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EFFECTS OF CATALYST COMPOSITION ON METHANOL SYNTHESIS FROM CO_2/H_2

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Abstract—Effects of catalyst composition have been studied for Cu/support and Cu/ZnO/supports in methanol synthesis from CO_2/H_2. A strong effect of support has been observed. Different supports brought about different behavior in temperature-programmed reduction of copper, different copper surface areas, and different catalytic activity and selectivity. It seemed possible to find catalyst supports that might perform better than commercial $Cu/ZnO/Al_2O_3$ catalysts. A correlation was observed between catalytic activity and the copper surface area which was varied by using different supports. However, the supports appeared to influence other catalytic properties as well, for example, the surface oxygen coverage.

Key words: Methanol Synthesis, CO_2/H_2, Copper Catalysts, Support Effects, Copper Area

INTRODUCTION

Carbon dioxide is the most important "greenhouse gas" which may cause the global warming. Various measures have been proposed to stabilize the atmospheric CO_2 concentration which include chemical fixation and recycling the emitted CO_2 [Lee and Lee, 1993]. Conversion of CO_2 to methanol by catalytic hydrogenation (Reaction 1) has been recognized as a promising route for the purpose because of a potentially large demand for methanol as a fuel and a basic chemical [Arakawa et al., 1992].

$$CO_2+3H_2 \rightarrow CH_3OH+H_2O \quad (1)$$

The process is closely related to established methanol synthesis technology from CO/H_2 (Reaction 2) because current industrial feeds contain ca. 5 vol% of CO_2 in addition to CO/H_2 [Bart and Sneeden, 1987].

$$CO+2H_2 \rightarrow CH_3OH \quad (2)$$

The processes are operating at 50-100 bar and 220-240°C with catalysts composed of $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ [Bart and Sneeden, 1987]. Although the catalysts are highly effective for the current CO-rich feeds, they may not necessarily be as effective for CO_2-rich feeds. Indeed, modified catalysts have been reported which perform better than the current catalysts for CO_2/H_2 reactions although most new catalysts contain copper as the main component [Amenomiya et al., 1985, 1988; Denise et al., 1986a, 1986b, 1989; Ramaroson, 1982; Fujitani, 1994].

In this work, we prepared many two component catalysts containing copper as the main component and three component catalysts containing Cu/ZnO as the basis. Catalysts were characterized by temperature-programmed reduction (TPR), BET area (S_{BET}) measurement and surface copper area (S_{Cu}) by N_2O titration. Attempt was made to correlate the properties of a catalyst with its reactivity in methanol synthesis from CO_2/H_2.

EXPERIMENTAL

Catalyst used in this study was prepared by a conventional coprecipitation method. It was precipitated from an aqueous solution of $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (all Alfa, total cation concentration 1 M) by dropwise addition of a 1 M aqueous solution of Na_2NO_3 (Alfa) at 80°C to a final pH of 7. The precipitate was then filtered, dried, and then calcined in air at 350°C for 12 h. For other catalysts, copper was combined with SiO_2 (Zerosil, Alfa), TiO_2 (Alfa), Al_2O_3 (Alfa), MgO (Alfa), ZrO_2 (prepared from $ZrOCl_2$ by precipitation), MoO_3 (Aldrich), V_2O_5 (Junsei), $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich) and $Zn(NO_3)_2 \cdot 6H_2O$ by precipitation or coprecipitation following the similar procedure. The resulting powders were ground and sieved to obtain mesh sizes of 100-140. Prior to synthesis reaction, typically 0.5 g of the calcined catalyst was reduced in a flowing 20% H_2/He mixture (34 μmol s^{-1}) at atmospheric pressure and temperatures increasing at a rate of 150°C h^{-1} up to 250°C and then in pure H_2 (27 μmol s^{-1}) at 250°C for 3.5 h.

