Mechanistic Study of the Hydrogenation of Carbon Dioxide to Methanol over Supported Rhenium and Copper-Zinc Catalysts

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The reaction of a mixture containing ^{13}CO, CO_2, and H_2 was carried out in order to elucidate the reaction mechanisms of carbon dioxide hydrogenation to methanol over supported Re catalysts as well as Cu–Zn oxide catalysts. The reactions of formic acid and formaldehyde with hydrogen were also examined. From the incorporation of ^{13}C in the product methanol, it could be distinguised whether the carbon dioxide hydrogenation to methanol proceeds through formation and successive hydrogenation of CO or by direct hydrogenation of CO_2. Methanol is formed almost exclusively by direct hydrogenation of CO_2 over CuO–ZnO based catalysts. However, the two reaction routes operate over Re/ZrO_2 and Re/CeO_2, the contribution of route via CO being higher over Re/ZrO_2 than over Re/CeO_2. The reactions of formic acid and formaldehyde with hydrogen suggest that the surface formate and the adsorbed formaldehyde are involved in the methanol formation, and that the conversion of the formate to the adsorbed formaldehyde is a key step.

In sharp contrast to the extensive studies involving hydrogenation of CO to methanol, hydrogenation of CO_2 to methanol has left some uncertainties regarding the mechanisms. One of the discussion points concerning the mechanism of methanol synthesis is the reaction intermediates. The other point to be discussed is the source of carbon for the product methanol. One candidate is CO_2 and the other is CO resulting from a reverse water–gas shift reaction of CO_2 and H_2.

Two kinds of catalysts used for the methanol synthesis from CO_2 and H_2 are supported transition metals and CuO–ZnO based catalysts. The mechanisms of methanol synthesis seem to be dependent upon the type of catalyst.

As the intermediate of methanol synthesis, surface formate species has been proposed for both supported transition metal catalysts and Cu–Zn oxide catalysts. Ramaroson et al. studied the mechanisms of the formation of C_1 products from CO_2 and H_2 over Pd/SiO_2 and Pd/Al_2O_3 by a chemical trapping method.1) They proposed that the first step involves the formation of formate by CO_2 insertion into a hydroxide site. Solymosi et al. confirmed by IR spectroscopy the formation of formate in the hydrogenation of CO_2 over supported Rh catalysts.2) They proposed that hydrogen activated on the Rh migrates onto the support and reacts with hydrocarbonate to yield the formate ion.

Over CuO-ZnO based catalysts, Kieffer et al.3) and Ramaroson et al.4) have reported that the formation of formate as an intermediate for the methanol synthesis from CO_2 and H_2 was observed by a chemical trapping method. Amenomiya et al. observed the formation of formate during CO_2 hydrogenation.5) They proposed that the formate is formed by the insertion of CO_2 into a hydroxide site, and that the formate species is a common intermediate to methanol synthesis as well as to CO formation by a reverse water–gas shift.

To clarify whether methanol is formed directly from CO_2 or through the formation of CO followed by hydrogenation, isotope-labeling studies were performed. Chinchen et al. used $^{14}CO_2$ or ^{14}CO in a mixture of $CO_2/CO/H_2$, and found that CO_2 is the major reactant for methanol synthesis over $CuO–ZnO–Al_2O_3$ under industrial conditions.6) Liu et al. used ^{18}O-labeled CO_2 for methanol synthesis over a Cu–Zn oxide catalyst.7) Their results have indicated that there are at least four parallel reactions: $CO–CO_2$ exchange, CO hydrogenation, CO_2 hydrogenation, and a water–gas shift.

Erdoeheloyi et al. studied the hydrogenation of CO_2 over supported Pd.8) The results failed to suppoort the idea that methanol is produced in a direct reaction of CO_2 and not through the formation of CO and its consecutive hydrogenation.

It seems that over CuO–ZnO based catalysts, methanol is formed directly from CO_2. However, it is not certain whether the same conclusion can be made regarding methanol synthesis over supported transition metal catalysts.

