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Methanol Synthesis from CO_2 and H_2 over $Cu/ZnO/Ga_2O_3$ Catalyst

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The methanol synthesis activity per unit copper surface area of Cu/ZnO catalyst combined with Ga_2O_3 was higher than those of Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalyst in the hydrogenation of carbon dioxide.

The methanol synthesis from CO_2 and H_2 has recently received much attention as one of the promising process for the utilization of CO_2. It has been reported that Cu/ZnO catalysts are highly effective for this reaction.[1,2] The effect of addition of various oxides to Cu/ZnO catalyst have been widely investigated. It was reported that $Cu/ZnO/Al_2O_3$,[3,4] $Cu/ZnO/ZrO_2$,[5] and $Cu/ZnO/Cr_2O_3$[2] were good methanol synthesis catalysts with high activity and selectivity. We have recently found Cu/ZnO catalyst combined with Ga_2O_3 is highly active for methanol synthesis from CO_2 and H_2. In the present work, the activity and the methanol selectivity of $Cu/ZnO/Ga_2O_3$ catalysts were examined and they were compared with those of Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalysts. Cu/ZnO, $Cu/ZnO/Ga_2O_3$ and $Cu/ZnO/Al_2O_3$ catalysts were prepared by a copresipitation method. A mixed aqueous solution of metal nitrates (total metal concentration 1 mol/l) and an aqueous solution of Na_2CO_3 (1.1 mol/l) were added dropwise to distilled water. Subseqently, the precipitate was filtered out, washed with distilled water, dried in air at 100 °C overnight, and calcined in air at 350 °C for 2 h, and screened to a size between 60 and 80 mesh. All the catalysts were reduced with a gas mixture of H_2 (10%) and He (90%) at 250 °C for 2 h in a reactor at a total pressure of 50 kg/cm^2G. A hydrogenation reaction of CO_2 with H_2 was carried out in a flow reactor. A gas mixture of H_2 and CO_2, of which the mole ratio of H_2 to CO_2 was 3, was fed through under a total pressure of 50 kg/cm^2G. The reaction products were analyzed by gas chromatography. The copper surface area of each of the catalysts was measured by the technique of N_2O reactive frontal chromatography.[6] Methanol and CO were mainly produced and a trace amount of methane, dimethylether and metheylformate were also detected.

Table 1 gives the activities (conversion of CO_2) and methanol selectivities of Cu/ZnO, $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Ga_2O_3$ catalysts with various composition for the hydrogenation of CO_2. In the case of $Cu/ZnO/Ga_2O_3$ catalysts, the highest methanol synthesis activity, i.e., mass time yield (MTY), was obtained at 25 wt% of Ga_2O_3 content. And the activity of this $Cu/ZnO/Ga_2O_3$ catalyst was higher than those of Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalysts. Figure 1 shows the methanol synthesis activities of Cu/ZnO, $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Ga_2O_3$ catalysts as a function of copper surface area. This clearly shows that for each of the catalyst system there

Table 1. Activity and Cu surface area Cu/ZnO, $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Ga_2O_3$ catalysts[a)]

Catalyst composition[c)]	Reaction temp °C	Conversion %	Selectivity %	MTY[b)] $g\text{-}CH_3OH/kg\text{-}cat{\bullet}h$	Cu surface area $m^2/g\text{-}cat$
Cu/ZnO	200	5.8	77.2	286	27.8
50/50	250	17.4	42.1	514	
$Cu/ZnO/Al_2O_3$	200	5.7	74.0	285	35.4
50/40/10	250	19.7	48.1	637	
$Cu/ZnO/Ga_2O_3$	200	6.9	73.2	319	25.0
50/45/5	250	20.4	47.6	379	
$Cu/ZnO/Ga_2O_3$	200	7.1	72.6	321	26.9
50/40/10	250	21.5	50.2	679	
$Cu/ZnO/Ga_2O_3$	200	7.4	76.4	363	28.4
50/30/20	250	22.1	52.2	736	
$Cu/ZnO/Ga_2O_3$	200	7.7	77.6	375	29.9
50/25/25	250	22.1	53.2	738	
$Cu/ZnO/Ga_2O_3$	200	6.7	73.4	318	27.5
50/20/30	250	21.1	48.0	645	
$Cu/ZnO/Ga_2O_3$	200	3.8	69.1	203	17.5
50/10/40	250	17.1	39.6	405	
Cu/ZnO	200	2.4	67.5	128	14.2
50/50	250	14.4	32.9	350	