Specific surface area was determined by the N_2 BET method on a Micromeritics constant-volume adsorption system (Accusorb 2100E). Exposed copper surface area was determined by the N_2O titration on a Pyrex flow system following the procedure described by Chinchen et al. [1987]. Reduced catalysts were flushed by He at 60°C and N_2O was supplied at 14 μmol s^{-1}. N_2O reacts with surface copper leaving behind surface oxygen $(Cu\text{-}O\text{-}Cu)_s$ and produces N_2 according to the following stoichiometry.

$$N_2O(g)+2Cu(s) \rightarrow N_2(g)+(Cu\text{-}O\text{-}Cu)_s \quad (3)$$

The amount of the produced N_2 was measured by a thermal conductivity detector (TCD) and a typical chromatogram is shown in Fig. 1. The surface copper area S_{Cu} is calculated from integrated N_2 area and assuming a copper atom density of 1.46×10^{19} m^{-2} [Chinchen et al., 1987]. TPR was performed on the same apparatus. Typically 25 mg of a calcined catalyst was flushed in He at

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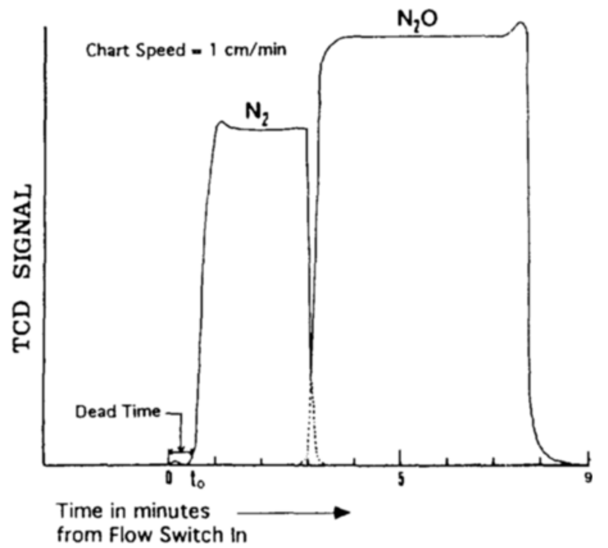

Fig. 1. A typical N_2O titration chromatogram for the determination of copper surface area.

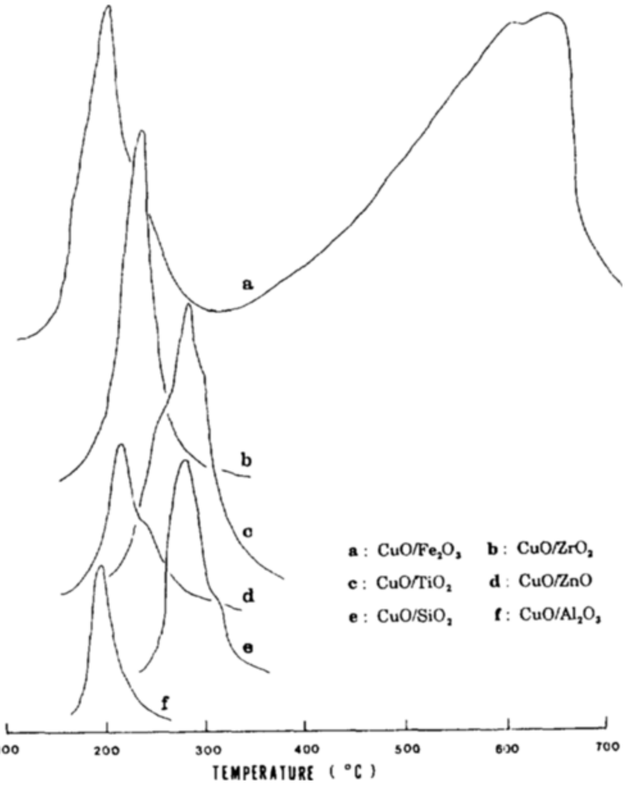

Fig. 2. TPR spectra (hydrogen consumption) of two component catalysts containing 24 wt% copper.

150°C to remove adsorbed water. After cooling to room temperature, temperature was increased at a rate of 3.4°C min^{-1} in a flow of 5% H_2 in N_2. The consumption of H_2 was continuously monitored by TCD.

The detailed procedure for the methanol synthesis reaction has been described elsewhere [Lee et al., 1993]. An in-house modification of a commercial Sotelem RDP-830 reaction system was employed as a pressurized flow reactor. Reaction products were analyzed by an on-line gas chromatography (Hewlett-Packard 5890) equipped with a 2.5 m long Porapak T column and a thermal conductivity detector.

