comparison with the outlet partial pressure of CO formed in the course of the CO_2–H_2 reaction (Fig. 1), it is clear that the initial rate of CO formation from CO_2 alone (Fig. 2) is practically the same as that from the CO_2–H_2 mixture. This is consistent with the recent results by Nakamura *et al.* (*16*), who reported that the RWGS reaction proceeded through the dissociation of CO_2 on Cu(110). Therefore we concluded that over Cu/ZnO catalyst CO_2 dissociates to CO and the surface oxygen species either in CO_2 or in the CO_2–H_2 mixture. The initial rate of the dissociation is unaffected by the presence of H_2 in the gas phase.

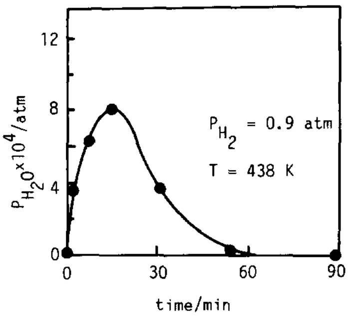


FIG. 3. H_2O formation via hydrogenation of the surface oxygen species over Cu/ZnO catalyst.

When CO_2 or H_2 was fed over the ZnO catalyst, no reaction occurred under the present reaction conditions. On the other hand, over unsupported Cu and Cu/SiO_2 catalysts, the reaction with CO_2 or H_2 occurred in a fashion similar to that over Cu/ZnO catalyst. This strongly suggests that the surface oxidation and reduction occurred with CO_2 and H_2 over the Cu surface.

In order to elucidate the surface oxidation and reduction in more detail, we performed some experiments on the Cu/ZnO catalyst. After various amounts of the surface oxygen species were formed by CO_2 dissociation at 438 K, the number of metallic Cu sites was determined by titration with N_2O at 333 K. On the feed of N_2O, only N_2 was detected in the effluent. Figure 5 shows the relationship between the total amount of N_2 formed and that of the surface oxygen species estimated from the amount of CO formed. The amount of N_2 formed decreases as the surface oxygen species increases in a 1 : 1 ratio. This strongly suggests that the surface Cu(I) ox-

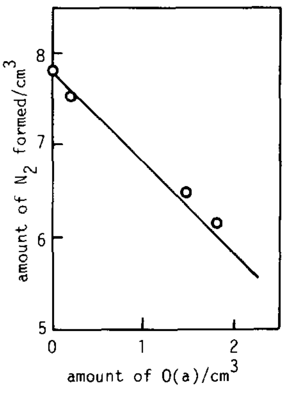


FIG. 5. Correlation between the total amount of N_2 formed and that of the surface oxygen species.

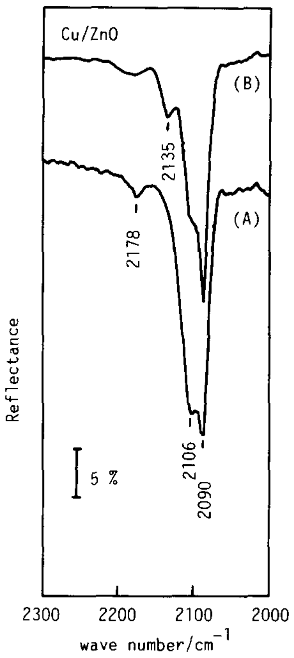


FIG. 7. IR spectra of CO adsorbed on the Cu/ZnO catalyst. CO was adsorbed at room temperature (A) after H_2 reduction followed by He treatment at 583 K and (B) after oxidation with CO_2 at 438 K for 1 h followed by He treatment at 438 K. Spectra were taken after CO in the gas phase was flushed with He.

ide was formed by the dissociation of CO_2, since this species is formed by N_2O decomposition over metallic Cu surface (*24, 25*).

