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Hydrogenation of Carbon Dioxide over Cu–Zn–Cr Oxide Catalysts

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The hydrogenation of carbon dioxide for methanol synthesis was studied over Cu–Zn–Cr oxide catalysts, which were prepared by using CrO_3 as a source of chromium. From the results of improving this type of catalysts, a catalyst prepared by the addition of copper–zinc carbonate to an aqueous solution of CrO_3 was confirmed to be the most effective in this study. The detailed reaction behaviors, such as the dependence on the pressure, temperature and space velocity, were studied using this catalyst.

Recently, the fixation of carbon dioxide has become more important due to the global warming induced by the exhaust of large amounts of carbon dioxide. Furthermore, carbon dioxide is a significant carbon resource. Methanation[1)] or methanol synthesis[2)] have been energetically studied recently. C_2^+ hydrocarbons, such as liquefied petroleum gas or gasoline, are also desirable products. Hybrid catalysts comprising methanol synthesis catalysts and zeolites have shown hopeful results from the viewpoints of the synthesis of hydrocarbons. Although the hydrogenation of carbon monoxide was successful by using hybrid catalysts,[3)] the application of hybrid catalysts to the hydrogenation of carbon dioxide was not very satisfactory and the yields of hydrocarbons were low in most cases.[4)] We recently reported that Cu–Zn–Cr oxide prepared from CuO, ZnO, and CrO_3 was remarkably suitable for hybrid catalysts for the hydrogenation of carbon dioxide.[5)]

The preparation of Cu–Zn–Cr oxide catalysts from CuO, ZnO, and CrO_3, reported by Ogino et al.,[6)] is a unique method in contrast to coprecipitation, which is the most common one. Although those catalysts, Cu–Zn–Cr oxides, were used for the hydrogenation of carbon monoxide, their applications to the hydrogenation of carbon dioxide have been scarcely reported.[7)] On the other hand, the hybrid catalyst is a combined system which works for both the synthesis and conversion of methanol. Therefore, the detailed behaviors of Cu–Zn–Cr oxide as a methanol synthesis catalyst should be investigated for the sake of both revealing the mechanism of the hybrid catalyst and preparing more effective ones. We now wish to report on our latest results concerning the catalytic property of Cu–Zn–Cr oxide and their improvements for methanol synthesis in the hydrogenation of carbon dioxide.

Experimental

Preparation of Catalysts. Cu–Zn–Cr oxides were prepared by the following five methods. Method A was the same as that reported by Ogino et al.[6)] Methods B, C, D, and E were first investigated in this paper.

Method A: CuO was added to an aqueous solution of CrO_3 with physical mixing. After 1 h, ZnO was introduced into the resulting mixture.

Method B: A mixture of CuO and ZnO was added to an aqueous solution of CrO_3.

Method C: At first, a carbonate gel was prepared by the coprecipitation of copper and zinc nitrate with Na_2CO_3.[8)] After sufficient washing and drying at 120 °C, the obtained carbonate gel was added to an aqueous solution of CrO_3.

Method D: A mixed oxide, CuO–ZnO, after the calcination of the coprecipitated carbonate obtained in method C at 350 °C for 3 h was added to an aqueous solution of CrO_3.

Method E: CuO and ZnO were added in reversed order of method A. ZnO was at first added to an aqueous solution of CrO_3 with physical mixing, after 1 h CuO was introduced into the resulting mixture. All pastes obtained by methods A, B, C, D, and E were dried under atmospheric pressure without heating. Calcination was not performed.

The Cu–Zn catalyst in Table 1 (Run 1) was prepared by the kneading of CuO with ZnO using water. The Cu–Cr and Zn–Cr catalysts were obtained from the mixing of CuO or ZnO with an aqueous solution of CrO_3, respectively.

Cu–ZrO_2 and Cu–Zr–Cr oxide were prepared as follows. Copper and zirconium nitrates were coprecipitated with Na_2CO_3, as reported.[2c)] After sufficient washing and drying at 120 °C for 4 h, a carbonate gel of copper and zirconium was obtained. Cu–ZrO_2 was obtained by calcination of the gel at 350 °C for 4 h. Cu–Zr–Cr oxide was prepared by mixing the Cu–Zr carbonate gel with an aqueous solution of CrO_3 in the same manner as that for Cu–Zn–Cr oxide (Method C).