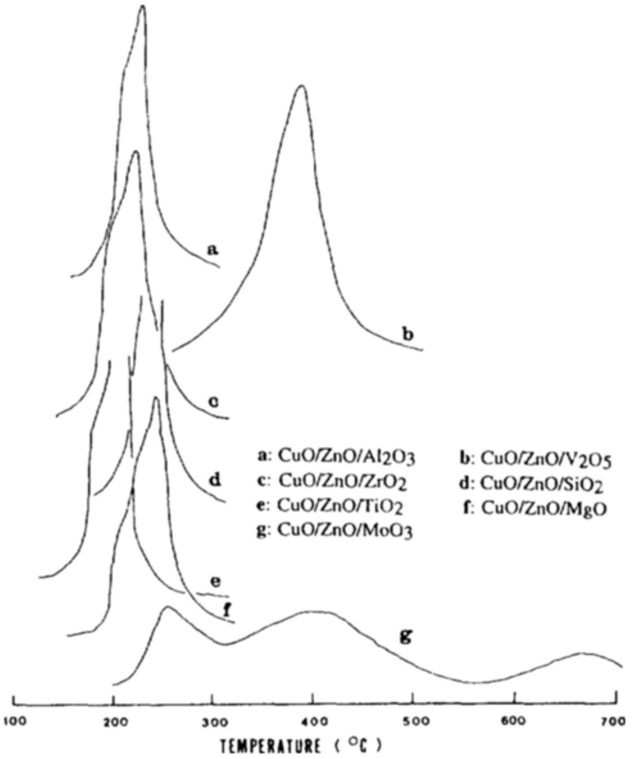

Fig. 3. TPR spectra (hydrogen consumption) of three component catalysts containing Cu/ZnO (20 wt%/56 wt%).

RESULTS AND DISCUSSION

1. Temperature-Programmed Reduction (TPR)

The support materials chosen in this study have been known to be effective in methanol synthesis from CO_2/H_2 or CO/H_2 [Bart and Sneeden, 1987]. The results of TPR for the calcined samples are shown in Fig. 2 and 3. The reducibility of copper represented by the peak temperature depended markedly on the employed support for both two and three component catalysts. Catalysts containing Fe_2O_3 showed high temperature reduction peaks of Fe_2O_3. For two component catalysts, the ease of reduction followed the order of $Fe_2O_3>Al_2O_3>ZnO>ZrO_2>SiO_2$-$TiO_2$. Some peaks apparently consisted of two or three unresolved peaks, indicating the presence of species with different degrees of reducibility. For example, it has been shown that bulk CuO is more difficult to be reduced than small copper crystallites, yet the reduction of copper in close interaction with the other phase is even harder in spite of its small size [Matulewicz et al., 1984; Fleisch et al., 1984]. Interestingly, the amount of hydrogen consumption was also different among the catalysts although all catalysts contained 24 wt% copper. Peak area decreased as follows: $Fe_2O_3>ZnO$-ZrO_2-$TiO_2>SiO_2>Al_2O_3$. Since all the support except Fe_2O_3 are not reduced below 350°C, the peaks are due to the reduction of copper oxide. Hence, different peak positions and areas reflect different physical and chemical states of copper oxide precursor due to support effects. Different precursor states are also believed to lead to different states of copper in reduced catalysts. Three com-

Table 1. Effect of copper loading on catalytic properties[a]

Catalyst	Weight ratio	S_{BET} (m^2g^{-1})	S_{Cu} (m^2g^{-1})	N_s/N_T[b] (%)	CO_2 conversion (%)	CH_3OH selectivity (%)	Turnover rate[c] (10^{-3} s^{-1})
Cu/ZnO	17/83	14.3	1.8	1.7	1.4	71.2	9.5
	30/70	11.8	2.7	1.4	1.9	69.3	8.7
	45/55	9.8	2.8	0.96	2.6	73.1	11.2
Cu/ZrO_2	2/98	51.6	2.1	16.0	0.08	-	0.47
	10/90	64.4	2.4	3.8	0.13	35.9	0.67
	40/60	40.4	1.8	0.70	0.22	56.9	1.5
$Cu/ZnO/Al_2O_3$	9/7/84	262.4	4.6	7.7	4.1	25.3	10.9
	29/44/27	48.4	7.4	4.0	4.4	49.1	7.3
	49/36/15	34.9	5.3	1.7	4.6	58.1	10.7
$Cu/ZnO/ZrO_2$	24/12/64	10.2	6.1	3.8	4.8	52.4	9.7
	26/65/09	15.8	2.2	1.3	2.0	72.8	8.2
	37/45/18	23.2	5.1	2.2	3.5	58.7	8.5

[a] Reaction conditions: 230℃, 20 bar, $H_2/CO_2=3$, GHSV=6000 h^{-1}.