In our previous papers, methanol syntheses from CO_2 and H_2 were carried out over supported Re catalysts and Cu–Zn oxide supported on various metal oxides in order to examine the support effects.9,10) The activity and selectivity depend on the type of support for both the Re and Cu–Zn oxide catalysts. It is also suggested that different mechanisms are operating in methanol formation over Re/ZrO_2 and Re/CeO_2. In the present study, the mechanisms of hydrogenation of CO_2 were studied regarding both supported Re and Cu–Zn oxide catalysts by the use of ^{13}C-labeled CO in order to clarify the origin of carbon in the products. The reaction of formic acid or formaldehyde with hydrogen was carried out in order to examine the intermediates for methanol.

Experimental

Preparation of Catalysts. Supported Re catalysts were prepared by impregnating CeO_2 and ZrO_2 (20—40 mesh) with an NH_4ReO_4 solution (1 M, 1 M=1 mol dm^{-3}), followed by drying in a vacuum and successively reducing with hydrogen first at 200 °C for 2 h, then 400 °C for 4 h, and finally at a reaction temperature of 200 °C for 2 h before use. The content of Re was adjusted to be 1.5 wt% for both catalysts.

The Cu–Zn oxide catalyst was prepared by the hydrolysis of a mixed solution containing 1 M $Cu(NO_3)_2$ and 1 M $Zn(NO_3)_2$ with 1 M aqueous solution, followed by washing and drying. The dried catalyst was calcined in air at 350 °C for 3 h and then at 500 °C for 1 h. The mole percents of CuO was adjusted to be 50%.

The Cu–Zn oxide catalysts supported on ZrO_2, MgO, Al_2O_3, and Cr_2O_3 were prepared by the direct addition of $Zr(OH)_4$, $Mg(OH)_2$, $Al(OH)_3$, and $Cr(OH)_3$, respectively, to the $Cu(OH)_2$–$Zn(OH)_2$ coprecipitates obtained as above; this was followed by drying and calcining also in a manner similar to the above. The mole percents of CuO, ZnO, and support metal oxides were adjusted to be 42, 47, and 11% for CuO–ZnO–ZrO_2, 47, 47, and 6% for CuO–ZnO–MgO and CuO–ZnO–Al_2O_3, 34.5, 34.5, and 11% for CuO–ZnO–Cr_2O_3.

Isotope Labeling Reaction. A mixture containing CO_2 (140 Torr, 1 Torr=133.322 Pa), H_2 (420 Torr) and ^{13}CO (10 Torr) was used as a reactant. The ^{13}CO was purchased from Cambridge Isotope Laboratories; its isotopic purity was 99%. Hydrogen was purified by passage through 13X molecular sieves. The CO_2 was purified by freeze-thaw cycles. A recirculation reactor having a volume of 267 cm^3 was employed. A catalyst sample (0.30 g) was placed in the reactor and reduced with hydrogen flow at 300 °C for 6 h. After evacuating the hydrogen for 30 min, the reactant was introduced into the reaction system. All reactions were carried out at 200 °C. During the reaction, a trap placed in the loop of the recirculation reactor was kept at −78.5 °C, so that the formed methanol could be trapped so as to keep the vapor pressure of methanol negligibly low in order to avoid a reverse reaction. For product analysis, the catalyst bed was closed from the recirculation loop and the trap was heated to room temperature. The reaction mixture was then withdrawn. A part of the withdrawn reaction mixture was analyzed by gas chromatography. The other part was subjected to mass spectrometric analysis.

Reaction of Formic Acid or Formaldehyde with Hydrogen. For the reaction of formic acid or formaldehyde with hydrogen, the same recirculation reactor was employed. After pretreatment, the catalyst was exposed to 12 Torr formic acid or formaldehyde at room temperature for 30 min. Then, 420 Torr hydrogen was introduced, and the catalyst was heated to a reaction temperature of 200 °C. The products were analyzed by a gas chromatograph using Porapak-Q column.

XPS Measurements. XPS were measured by using an Escalab MK II spectrometer equipped with an in situ reaction cell inside the pretreatment chamber. Mg *Kα* was used as a radiation source. A plate sample was evacuated at room temperature in the pretreatment chamber, then transferred to a small reactor where the reduction with hydrogen stream was carried out at 300 °C for 2 h. After the prereduced sample was transferred to the pretreatment chamber, evacuated, and transferred to the analyzing chamber, the Cu2p spectra were measured.