Reaction Procedures. The hydrogenation of carbon dioxide was carried out using a pressurized flow-type fixed-bed reactor. The reactor was made of a stainless-steel tube with an inner diameter of 9 mm. In a typical experiment, 1 g of catalyst (24—40 mesh) was packed in the reactor, and was activated in a stream of diluted hydrogen (1%H_2 in N_2) at 250 °C for 12 h. After pre-reduction, a reaction gas ($H_2/CO_2=3$) was introduced into the reactor under 50 $kg\,cm^{-2}$. The effluent gas was analyzed by an on-line gas chromatograph using Porapak Q for carbon dioxide, MS-13X for methane and carbon monoxide, PEG for methanol and VZ-10 for C_2^+ hydrocarbons. The tubing from the catalyst bed to the gas chromatograph was heated at 100—150 °C so as to avoid any condensation fo the products.

Characterization of Catalysts. The BET surface area of each catalyst was determined by N_2 desorption. The patterns of X-ray diffraction were obtained by using a Rigaku X-ray diffraction meter with Cu $K\alpha$ radiation.

Table 1. Hydrogenation of Carbon Dioxide over Cu–Zn–Cr Oxide

Run	Catalyst[a]		Conversion	Selectivity (%)		Yield of	BET
	(Molar ratio)		of CO_2 (%)	MeOH	CO	MeOH (%)	$(m^2 g^{-1})$[b]
1	Cu–Zn	(1 : 1)[c]	3.5	100	0	3.5	3.3
2	Cu–Cr	(2 : 1)	12.9	36.9	63.1	4.8	118.0
3[d]	Cu–Cr	(2 : 1)	23.8	21.6	78.4	5.1	—
4[e]	Cu–Cr	(2 : 1)	29.1	10.9	89.1	3.2	—
5	Zn–Cr	(2 : 1)	0.2	100	0	0.2	103.1
6[e]	Zn–Cr	(2 : 1)	28.4	8.7	91.3	2.5	—
7	Cu–Zn–Cr	(2 : 2: 1)	24.8	58.6	41.4	14.6	105.5
8	Cu–ZrO_2	(4 : 6)[f]	4.7	47.8	52.2	2.2	31.3

Conditions: 50 kg cm^{-2}, 250 °C, SV=3000 ml g-cat^{-1} h^{-1}, H_2/CO_2=3. a) Catalysts prepared by Method A were used. b) After used for the reaction. c) Kneading of CuO with ZnO. d) 300 °C. e) 350 °C. f) Coprecipitation.

Results and Discussion

Effect of Copper and Zinc on Methanol Synthesis. The results of the hydrogenation of carbon dioxide are shown in Table 1 using various catalysts prepared by Method A. The addition of CrO_3 increased the catalytic activity remarkably. Although the activity of the Cu–Zn catalyst by kneading (Run 1) was low, those of Cu–Zn–Cr oxide (2 : 2 : 1) catalysts were greatly improved (Run 7). The patterns of CuO and ZnO in X-ray diffraction, which were clearly observed in the kneading catalyst before being used for the reaction, were not found in Cu–Zn–Cr oxide, as reported by Ogino et al.[6] It seems that CuO and ZnO reacted with chromic acid in the preparation of Cu–Zn–Cr oxides.

The effects of copper and zinc species on the catalytic activity of methanol synthesis were also studied. Cu–Cr oxide obtained from CuO and CrO_3 gave methanol in low yield (4.8%; Run 2). A better yield of methanol was found at 300 °C over Cu–Cr oxide (Runs 2—4), although the optimum temperature was approximately 250 °C in the case of Cu–Zn–Cr oxide, as mentioned later. On the other hand, the Zn–Cr oxide catalyst had an extremely low catalytic activity (Run 5) and the yield of methanol was only 2.5%, even at 350 °C (Run 6).