[b] % surface copper atom relative to total copper.

[c] The rate of CO_2 conversion per second per surface copper atom measured by N_2O titration.

Table 2. Catalytic properties of two component catalysts (24 wt% Cu/support)

Support	S_{BET} (m^2g^{-1})	S_{Cu} (m^2g^{-1})	N_s/N_T[b] (%)	CO_2 conversion (%)	Selectivity (%)			Turnover rate[c] ($10^{-3}s^{-1}$)
					CH_3OH	CO	CH_4	
Al_2O_3[d]	173.8	3.5	2.2	2.5	56.0	42.5	0.6	5.5
Fe_2O_3[e]	71.5	9.0	5.8	6.3	6.6	25.4	32.9	5.4
SiO_2	218.0	4.7	3.0	4.2	1.9	97.3	0.8	6.7
TiO_2	4.6	0.96	0.61	0.6	29.8	67.5	2.7	4.8
ZnO	41.7	15.4	9.9	8.8	46.6	53.2	0.2	4.4
ZrO_2	124.9	1.9	1.2	3.0	28.2	71.4	0.4	12.1

[a] Reaction conditions: 230℃, 30 bar, $H_2/CO_2=3$, GHSV=6000 h^{-1}.

[b] % surface copper atom relative to total copper.

[c] The rate of CO_2 conversion per second per surface copper atom measured by N_2O titration.

[d] The balance of the selectivity was to dimethyl ether.

[e] The balance of the selectivity was to hydrocarbons.

ponent catalysts based on Cu/ZnO also showed significant support effects in TPR spectra (Fig. 3). The ease of reduction followed the order of $TiO_2>Al_2O_3$-$ZrO_2>MgO$-$SiO_2>MoO_3>V_2O_5$.

2. Effect of Copper Loading

Table 1 shows effects of copper loading for four catalysts. BET areas decreased as copper loading was raised for two component catalysts (Cu/ZnO, Cu/ZrO_2). For three component catalysts ($Cu/ZnO/Al_2O_3$, $Cu/ZnO/ZrO_2$), higher S_{BET} values were obtained for catalysts containing higher concentrations of Al_2O_3 or ZrO_2. Thus, most BET areas appear to originate from the supports. The copper area S_{Cu} measured by N_2O titration showed a maximum as copper loading was increased. The N_s/N_T in Table 1 is % surface copper relative to total copper and shows monotonic decreases with increasing copper loadings. Increased copper loadings also led to increased CO_2 conversions and methanol selectivity in methanol synthesis from CO_2/H_2 at 230℃ and 20 bar. Improved selectivity was due to suppressed formation of CO and CH_4. In general, as will be discussed shortly, ZnO was more effective than ZrO_2 as a support for two component catalysts, and three component catalysts performed better than two component catalysts.

3. Two Component Catalysts

Catalytic properties of two component catalysts are summarized in Table 2. As mentioned, copper content was fixed at 24 wt%. Wide variations are evident in S_{BET} and S_{Cu} values depending on the employed support. The S_{Cu} decreased in the following order: $ZnO>Fe_2O_3>SiO_2>Al_2O_3>ZrO_2>TiO_2$. Correlation between S_{BET} and S_{Cu} is weak. The reactivity of catalysts also showed a marked support effect in methanol synthesis from CO_2/H_2 at 230℃ and 30 bar. The Cu/Fe_2O_3 catalyst produced 35.2% hydrocarbons ($>C_2$) and Cu/Al_2O_3 yielded 2.0% dimethylether. Both of these products should be formed on supports. Other catalysts produced only CH_3OH, CO, and CH_4 as shown in Table 2. Figure 4 shows graphically CO_2 conversion and methanol selectivity for this series of two component catalysts. The supports were lined up in the order of increasing surface copper areas. CO_2 conversion decreased as $ZnO>Fe_2O_3>SiO_2>ZrO_2>Al_2O_3>TiO_2$. Note that this is very close to an order of decreasing S_{Cu}, suggesting that it is probably the most important parameter determining the reactivity of two component catalysts. The methanol selectivity followed the order of $Al_2O_3>ZnO>TiO_2>ZrO_2>Fe_2O_3>SiO_2$.

