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Support Effect of Zinc Oxide Catalyst on Synthesis of Methanol from CO_2 and H_2

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Synopsis. The synthesis of methanol from CO_2+H_2 was carried out at 340—400 °C under total pressure of 10 atm over ZnO supported on MgO, Al_2O_3, SiO_2, TiO_2, ZrO_2, and Nb_2O_5. The ZnO/ZrO_2 catalyst showed high activity and selectivity for methanol formation. The hydrogenation of CO_2 was more selective for methanol synthesis than that of CO.

The hydrogenation of CO has been extensively studied for the synthesis of hydrocarbons and alcohols.[1] For the production of methanol from $CO+H_2$, several catalysts such as ZnO-Cr_2O_3, CuO-ZnO-Al_2O_3, CuO-ZnO-Cr_2O_3 are known to be efficient.[2] However, the study of CO_2 hydrogenation has been much less extensive than those of CO hydrogenation. Although, for the synthesis of methanol from CO_2+H_2, several catalysts such as CuO,[3] Pd,[4] Re,[5] or Pt[6] supported on metal oxides are reported, no study has been made of ZnO supported on metal oxides. Thus, the support effect of ZnO catalyst on CO_2 hydrogenation has been examined in the present work.

Experimental

Zinc oxides supported on various oxides were prepared by impregnating ZrO_2, TiO_2, SiO_2, Al_2O_3, or Nb_2O_5 with an aqueous solution of zinc nitrate followed by calcining at 500 °C for 3 h and reducing at 400 °C in a stream of hydrogen before use. In the case of ZnO/MgO, a methanol solution of zinc nitrate was used to avoid the partial dissolution of MgO in water. The content of ZnO was 10 wt % for all catalysts. Zinc oxide itself was prepared by hydrolyzing an aqueous solution of zinc nitrate with aqueous ammonia followed by treating similarly as above. Commercial catalysts of methanol synthesis from CO and H_2 used for comparison were Toyo CCI, KMA (ZnO-Cr_2O_3), and MDC-02 (CuO-ZnO-Al_2O_3) which were treated similarly as above.

The reaction was carried out at 340—400 °C under 10 atmospheric pressure by use of a conventional flow reactor. The molar ratio of CO_2/H_2 or CO/H_2 in the premixed gas obtained from Nippon Sanso Co. was 1/3. The flow rate of the gas was 12.5 mmol h^{-1} under standard condition, GHSV being 600—1200 h^{-1}. The reaction products were analyzed by gas chromatography.

Results and Discussion

Table 1 shows the results of the hydrogenation of CO_2 over supported ZnO catalysts. Main products were, besides CO, methanol and dimethyl ether. The ZnO and ZnO/MgO catalysts showed 100 % selectivity for methanol formation, but their activities (rate of methanol formation) were low. On the other hand, the activities of ZnO/Al_2O_3, ZnO/SiO_2, and ZnO/TiO_2 were higher, but their selectivities were lower. The ZnO/ZrO_2 catalyst exhibited not only high activ-

Table 1. Hydrogenation of CO_2 over Supported ZnO Catalysts
($CO_2/H_2=1/3$, Total Pressure = 10 atm)

Catalyst (weight)	Reaction temp / °C	Rate of $MeOH+Me_2O$ formation / 10^{-4} mol h^{-1} g^{-1}	Selectivity/%		Rate of CO formation / 10^{-4} mol h^{-1} g^{-1}
			MeOH	Me_2O	
ZnO (3.0 g)	360	0.07	100.0	—	0.8
	400	0.08	100.0	—	2.5
ZnO/MgO (1.5 g)	360	0.02	100.0	—	0.1
	400	0.08	100.0	—	0.6
ZnO/Al_2O_3 (1.0 g)	360	0.18	40.8	59.2	1.3
	380	0.5	38.0	62.0	3.7
ZnO/SiO_2 (1.0 g)	360	0.13	97.8	2.2	0.3
	400	0.35	86.9	13.1	1.3
ZnO/TiO_2 (2.0 g)	340	0.3	86.9	13.1	0.6
	360	0.7	77.0	23.0	1.2
ZnO/ZrO_2 (2.0 g)	340	0.4	99.9	trace	0.4
	360	0.8	99.2	0.8	1.1
ZnO/Nb_2O_5 (2.0 g)	360	trace	—	—	1.5
KMA[a] (2.0 g)	360	0.8	99.8	0.2	10.6
MDC-2[a] (2.0 g)	340	0.5	89.7	(10.3)[b]	10.2