Results and Discussion

Regarding the reaction of the mixture containing CO_2, ^{13}CO and H_2, the experimental results are shown in Table 1. Over Re catalysts, methane was produced as well as methanol. In particular, the formation of methane exceeded to a considerable extent over Re/ZrO_2. In contrast to the case of the Re catalysts, methane was not formed over Cu–Zn oxide catalysts. Practically no reaction was appreciable over CuO–ZnO–Cr_2O_3.

The percentages of the ^{13}C content in each product are plotted against the reaction time in Figs. 1 and 2 for Re/ZrO_2 and Re/CeO_2, respectively. If the product is formed directly from CO_2, the ^{13}C content in the product will be 0% at a conversion of 0%. On the contrary, the

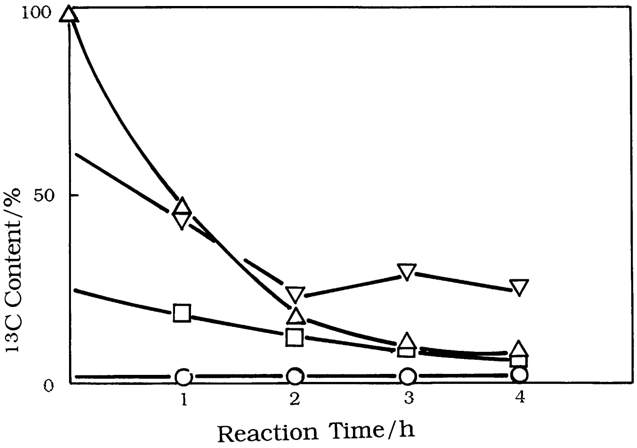


Fig. 1. Variations in the ^{13}C contents of each product in the reaction of H_2+CO_2+^{13}CO over Re/ZrO_2 as a function of the reaction time. △: CO, ○: CO_2, □: CH_3OH, ▽: CH_4.

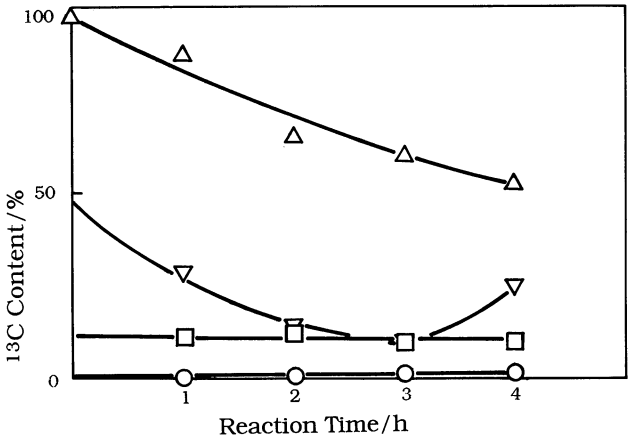


Fig. 2. Variations in the ^{13}C contents of each product in the reaction of H_2+CO_2+^{13}CO over Re/CeO_2 as a function of the reaction time. △: CO, ○: CO_2, □: CH_3OH, ▽: CH_4.

Table 1. Product Distribution and ^{13}C Isotopic Distribution in the Reaction of H_2, CO_2, and ^{13}CO[a)]