To confirm the formation of the surface Cu(I) oxide, XPS spectra of the catalyst were measured (Fig. 6). Spectrum A illustrates the X-ray induced Cu(LMM) Auger spectrum of the reduced catalyst. Spectra B and C illustrate those obtained after the catalyst was oxidized with CO_2 at 438 K for 1 h and 4 h, respectively. It is evident that the peak assigned to metallic copper (918.8 eV) decreases in intensity and that assigned to Cu(I), which is located at 917.2 eV, gradually increases in intensity as a result of oxidation with CO_2.

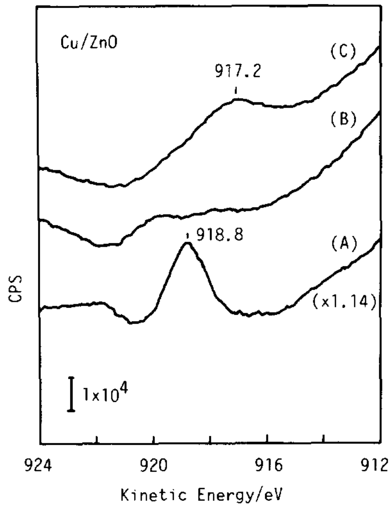
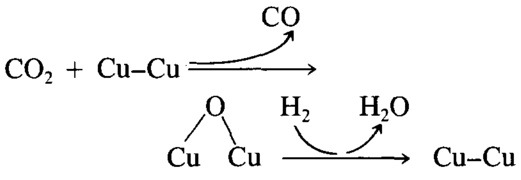


FIG. 6. X-ray induced Cu(LMM) Auger spectra of the catalyst. (A) after H_2 reduction followed by evacuation at 573 K. (B) and (C) after oxidation with CO_2 at 438 K for 1 h and 4 h, respectively.

The presence of Cu(I) was further supported by the observations with diffuse reflectance FT-IR spectroscopy. Figure 7 shows the IR spectra of CO adsorbed on the reduced and the oxidized catalyst. After reduction with H_2, the catalyst was treated with He at 573 K for 15 min and exposed to a CO stream for 15 min at room temperature. Spectrum A was recorded after CO in the gas phase was flushed with He. Absorptions occur at 2178, 2106, and 2090 cm^{-1}. The absorptions at 2106 and 2090 cm^{-1} are assigned to CO absorbed on metallic Cu (*26–29*), while that at 2178 cm^{-1} is assigned to CO adsorbed on ZnO (*30*). After being subjected to oxidation in a CO_2 stream at 438 K, the catalyst was treated with He at 438 K and then exposed to a CO stream for 15 min at room temperature. Spectrum B was recorded after CO in the gas phase was flushed with He. As spectrum B shows, on the oxidized catalyst the absorption due to CO adsorbed on Cu(I) sites is evidently seen at 2135 cm^{-1} (*31–34*) along with those adsorbed on metallic Cu sites. On the other hand, on the catalyst re-reduced with H_2, the absorption at 2135 cm^{-1} disappeared.

In a similar manner, over the catalyst subjected to the RWGS reaction the surface oxygen species were titrated with H_2 and the valence states of Cu were determined by XPS. After attainment of the steady state of reaction, the mixture was flushed with a He stream for 10 min and a H_2 stream was fed over the catalyst. However, no H_2O was detected in the effluent, suggesting that the amount of the surface oxygen species was negligible. Consistent with these findings the Cu(LMM) Auger peak ascribed to metallic copper was observed, while no peaks ascribed to Cu(I) and Cu(II) were observed. These findings strongly suggested that the reduction of the oxygen species proceeded faster than the oxidation of the catalyst with CO_2 at the steady state of the RWGS reaction.

Based on these results, we conclude that the RWGS reaction proceeds via the scheme



involving the oxidation and reduction of the Cu surface, Cu(O) $\rightleftharpoons$ Cu(I), with CO_2 and H_2, the oxidation with CO_2 being the rate determining step of the reaction.

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