a) Commercial catalysts of Toyo CCI. The composition of KMA and MDC-2 are known to be ZnO-Cr_2O_3 and CuO-ZnO-Al_2O_3, respectively. b) No ether is formed, the selectivities of CH_4 and C_2^+ being 5.7 and 4.6%, respectively.

Table 2. Hydrogenation of CO over ZnO/TiO_2 ($CO/H_2=1/3$, Total Pressure = 10 atm)

Catalyst	Reaction temp °C	Rate of $MeOH+Me_2O$ formation 10^{-4} mol h^{-1} g^{-1}	Selectivity/%		Rate of CO_2 formation 10^{-4} mol h^{-1} g^{-1}
			MeOH	Me_2O	
ZnO/TiO_2	340	0.7	29.2	70.7	0.8
	360	2.2	9.9	90.0	1.0

ity, but also high selectivity. Little activity was found in the case of ZnO/Nb_2O_5.

These results can be interpreted in terms of acid-base properties of the catalyst supports. Dimethyl ether which is known to be formed by dehydration of methanol was formed over the acidic catalyst supports (Al_2O_3, TiO_2, and SiO_2). The stronger the acid strength of the oxides, the larger the amount of dimethyl ether. Thus, the high selectivity for formation of methanol was obtained over basic or less acidic catalyst or supports (ZnO, MgO, and ZrO_2). In the hydrogenation of CO over Rh supported on various metal oxides, Ichikawa[7)] reported that the selectivity for methanol formation was high over Rh supported on basic oxides such as BeO, MgO, CaO, and ZnO. In the case of Pt supported on metal oxides, the selectivity for methanol formation was also high over Pt supported on a basic MgO in the hydrogenations of both CO and CO_2.[6)] Hence, the use of basic supports seem to be advantageous for methanol synthesis regardless of the kinds of metals and the difference between CO and CO_2.

Commercial catalysts of methanol synthesis from $CO + H_2$ showed considerably high activities and KMA gave a high selectivity for methanol formation. However, the rate of CO formation was much higher over both KMA ($ZnO\text{-}Cr_2O_3$) and MDC-2 ($CuO\text{-}ZnO\text{-}Al_2O_3$) than over the other catalysts.

The rate of formation of methanol and dimethyl ether from CO_2+H_2 was low in the initial stage of the reaction, but gradually increased and reached steady states in 2—4 h over all the catalysts. The selectivity for methanol formation gradually increased as the reaction proceeded. This suggests the gradual change of surface active species to favor methanol formation. In fact, the activity and the selectivity of ZnO/TiO_2 for methanol formation in the initial stage of the reaction increased when treated with the mixture gas of H_2O+H_2. Therefore, water molecules are one of the factors to enhance the catalytic activity.

To clarify the difference in reactivity between CO_2 and CO, the reaction of CO_2+H_2 was compared with that of $CO+H_2$ over the ZnO/TiO_2 catalyst. As seen from the comparison of Table 2 with Table 1, the reactivity of CO was higher than that of CO_2, however the selectivity for methanol formation in the reaction of $CO+H_2$ was much lower than that in the reaction of CO_2+H_2. Denise and Sneeden[8)] made a comparison of methanol synthesis from CO with that of CO_2 over CuO/ZnO and found that the hydrogenation of CO_2 is more reactive than that of CO at lower temperatures, though the latter is more reactive than the former at higher temperatures. These indicate that the superiority of CO_2 hydrogenation to CO hydrogenation for methanol synthesis depends on the kinds of catalysts and reaction conditions.

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