The best result was obtained by a combination of copper, zinc, and chromium (Cu : Zn : Cr=2 : 2 : 1). Copper species seem to play the most important role in methanol synthesis. The addition of the zinc species to Cu–Cr oxide lowered the optimum temperature for methanol synthesis from 300 to 250 °C. The synergistic effect of the coprecipitated Cu–ZnO catalysts on the methanol synthesis from syngas has often been discussed.[9] A similar phenomenon, induced by the coexistence of copper and zinc species, was also observed, even in the hydrogenation of carbon dioxide over Cu–Zn–Cr oxide.

The relation between the productivity of methanol and the content of copper in Cu–Zn–Cr oxide (by Method A), where the ratio of the zinc and chromium was fixed (2 : 1), was also studied; the results are given in Fig. 1. The activities of a catalyst without copper (Cu: 0%) and of CuO alone (Cu: 100%) were extremely low; the maximum activity was observed when the content of copper was about 40% (Cu : Zn : Cr=2 : 2 : 1). On the other hand, the relationship betwen the productivity of methanol and the BET surface area was not observed.

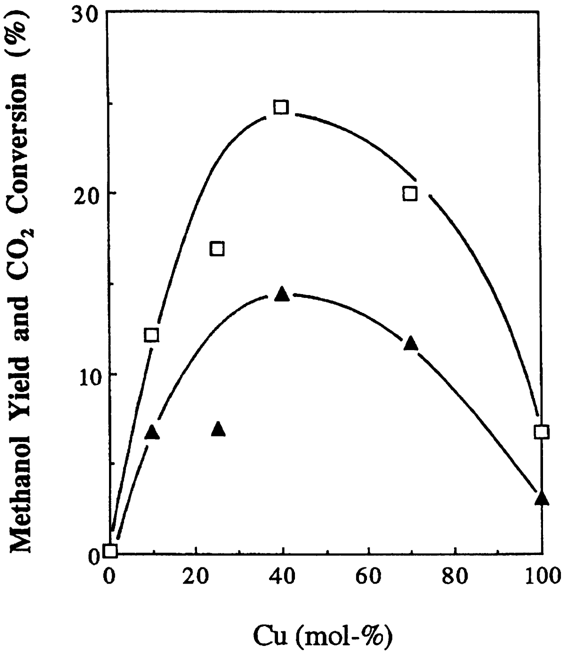

Fig. 1. Effect of the copper content on the productivity of methanol over Cu–Zn–Cr oxide (Zn : Cr=2 : 1) prepared by the Method A. (▲: MeOH Yield, □: CO_2 Conversion; 50 kg cm^{-2}, 250 °C, SV=3000 ml g-cat.$^{-1}$ h^{-1}).

It was recently reported that Cu–ZrO_2 catalysts were also effective for the hydrogenation of carbon dioxide.[2c] However, Cu–ZrO_2 (4 : 6) had extremely low activity under our conditions (Run 8).

Improvement of Cu–Zn–Cr Oxide. Although a method of Ogino et al. (Method A) was unique and effective, it was not modified for the hydrogenation of carbon dioxide.[7] In addition, recent research has found that the hydrogenation of carbon dioxide is not always

Table 2. Comparison of the Catalytic Activity of Various Catalysts

Run	Catalyst (Molar ratio)	Method	Conversion of CO_2 (%)	Selectivity (%) MeOH	Selectivity (%) CO	Yield of MeOH (%)	BET $(\mathrm{m^2/g^{-1}})$[a]
1	Cu–Zn–Cr (6 : 14 : 5)	A	24.0	57.8	42.2	13.9	144.2
2	Cu–Zn–Cr (6 : 14 : 5)	B	22.0	54.4	44.6	12.0	108.7
3	Cu–Zn–Cr (6 : 14 : 5)	C	25.6	63.3	36.7	16.2	47.4
4	Cu–Zn–Cr (2 : 2 : 1)	C	23.5	56.1	43.9	13.2	52.6
5	Cu–Zn–Cr (6 : 14 : 5)[b]	C	21.1	60.3	39.7	12.7	42.0
6	Cu–Zn–Cr (6 : 14 : 5)	D	23.5	55.8	44.2	13.1	198.4
7	Cu–Zn–Cr (6 : 14 : 5)	E	15.3	45.4	54.6	6.9	87.5
8	Cu–ZnO (3 : 7)	c)	22.4	53.5	46.5	12.0	20.7
9	Cu–Zr–Cr (8 : 12 : 5)	C	20.4	12.5	87.5	2.6	11.9