Catalyst	Reac. time	Product composition/%					^{13}C Content in each product/%			
	h	CO	CH_4	CH_3OH	CO_2	C_2	CO	CH_4	CH_3OH	CO_2
Re/CeO_2	1	7.7	0.2	0.1	92.0	0.1	80.7	28.5	11.0	0.5
	2	8.0	0.6	0.3	91.0	0.1	65.3	13.4	11.9	0.9
	3	8.6	0.8	0.5	90.1	0.1	60.2	9.4	9.6	1.3
	4	9.2	1.0	0.6	89.1	0.2	52.6	24.5	9.6	1.7
Re/ZrO_2	1	4.4	3.0	0.2	92.1	0.3	46.5	42.2	18.5	1.2
	2	4.2	6.1	0.3	88.8	0.6	17.6	23.4	11.5	1.4
	3	4.5	8.6	0.4	85.7	0.9	10.7	29.0	9.7	1.7
	4	9.5	10.6	0.4	78.5	1.1	8.2	25.1	7.1	2.0
CuO-ZnO	1	11.8	0	0.2	86.2	0	37.7	—	2.8	0
	2	13.0	0	0.6	84.2	0	37.4	—	2.1	0.4
	3	14.5	0	0.8	81.4	0	34.0	—	2.3	0.8
	4	16.0	0	1.0	79.3	0	31.4	—	2.0	0.8
CuO-ZnO-MgO	0.5	7.7	0	0.6	89.4	0	61.1	—	0.9	0.1
	1.0	10.4	0	0.9	85.4	0	43.5	—	1.8	0.4
	1.5	13.3	0	1.2	80.6	0	37.6	—	2.0	0.5
	2.0	16.0	0	1.0	76.3	0	26.5	—	1.9	0.7
CuO-ZnO-Al_2O_3	0.5	7.4	0	0.4	91.3	0	80.3	—		0
	1.0	8.8	0	1.2	88.1	0	66.6	—	1.3	0
	1.5	10.5	0	2.0	84.2	0	58.5	—	0.8	0.1
	2.0	12.3	0	2.7	80.3	0	46.6	—	0.5	0.2
CuO-ZnO-ZrO_2	0.5	9.6	0	0.2	88.9	0	81.9	—	1.0	0.2
	1.0	11.2	0	1.7	84.9	0	69.4	—	1.1	0.3
	1.5	12.9	0	2.0	80.8	0	59.9	—	1.8	0.3
	2.0	14.5	0	2.7	77.6	0	52.6	—	1.8	0.4
CuO-ZnO-Cr_2O_3	1	8.6	0	0	91.3	0	91.7	—	—	0.2
	2	8.4	0	0	91.5	0	90.3	—	—	0.2
	3	8.5	0	0	91.5	0	88.1	—	—	0.2
	4	8.9	0	0	91.0	0	81.4	—	—	0

a) Reaction conditions: Reactant: H_2 (420 Torr)+CO_2 (140 Torr)+^{13}CO (10 Torr), Catalyst: 300 mg, Reaction temperature: 200 °C.

^{13}C content will be 100% if the product is formed from CO. Although the values obtained by extrapolation to 0 conversion have some uncertainties, these are useful for determining the reaction route. Over a Re/ZrO_2 catalyst, the ^{13}C content in CH_4 was about 60—70% at a conversion of 0%, while that of CH_3OH was in the range of more than 25%. It is thus suggested that CH_4 is formed predominantly via CO, while CH_3OH is formed predominantly by a direct reaction of CO_2.

Over a Re/CeO_2 catalyst, the ^{13}C contents in both CH_4 and CH_3OH were low, compared to those produced over Re/ZrO_2. The percentages of the ^{13}C contents in CH_4 and CH_3OH at a conversion of 0% were about 50% and 10%, respectively. It is, therefore, suggested that the contributions of the routes via CO and via CO_2 are almost equivalent for CH_4 formation, and that CH_3OH is predominantly formed from CO_2. This indicates that the catalytic behavior is different over Re/ZrO_2 and Re/CeO_2 in CO_2 hydrogenation.

One more difference between Re/ZrO_2 and Re/CeO_2 was observed regarding the rate of a CO–CO_2 carbon exchange. Over both catalysts, the rate of incorporation of ^{12}C into CO was fast compared to the formation rates of CH_4 and CH_3OH. The rate of CO–CO_2 carbon exchange was much faster for Re/ZrO_2 than for Re/CeO_2.

The distribution of ^{13}C in the products produced over Cu–Zn oxide catalysts were quite different from those observed over the supported Re catalysts, such as CuO–ZnO–ZrO_2, as shown in Fig. 3. The ^{13}C contents in CH_3OH produced over Cu–Zn oxide catalysts were close to 0%. This demonstrates that product methanol is directly formed from CO_2. The contribution from the route via CO is negligible. This coincides with the conclusion reported by Chinchen et al. for Cu–Zn/Al_2O_3 catalyst.[6)]

Although the incorporation of ^{13}C into methanol was negligible, a CO–CO_2 carbon exchange occurred to a considerable extent. Two possibilities which account for the fast CO–CO_2 exchange against a negligible incorporation of ^{13}C into methanol are as follows. One possibility is that the intermediates for the formation of