Compared to TPR results in Fig. 2, it appears that active and selective supports Al_2O_3 and ZnO are the ones which showed low temperature reduction peaks in TPR. In contrast, SiO_2 and TiO_2 which showed high temperature reduction peaks showed poor selectivity. It is interesting to note that Al_2O_3 and ZnO, components of commercial $Cu/ZnO/Al_2O_3$, perform the best individually as well in both activity and selectivity.

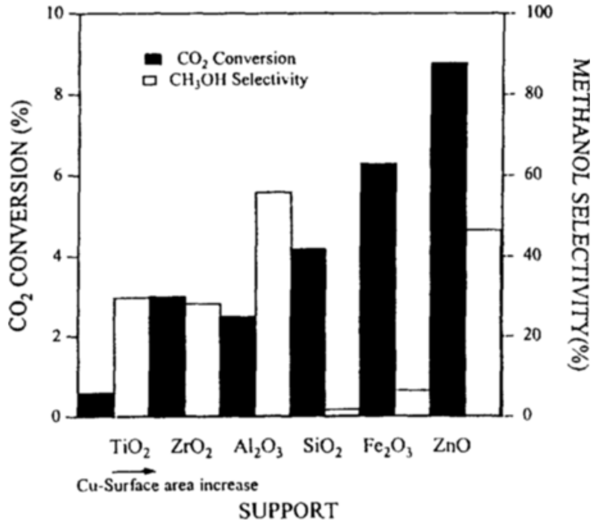

Fig. 4. Comparison of catalytic performance for two component catalysts containing 24 wt% copper in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $H_2/CO_2=3$. GHSV=6000 h^{-1}.

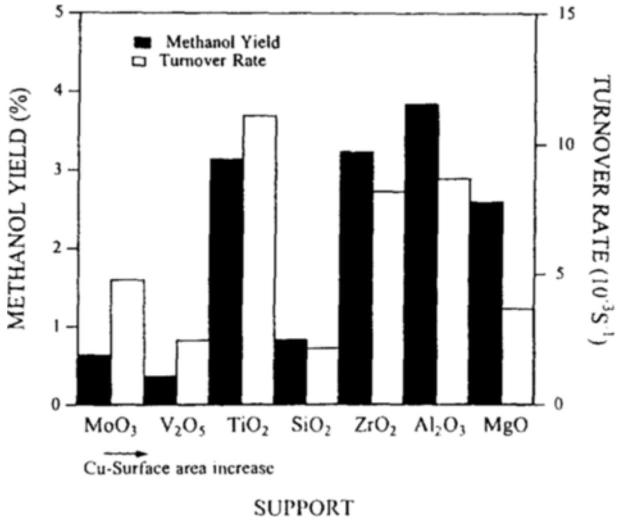

Fig. 5. Comparison of catalytic performance for three component catalysts containing 24 wt% copper in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $H_2/CO_2=3$. GHSV=6000 h^{-1}.

4. Three Component Catalysts

The characteristics of three component catalysts with Cu/ZnO (20 wt%/56 wt%) as common components are shown in Table 3. There was much less distribution of S_{Cu} values compared to two component catalysts. The S_{Cu} decreased in the order of MgO>Al_2O_3>ZrO_2>SiO_2>TiO_2>V_2O_5>MoO_3. A notable feature of the three component catalysts in methanol synthesis at 230°C and 30 bar was the greatly suppressed methane formation. Still, the support effect was significant although these catalysts contained two common components Cu/ZnO. Methanol yield (CO_2 conversion x methanol selectivity) and turnover rate (rate of CO_2 conversion per second per surface copper atom titrated by N_2O) are shown in Fig. 5. Cu/ZnO/Al_2O_3 containing the same components as commercial catalysts showed the highest methanol yield. TiO_2 and ZrO_2 were found to be almost as effective. The effectiveness of Al_2O_3 and ZrO_2 as supports of Cu/ZnO has also been reported [Xu et al., 1991]. In particular, Cu/ZnO/TiO_2 showed a higher turnover rate than Cu/ZnO/Al_2O_3, suggesting that a better catalyst based on this composition could be obtained if copper surface area is increased. It is also interesting to note that Cu/TiO_2, a poor catalyst as a two component catalyst, turned to an excellent one when combined with ZnO.