a)Reaction condition; $H_2/CO_2=3$, Total pressure=50 kg/cm^2G, Catalyst weight=1.0 g, Feed gas rate=300 cc/min. b)Mass time yield. c)Composition of catalyst is shown by wt%.

is a linear relationship between methanol synthesis activity and copper surface area, and also indicates that the specific methanol synthesis activity, i.e. MTY per copper surface area, of $Cu/ZnO/Ga_2O_3$ catalyst is about 40% higher than those of Cu/ZnO and $Cu/ZnO/Al_2O_3$. In addition, it was found that the copper surface area of the catalyst containing 20-30 wt% Ga_2O_3 was higher as compared with Cu/ZnO catalyst.

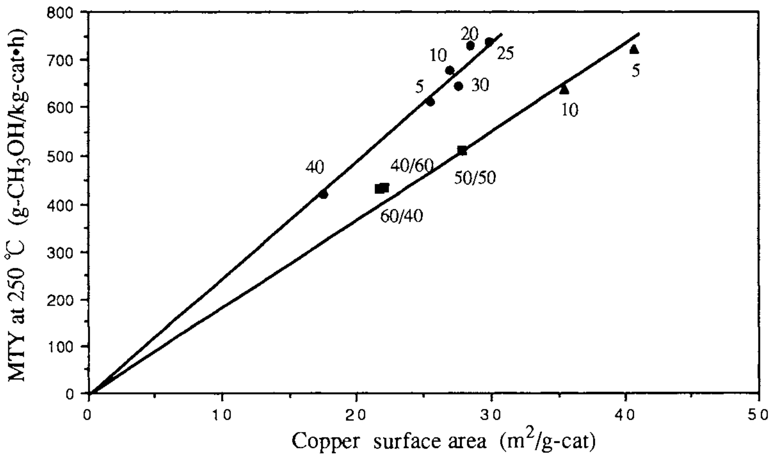

Fig. 1. Methanol synthesis activity (MTY) as a function of copper surface area.
■;Cu/ZnO catalysts [Cu(40)/ZnO(60), Cu(50)/ZnO(50), Cu(60)/ZnO(40)]
▲;Cu(50)/ZnO/Al_2O_3 catalysts [Al_2O_3 content, 5, 10 wt%]
●;Cu(50)/ZnO/Ga_2O_3 catalysts [Ga_2O_3 content, 5, 10, 20, 25, 30, 40 wt%]

In summary, it is clear that the addition of Ga_2O_3 to Cu/ZnO highly enhances the specific methanol synthesis activity of Cu/ZnO. At present, however, no clear explanation for the ositive effects of Ga_2O_3 incorporated can be offered. Further investigation on the role of Ga_2O_3 in $Cu/ZnO/Ga_2O_3$ catalyst will be preformed.

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Referances

1) B. Denise and R.P.A Sneeden, *Appl. Catal.*, **28**, 235(1986).
2) T.Tagawa, G.Pleizier, and Y. Amenomiya, *Appl. Catal.*, **18**, 285(1985).
3) Y. Amenomiya and T. Tagawa, "Proc. 8th Int. Congr. Catalysis," Verlag Chemie, Weinheim (1984), vol. II, p.557.
4) E. Ramarson, R. Kieffer, and A. Kiennemann, *Appl. Catal.*, **4**, 281(1983).
5) Z. Xu, Z. Qian, L. Mao, K.Tanabe, and H. Hattori, *Bull. Chem. Soc. Jpn.*, **64**, 1658(1991).
6) G. C. Chinchen, K. C. Waugh, and D.A.Whan, *Appl. Catal.*, **25**, 101(1986).

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