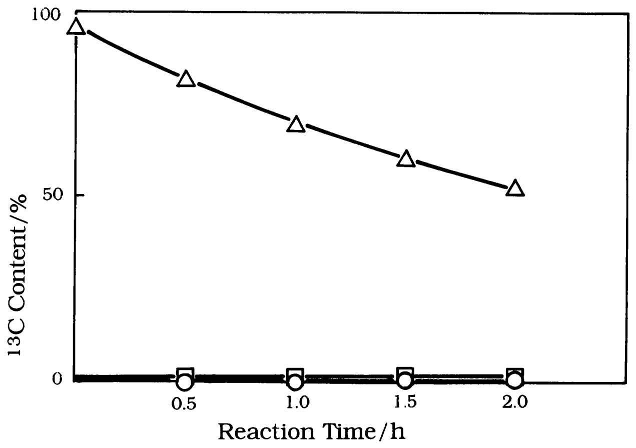


Fig. 3. Variations in the ^{13}C contents of each product in the reaction of $H_2+CO_2+^{13}CO$ over CuO-ZnO-ZrO_2 as a function of the reaction time. △: CO, ○: CO_2, □: CH_3OH.

methanol from CO_2 are not common to those for a CO-CO_2 carbon exchange. The other possibility is that the intermediates are common, but that the slow step in the formation of methanol is a conversion of the intermediates, leading to methanol.

Reactions of Formic Acid and Formaldehyde with Hydrogen. Formic acid is supposed to be adsorbed on the surface in the form of formate. The purpose of the reactions was to determine how the formate and the adsorbed formaldehyde are involved in the hydrogenation of carbon dioxide by a comparison of the product distribution with those obtained in the hydrogenation of carbon dioxide. In the reactions of formic acid and formaldehyde with hydrogen, all of the formic acid and formaldehyde were completely consumed within 1 h; the conversions were 100%. The product distributions in the reactions of formic acid and formaldehyde with hydrogen are given in Tables 2 and 3, respectively.

Over the Re/CeO_2 catalyst, the products in the reaction of adsorbed formic acid with H_2 comprised of CO_2, CH_4, and CO. No methanol formation was observed. Over the Re/ZrO_2 catalyst, however, the products comprised of CH_4 and CO, neither CO_2 nor methanol was observed. It should be noted that CO_2 was not formed over Re/ZrO_2 at all, though CO_2 was the main product over Re/CeO_2.

Over Cu-Zn oxide catalysts, CO, CO_2, and methanol were produced; no methanol was formed over CuO-ZnO-Cr_2O_3. The production of methanol was the highest for CuO-ZnO-ZrO_2.

For all of the catalysts examined, the product distributions in the reaction of formic acid with hydrogen and in the hydrogenation of CO_2 show common features regarding the following three points: (1) The amount of methane greatly exceeded that of methanol over Re catalysts. (2) Over Cu-Zn oxide catalysts, methanol was formed; no methane was formed. (3) Over CuO-ZnO-Cr_2O_3, neither methanol nor methane were formed.

The reaction of formaldehyde with hydrogen gave product distribution quite different from that of formic acid with hydrogen. Over Re/ZrO_2 and Re/CeO_2 catalyst, methanol was formed considerably. In addition, the formation of CO_2, which was the main product in the reaction of formic acid with hydrogen on Re/CeO_2, was not observed.

Over Cu-Zn oxide catalysts, the products comprised mostly of methanol. Only small amounts of CO_2 and CO were formed in the reaction of formaldehyde with hydrogen. It is to be noted that with Cu-Zn oxide

Table 2. Product Distribution of the Reaction of Formic Acid with Hydrogen

Catalyst	Reaction time/h	Yield/%				
		CO	CH_4	CO_2	C_2	CH_3OH
Re/CeO_2	1	8.6	3.8	87.6	0	0
	2	12.9	12.5	74.1	0.5	0
Re/ZrO_2	1	4.3	94.8	0	0.9	0
	2	6.5	93.1	0	0.5	0
CuO-ZnO	1	32.6	0	62.7	0	4.7
	3	28.8	0	60.2	0	11.0
CuO-ZnO-Al_2O_3	1	19.6	0	70.2	0	10.2
	2	34.7	0	40.0	0	25.3
CuO-ZnO-ZrO_2	1	15.7	0	44.9	0	39.4
	2	20.3	0	34.1	0	45.6
CuO-ZnO-Cr_2O_3	1	56.4	0	43.6	0	0
	2	56.7	0	42.3	0	0

a) Reaction conditions: Reactant: HCOOH (12 Torr)+H_2 (420 Torr), Catalyst: 300 mg, Reaction temperature: 200 °C.