Like the two component catalysts, active catalysts are the ones that showed low reduction temperatures in TPR (Fig. 3). Hence, one reason for different activity might arise from the different degree of reduction. The poor activity of Cu/ZnO/V_2O_5 is most probably due to incomplete reduction of CuO. But other catalysts should be mostly reduced under our reduction condition (250°C). Furthermore, different degree of reduction was at least partly accounted for in the calculation of turnover rates. The large spread of turnover rates none the less suggests that there are other important factors determining the catalyst activity.

In both two and three component catalysts, SiO_2 support showed relatively high S_{Cu} values, yet very poor methanol yield. Cu/SiO_2 showed high selectivity to CO and Cu/ZnO/SiO_2 showed a poor activity of CO_2 conversion. Similar effect has been observed by Ramaroson et al. [1982]. Since Chinchen et al. [1986] reported that Cu/SiO_2 showed a turnover rate similar to that of Cu/ZnO/Al_2O_3 in methanol synthesis from CO/H_2 containing ca. 5% CO_2, it appears that the support effect depends on synthesis gas composition [Denise, 1986a]. Cu/ZnO/MgO had the highest S_{Cu} value. However, the methanol yield was lower than some active catalysts with lower S_{Cu} values. It has been reported that MgO forms a solid solution with ZnO and inhibits the methanol synthesis from $CO/CO_2/H_2$ [Höppener et al., 1986].

Table 3. Catalytic properties of three component catalysts (20 wt% Cu/56 wt% ZnO/support[a])

Support	S_{BET} (m^2g^{-1})	S_{Cu} (m^2g^{-1})	N_s/N_T[b] (%)	CO_2 conversion (%)	Selectivity (%)			Turnover rate[c] ($10^{-3}s^{-1}$)
					CH_3OH	CO	CH_4	
Al_2O_3	55.5	7.6	5.9	8.6	44.8	55.2	0.0	8.7
MgO	47.1	9.1	7.0	4.4	59.1	40.	0.2	3.7
SiO_2	78.7	4.9	3.8	1.4	59.7	39.5	0.8	2.2
TiO_2	19.8	4.2	3.2	6.1	51.7	48.1	0.2	11.1
MoO_3	13.8	2.3	1.8	1.5	43.2	55.8	1.0	4.8
ZrO_2	40.0	6.5	5.0	6.9	47.1	52.8	0.1	8.2
V_2O_5	15.9	3.8	3.0	1.3	28.4	70.3	1.3	2.5

[a] Reaction conditions: 230°C, 20 bar, $H_2/CO_2=3$, GHSV=6000 h^{-1}.

[b] % surface copper atom relative to total copper.

[c] The rate of CO_2 conversion per second per surface copper atom measured by N_2O titration.

4. Correlation between Copper Surface Area and Catalytic

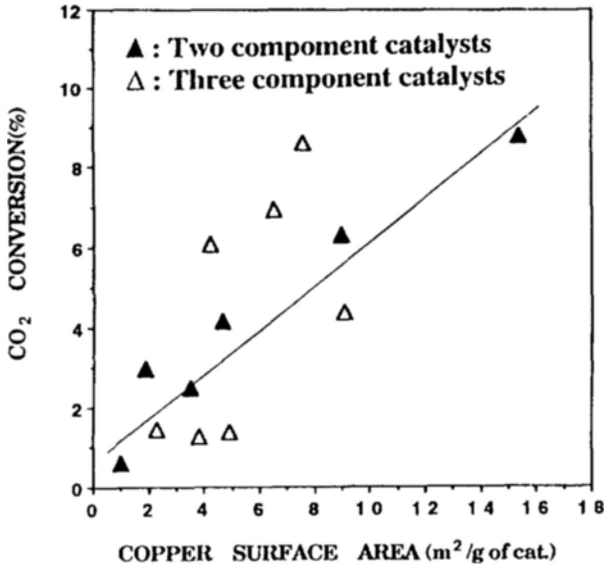

Fig. 6. Dependence of CO_2 conversion on copper surface area in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $H_2/CO_2=3$. GHSV$=6000$ h^{-1}.