Conditions: 50 kg cm^{-2}, 250 °C, SV=3000 ml g-cat.$^{-1}$ h^{-1}, $H_2/CO_2=3$. a) After used for the reaction. b) Calcinated at 350 °C for 3 h. c) Coprecipitation.

similar to that of carbon monoxide.[2,10] It seems that the methods of mixing the copper and zinc species with CrO_3 are very important, especially for the hydrogenation of carbon dioxide, since the structure of copper and zinc oxide mainly influences their catalytic activity.[9] We thus tried to compare Method A (Ogino's method) with other methods (Methods B, C, D, and E) in a catalyst, Cu–Zn–Cr oxide (6 : 14 : 5). Since the copper–zinc species were prepared by coprecipitation, the ratio (3 : 7) of copper and zinc, which was regarded as being the best, was employed.[8] The content of chromium was fixed at 20%. Consequently, the ratio of copper, zinc, and chromium was determined to be 6 : 14 : 5. The results are summarized in Table 2.

As shown from Runs 1, 2, 3, 6, and in Table 2, a catalyst prepared by Method C (the mixing of a carbonate gel of copper and zinc with CrO_3) showed the best result in this study (Run 3). In the cases of both using a simple mixture of CuO and ZnO (Method B; Run 2) and of using a mixed oxide of copper and zinc (Method D; Run 6), the yields of methanol were approximately the same as that of a catalyst by Method A (Run 1). A catalyst prepared by the initial addition of ZnO to an aqueous solution of CrO_3 (Method E) had the worst activity (Run 7). Furthermore, a catalyst prepared by Method C was remarkably superior to a typical coprecipitated Cu–ZnO catalyst (Run 8). From the result of a calcinated Cu–Zn–Cr oxide (Run 5), this treatment was found to decrease the catalytic activity of Cu–Zn–Cr oxide. In addition, a catalyst produced by Method C, where the ratio of copper, zinc, and chromium was 2 : 2 : 1, also had a lower activity (Run 4). This result indicated that the ratio (3 : 7) of copper and zinc was favorable, even in this case.[8]

For the sake of revealing the difference in the activity of various catalysts (Methods A—E), the X-ray diffraction patterns of catalysts after being used for methanol synthesis were compared. Only the broad peaks of Cu_2O were observed in the catalysts prepared by Methods A and D. In the case of the catalysts prepared by Methods B and E, metallic copper along with Cu_2O were detected. On the other hand, the X-ray diffraction patterns of the catalyst prepared by Method C, which was confirmed to be the most effective in our study, were quite different from the others. Clear peaks of ZnO were observed with broad peaks of metallic copper and Cu_2O. Therefore, the crystal growth of ZnO remarkably occurred in this case. ZnO is thought to contribute to the stabilization of the active copper species,[9a] causing a difference in the activity of the catalysts. Although the detailed reason for the differences in the catalytic activity was not clear, it was confirmed that the method for mixing copper and zinc species was very important, even in the case of these Cu–Zn–Cr oxide catalysts.

On the other hand, Cu–Zr–Cr oxide prepared by Method C was examined as well (Run 9). Its catalytic activity for methanol synthesis was extremely low, even though the conversion of carbon dioxide was approximately the same as that for Cu–Zn–Cr oxides.

Catalytic Behaviors of Cu–Zn–Cr Oxide. The reaction behaviors of methanol synthesis were studied by using Cu–Zn–Cr (6 : 14 : 5; Run 3 in Table 2), which was the best one in this study. The effect of the pressure was examined, and the results are given in Fig. 2. Although both the yield and the selectivity of methanol increased with the reaction pressure, carbon monoxide decreased only slightly. While methanol synthesis was advantageous under high pressure, the reaction pressure did not dominate the productivity of carbon monoxide. Therefore, the decrease in carbon monoxide suggested that methanol was also obtained from carbon monoxide.