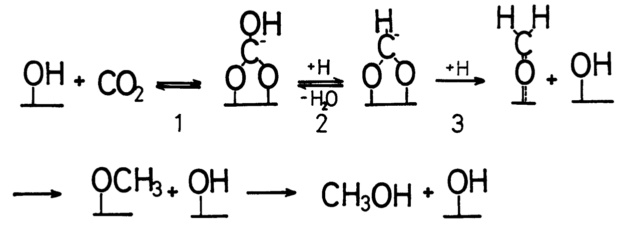
Table 3. Product Distribution of the Reaction of Formaldehyde with Hydrogen[a)]

Catalyst	Reaction time/h	Yield/%				
		CO	CH_4	CO_2	C_2	CH_3OH
Re/CeO_2	1	7.2	59.7	0	0.8	32.1
	2	10.3	77.9	0	0.9	11.0
Re/ZrO_2	1	7.3	85.2	0	0	7.5
	2	0	95.4	0	0	0
CuO-ZnO	1	6.2	0	11.9	0	81.9
	2	5.3	0	5.9	0	88.7
$CuO-ZnO-Al_2O_3$	1	2.0	0	0	0	98.0
	2	3.2	0	0.8	0	96.0
$CuO-ZnO-ZrO_2$	1	2.1	0	1.0	0	96.9
	2	6.5	0	1.6	0	91.8
$CuO-ZnO-Cr_2O_3$	1	3.4	0	1.9	0	94.6
	2	6.1	0	3.0	0	90.9

a) Reaction conditions: HCHO (12 Torr)+H_2 (420 Torr), Catalyst: 300 mg, Reaction temperature: 200 °C.

catalysts methanol was formed, even over CuO-ZnO-Cr_2O_3, over which no methanol was formed from formic acid. This indicates that the conversion of adsorbed formic acid to adsorbed formaldehyde is very slow over CuO-ZnO-Cr_2O_3 catalysts.

Some common features between CO_2 hydrogenation and the reaction of formic acid with hydrogen and the predominant formation of methanol in the reaction of formaldehyde suggest the following reaction route. At first, formate is formed from CO_2 and hydrogen; the formate converts into the adsorbed formaldehyde. The adsorbed formaldehyde is hydrogenated to yield methanol. The formation of formate may proceed by the insertion of CO_2 into the hydroxide site, as suggested by Amenomiya et al.[5)] A scheme for methanol formation may be as shown below:



Scheme 1.

Since CO-CO_2 carbon exchange is fast, and essentially no incorporation of ^{13}C into methanol was observed in the reaction of ^{13}CO, CO_2, and H_2, a CO-CO_2 carbon exchange proceeds by intermediates which are different from the formate shown above.

The conversion of the formate into the adsorbed formaldehyde (step 3) is the key step in methanol synthesis. Once the adsorbed formaldehyde is formed, methanol is easily yielded, as is evidenced by the selective formation of methanol in the reaction of formaldehyde with hydrogen.

Over a CuO-ZnO-Cr_2O_3 catalyst, methanol was not formed, neither in CO_2 hydrogenation nor in the reaction of formic acid with hydrogen; methanol, however, was selectively formed in the reaction of formaldehyde with