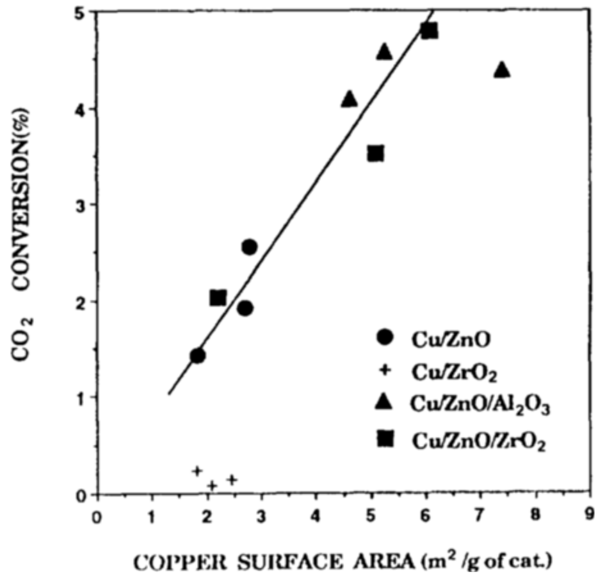

Fig. 7. Dependence of CO_2 conversion on copper surface area for catalysts with different copper loading in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $H_2/CO_2=3$. GHSV$=9600$ h^{-1}.

Activity

Despite a long experience of commercial operations and extensive studies on the fundamental aspects of the process, the active copper species in $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ is still under debate [Bart and Sneeden, 1987]. Chinchen et al. [1986] proposed metallic copper Cu^0 based on their observation that methanol synthesis activity from $CO/CO_2/H_2$ is proportional to copper metal area titrated by N_2O for $Cu/ZnO/Al_2O_3$, Cu/SiO_2, Cu/Al_2O_3, Cu/MgO, Cu/MnO, and Cu/ZnO. However, there is an opinion that the correlation does not *a priori* permit the identification of the active sites as being Cu^0 [Ramaroson et al., 1982]. Furthermore, Bartley and Burch [1988] reported that there was no correlation between the Cu surface area and the methanol synthesis activity when different supports were employed.

Figure 6 shows the relationship between Cu surface area before the reaction and CO_2 conversion for two and three component catalysts. In general, there is no question that there is a correlation between the two quantity. Yet, there is a considerable scattering of data from the correlation line. Since the N_2O titration itself was found to be a quite reproducible technique, the scatter of the points should be considered as an indication that there may be other variables which must be taken into account. Recently, it has been suggested that oxygen coverage of copper surface during the reaction is an important variable which is varied by addition of promoters [Fujitani et al., 1994] or by employing different reaction conditions [Lee et al., 1993]. Figure 7 shows the same correlation for catalysts of different Cu loading. Much improved correlation is observed for catalysts containing Cu/ZnO. But Cu/ZrO_2 is far below the correlation line. Thus it could be concluded that the correlation between copper surface area and catalytic activity is good for catalyst series with similar chemical properties including composition. However, the supports can affect other catalytic properties as well, for example, the surface oxygen coverage.

CONCLUSIONS

There is a strong support effect in methanol synthesis from CO_2/H_2 over copper based catalysts. Different supports cause different reduction behavior, different copper surface areas and different catalytic activity and selectivity. It seems possible to find catalyst supports that may perform better than commercial Cu $/ZnO/Al_2O_3$. There exists a correlation between catalytic activity and copper surface area which can be varied by using different supports. However, the supports appear to affect other catalytic properties as well, for example, the surface oxygen coverage.

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REFERENCES

Arakawa, H., Dubois, J.-L. and Sayama, K., "Selective Conversion of Carbon Dioxide to Methanol by Catalytic Hydrogenation over Promoted Copper Catalyst", *Energy Convers. Mgmt.*, **33**, 521 (1992).

