

EFFECTS OF CATALYST COMPOSITION ON METHANOL SYNTHESIS FROM CO₂/H₂

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Abstract—Effects of catalyst composition have been studied for Cu/support and Cu/ZnO/supports in methanol synthesis from CO₂/H₂. 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/Al₂O₃ 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, CO₂/H₂ 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 CO₂ concentration which include chemical fixation and recycling the emitted CO₂ [Lee and Lee, 1993]. Conversion of CO₂ 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].



The process is closely related to established methanol synthesis technology from CO/H₂ (Reaction 2) because current industrial feeds contain ca. 5 vol% of CO₂ in addition to CO/H₂ [Bart and Sneed, 1987].



The processes are operating at 50-100 bar and 220-240°C with catalysts composed of Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ [Bart and Sneed, 1987]. Although the catalysts are highly effective for the current CO-rich feeds, they may not necessarily be as effective for CO₂-rich feeds. Indeed, modified catalysts have been reported which perform better than the current catalysts for CO₂/H₂ reactions although most new catalysts contain copper as the main component [Amenomiya et al., 1985, 1988; Denise et al., 1986a, 1986b, 1989; Ramarosan, 1982; Fujitani, 1994].

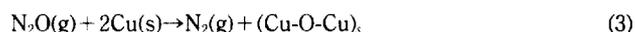
In this work, we prepared many two component catalysts containing copper as the main component and three component catalysts containing Cu/ZnO as the basis. Catalysts were characterized by temperature-programmed reduction (TPR), BET area (S_{BET}) measurement and surface copper area (S_{Cu}) by N₂O titration. Attempt was made to correlate the properties of a catalyst with

its reactivity in methanol synthesis from CO₂/H₂.

EXPERIMENTAL

Catalyst used in this study was prepared by a conventional coprecipitation method. It was precipitated from an aqueous solution of Cu(NO₃)₂·2.5H₂O, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O (all Alfa, total cation concentration 1 M) by dropwise addition of a 1 M aqueous solution of Na₂NO₃ (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 SiO₂ (Zerosil, Alfa), TiO₂ (Alfa), Al₂O₃ (Alfa), MgO (Alfa), ZrO₂ (prepared from ZrOCl₂ by precipitation), MoO₃ (Aldrich), V₂O₅ (Junsei), Fe(NO₃)₃·9H₂O (Aldrich) and Zn(NO₃)₂·6H₂O 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% H₂/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 H₂ (27 μmol s⁻¹) at 250°C for 3.5 h.

Specific surface area was determined by the N₂ BET method on a Micromeritics constant-volume adsorption system (Accusorb 2100E). Exposed copper surface area was determined by the N₂O titration on a Pyrex flow system following the procedure described by Chinchin et al. [1987]. Reduced catalysts were flushed by He at 60°C and N₂O was supplied at 14 μmol s⁻¹. N₂O reacts with surface copper leaving behind surface oxygen (Cu-O-Cu), and produces N₂ according to the following stoichiometry.



The amount of the produced N₂ 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 N₂ area and assuming a copper atom density of $1.46 \times 10^{19} \text{ m}^{-2}$ [Chinchin 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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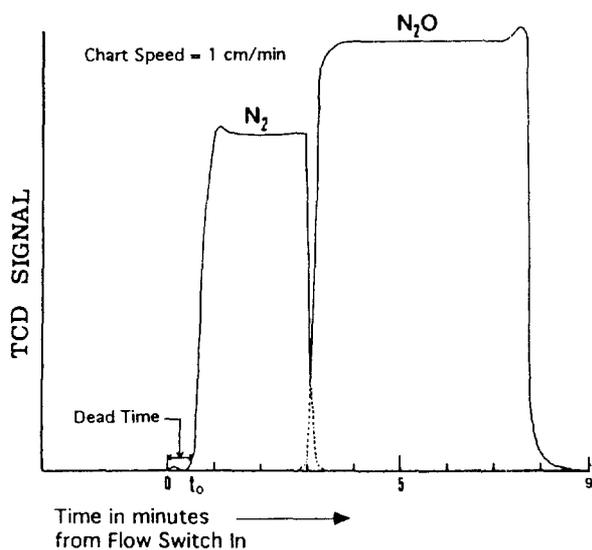


Fig. 1. A typical N₂O titration chromatogram for the determination of copper surface area.