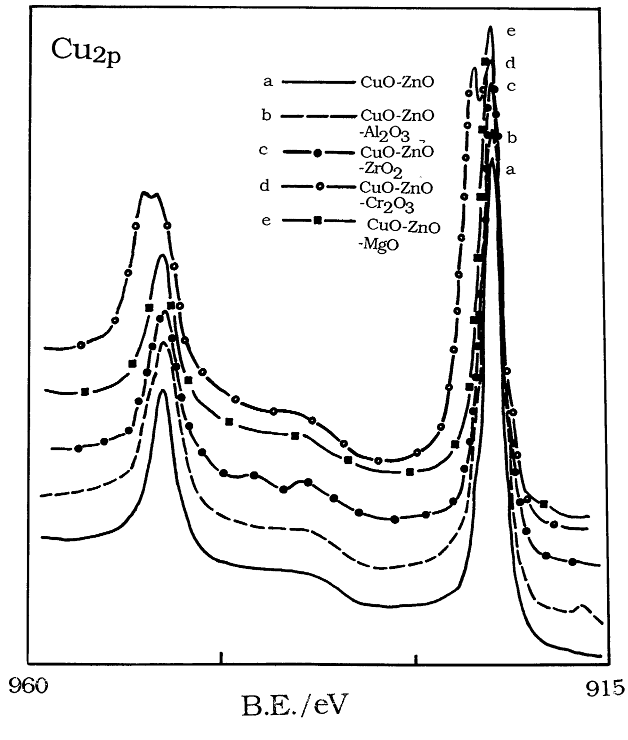


Fig. 4. XPS spectra of various Cu-Zn oxide catalysts after reduction with H_2 at 300 °C.

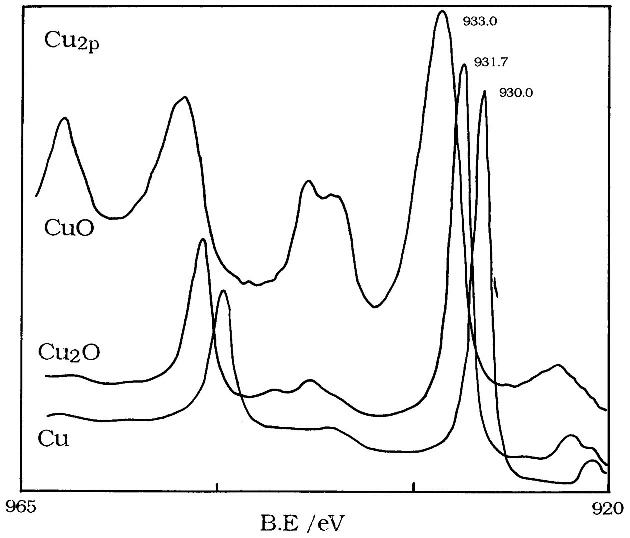


Fig. 5. XPS spectra of standard oxides of Cu.

hydrogen. The conversion of formate into the adsorbed formaldehyde is very slow over $CuO-ZnO-Cr_2O_3$. The state of Cu on $CuO-ZnO-Cr_2O_3$ should be different from those on the other supported CuO-ZnO catalysts. To examine the states of Cu, XPS was measured with $CuO-ZnO-Cr_2O_3$ together with the other Cu-Zn oxide catalysts. As shown in Fig. 4, $CuO-ZnO-Cr_2O_3$ showed two peaks in the Cu_{2p} region, while the other Cu-Zn oxide catalysts showed a single peak. The peaks are assigned to Cu^+, compared with the peaks for CuO, Cu_2O, and Cu^0, as shown in Fig. 5. The peak at 932.7 eV is positioned between those for Cu^{2+} and Cu^+. It is not certain why $CuO-ZnO-Cr_2O_3$ showed two peaks, but it can be said that Cu in the $CuO-ZnO-Cr_2O_3$ tends to stay at a higher oxidation state, compared with the other Cu-Zn oxide catalysts.

In our previous paper,[10] we proposed that Cu^+ in a Cu-Zn oxide solid solution is an active site for methanol formation from CO_2 and H_2.[10] The state of Cu in $CuO-ZnO-Cr_2O_3$ may be either partly oxidized Cu^+ or partly reduced Cu^{2+}. This causes the conversion of the formate to the adsorbed formaldehyde difficult.

With the Re/ZrO_2 catalyst, most of the methanol is formed through the reaction of CO with H_2, though the selectivity to methanol is very low under the reaction condition of subatomospheric pressure. With the Re/CeO_2 catalyst, one of the routes to methanol is considered to proceed by a direct hydrogenation of CO_2 in a similar manner to that shown in Scheme 1.

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