Amenomiya, Y., Emesh, A., Oliver, K. W. and Plezier, G., "Methanol Synthesis from CO_2+H_2. 1. Characterization of Catalysts by TPD", *Appl. Catal.*, **18**, 285 (1985).

Amenomiya, Y., Emesh, A., Oliver, K. W. and Plezier, G., "Copper-Zirconium Oxide Catalysts for Synthesis and Dehydrogenation of Methanol", *Proc. 9th Int. Congr. Catal. Calgary*, **2**, 634 (1988).

Bart, J. C. and Sneeden, R. P. A., "Copper-Zinc Oxide-Alumina Methanol Catalysts Reviewed", *Catal. Today*, **2**, 1 (1987).

Bartley, G. J. J. and Burch, R., "Support and Morphological Effects in the Synthesis of Methanol over Cu/ZnO, Cu/ZrO_2 and Cu $/SiO_2$ Catalysts", *Appl. Catal.*, **43**, 141 (1988).

Chinchen, G. C., Waugh, K. C. and Whan, D. A., "The Activity and State of Copper Surface in Methanol Synthesis Catalysts", *Appl. Catal.*, **25**, 101 (1986).

Chinchen, G. C., Hay, H. D., Vandervell, H. D. and Waugh, K. C., "The Measurement of Copper Surface Areas by Reactive Frontal Chromatography", *J. Catal.*, **103**, 79 (1987).

Denise, B. and Sneeden, R. P. A., "Oxide-Supported Copper Catalysts Prepared from Copper Formate: Differences in Behavior in Methanol Synthesis from CO/H_2 and CO_2/H_2 Mixture", *Appl. Catal.*, **28**, 235 (1986a).

Denise, B. and Sneeden, R. P. A., "Characterization of Cu/ZnO Methanol Synthesis Catalysts by Analytical Electron Microscopy", *J. Mol. Catal.*, **37**, 369 (1986b).

Denise, B., Cherifi, O., Bettahar, M. M. and Sneeden, R. P. A., "Supported Copper Catalysts Prepared from Copper(II) Formate. Hydrogenation of Carbon Dioxide Containing Feedstocks", *Appl. Catal.*, **48**, 365 (1989).

Fleisch, T. H. and Mieville, R. L., "Studies on the Chemical State of Cu during Methanol Synthesis", *J. Catal.*, **90**, 165 (1984).

Fujitani, T., Saito, M., Kanai, Y., Kakumoto, T., Watanabe, T., Nakamura, J. and Uchijima, T., "The Role of Metal Oxides in Promoting a Copper Catalysts for Methanol Synthesis", *Catal. Lett.*, **25**, 271 (1994).

Höppener, R. H., Doesburg, E. B. M. and Scholten, J. J. F., "Preparation and Characterization of Stable Copper/Zinc Oxide/Alumina Catalysts for Methanol Synthesis", *Appl. Catal.*, **25**, 109 (1986).

Lee, S. Y. and Lee, J. S., "Chemical Utilization of Carbon Dioxide", *Chemical Industry and Technology (Korean)*, **11**, 9 (1993).

Lee, J. S., Lee, K. H., Lee, S. Y. and Kim, Y. G., "A Comparative Study of Methanol Synthesis from CO_2/H_2 and CO/H_2 over a $Cu/ZnO/Al_2O_3$ Catalyst", *J. Catal.*, **144**, 414 (1993).

Matulewicz, E. R. A., De Keijser, M. S., Mol, J. C. and Kapteijn, F., "Characterization of Copper(II) Oxide-Zinc Oxide-Aluminum Oxide Methanol Synthesis Catalysts Using Temperature Programmed Reduction and Thermal Stability", *Thermochim. Acta*, **72**, 111 (1984).

Ramaroson, E., Kieffer, R. and Kiennemann, A., "Reaction of $CO-H_2$ on Copper-Zinc Catalysts Promoted by Metal Oxides of Group III and IV", *Appl. Catal.*, **4**, 281 (1982).

Xu, Z., Qian, Z., Mao, L., Tanabe, K. and Hattori, H., "Methanol Synthesis from CO_2 and H_2 over CuO-ZnO Catalysts Combined with Metal Oxides under 13 atm Pressure", *Bull. Chem. Soc. Jpn.*, **64**, 1658 (1991).