The dependence of the methanol yield on the temperature was studied (Fig. 3). Both the conversion of carbon dioxide and the yield of methanol increased with temperature below 250 °C. However, the yield of methanol decreased above 250 °C, in spite of a continuous increase in the conversion of carbon dioxide. The optimum temperature for methanol synthesis was confirmed to be approximately 250 °C.

The dependence of the methanol productivity on the space velocity of the feed gas was also studied. This study would be helpful for explaining the reaction pass of the hydrogenation of carbon dioxide.[10] The space ve-

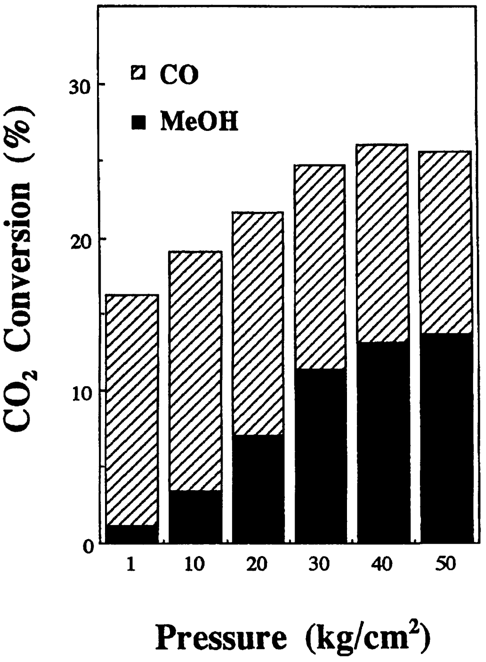

Fig. 2. Dependence of the productivity of methanol on the pressure over Cu–Zn–Cr oxide (6 : 14 : 5) prepared by the Method C. (250 °C, SV=3000 ml g-cat.$^{-1}$ h^{-1}).

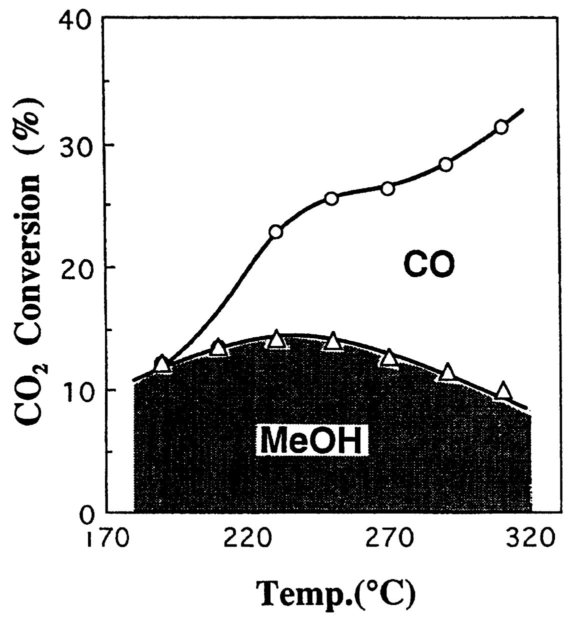

Fig. 3. Dependence of the productivity of methanol on the temperature over Cu–Zn–Cr oxide (6 : 14 : 5) prepared by the Method C. (50 kg cm^{-2}, SV=3000 ml g-cat.$^{-1}$ h^{-1}).

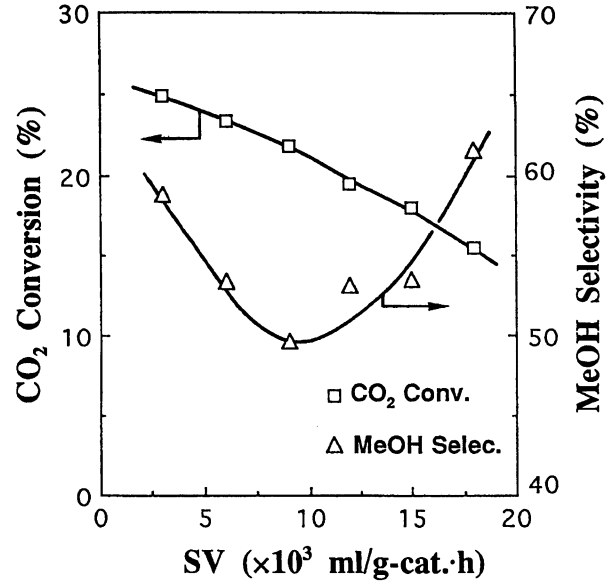

Fig. 4. Dependence of the productivity of methanol on the space velocity over Cu–Zn–Cr oxide (6 : 14 : 5) prepared by the Method C. (50 kg cm^{-2}, 250 °C).

locity was varied from 3000 to 18000 ml g-cat.$^{-1}$ h^{-1} in the hydrogenation reaction using the same Cu–Zn–Cr oxide catalyst at 250 °C and 50 kg cm^{-2} (Fig. 4). The conversion of carbon dioxide decreased along with an increase in the space velocity monotonously. The selectivity of methanol also decreased below 9000 ml g-cat.$^{-1}$ h^{-1}. However, the selectivity of methanol increased when the space velocity was greater than 9000 ml g-cat.$^{-1}$ h^{-1}. Similar results were reported by Arakawa et al.[11] They claimed from the results concerning both the dependence of the methanol productivity on the space velocity and in-situ FT-IR, that methanol was formed via carbon monoxide, mainly at a low space velocity (Eq. 1), and that the direct transformation of carbon dioxide to methanol occurred under high space-velocity conditions (Eq. 2). However, our results were not sufficient to discuss the reaction pass. As mentioned above, the specific behaviors as a methanol synthesis catalyst, compared with conventional coprecipitated catalysts, were not observed in our Cu–Zn–Cr oxide catalysts.[11] Therefore, the effectiveness of Cu–Zn–Cr oxide prepared by using CrO_3 for the hybrid catalysts was caused by mixing with zeolites.

$$CO_2 + 3H_2 \rightarrow CO \rightarrow CH_3OH \qquad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH \qquad (2)$$

The optimum temperature of the hybrid catalysts previously reported[5] was approximately 400 °C, while the most suitable temperature for methanol synthesis was about 250 °C. At high temperature, metallic copper must be sintered so as to decrease the catalytic activity. Therefore, the conditions of the catalysts at high temperature, for example 400 °C, was thought to be different from those at 250 °C. Then, the change in the catalytic activity of Cu–Zn–Cr oxide was studied when the reaction temperature was altered from 400 to 250 °C and from 250 to 400 °C. In the case that temperature was changed from 400 to 250 °C, the yield of methanol was relatively low after 1 h (11%) at earliest, but increased slightly with time and finally became stable after 3 h (16%). On the other hand, its catalytic activity just after the reaction temperature reached 400 °C from 250 °C (methanol yield: 6.5%) was higher than after 1 h at 400 °C (Methanol yield: 1%). After being used for the reaction at 400 °C, a moderate crystal growth of metallic copper was observed by X-ray diffraction compared with the catalyst used only for 250 °C. These results indicate that the conditions of the catalysts are different between 250 °C (favorable for methanol synthesis) and 400 °C (favorable for hydrocarbon synthesis over hybrid catalysts).

In the reaction of hybrid catalysts, carbon dioxide was converted into methanol over Cu–Zn–Cr oxide during the first stage, and methanol formed was transformed into hydrocarbons over zeolite during the next stage. Therefore, the methanol synthesis catalysts employed in hybrid catalysts require high catalytic activity of methanol formation at the temperature where zeolite exhibits its catalytic properties.

Conclusion

Cu–Zn–Cr oxide prepared by the mixing of copper and zinc species with CrO_3 were very effective for methanol synthesis by the hydrogenation of carbon dioxide. Especially, a catalyst prepared by Method C using a coprecipitated carbonate gel of copper and zinc, had a higher activity than catalysts prepared by Methods A, B, D, and E. However, the reaction behaviors of Cu–Zn–Cr oxide were approximately similar to those of conventional methanol synthesis catalysts.

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