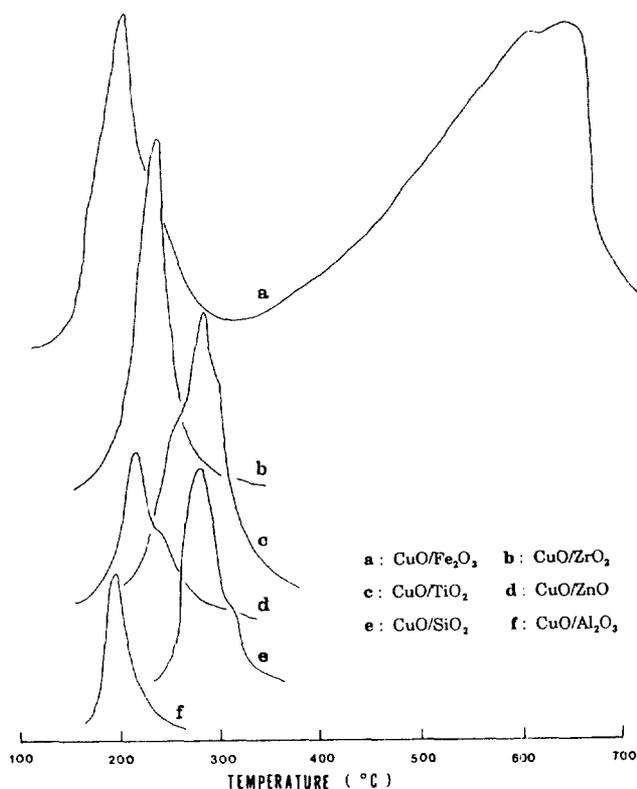


Fig. 2. TPR spectra (hydrogen consumption) of two component catalysts containing 24 wt% copper.

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% H₂ in N₂. The consumption of H₂ 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 Sotalem RDP-830 reaction system was employed as a pressurized flow reactor. Reaction products were

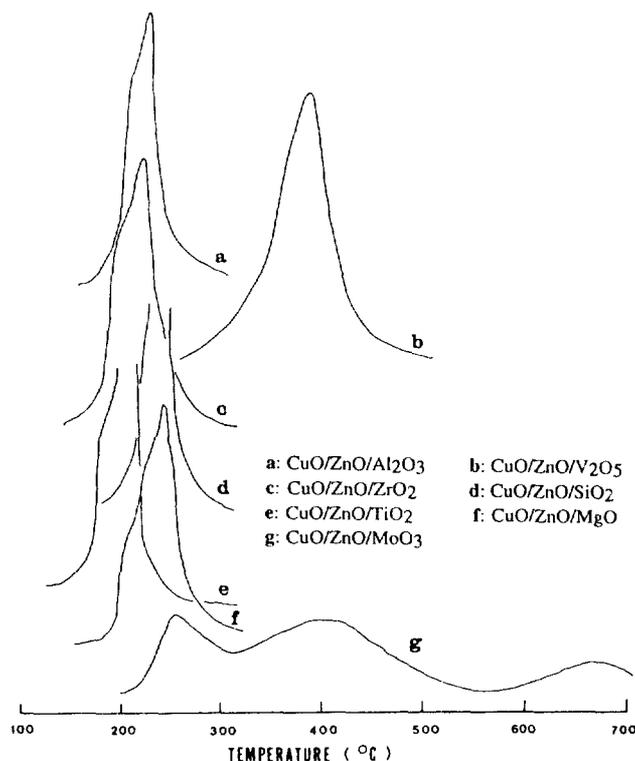


Fig. 3. TPR spectra (hydrogen consumption) of three component catalysts containing Cu/ZnO (20 wt%/56 wt%).

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.

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 CO₂/H₂ or CO/H₂ [Bart and Sneed, 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 Fe₂O₃ showed high temperature reduction peaks of Fe₂O₃. For two component catalysts, the ease of reduction followed the order of Fe₂O₃>Al₂O₃>ZnO>ZrO₂>SiO₂-TiO₂. 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: Fe₂O₃>ZnO-ZrO₂-TiO₂>SiO₂>Al₂O₃. Since all the support except Fe₂O₃ 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 ₃ OH 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 ₂ O 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

^aReaction conditions: 230°C, 20 bar, H₂/CO₂=3, GHSV=6000 h⁻¹.

^b% surface copper atom relative to total copper.

^cThe rate of CO₂ conversion per second per surface copper atom measured by N₂O 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 ₃ OH	CO	CH ₄	
Al ₂ O ₃ ^d	173.8	3.5	2.2	2.5	56.0	42.5	0.6	5.5
Fe ₂ O 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

^aReaction conditions: 230°C, 30 bar, H₂/CO₂=3, GHSV=6000 h⁻¹.

^b% surface copper atom relative to total copper.

^cThe rate of CO₂ conversion per second per surface copper atom measured by N₂O titration.

^dThe balance of the selectivity was to dimethyl ether.

^eThe 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 TiO₂>Al₂O₃>ZrO₂>MgO-SiO₂>MoO₃>V₂O₅.

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/ZrO₂). For three component catalysts (Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂), higher S_{BET} values were obtained for catalysts containing higher concentrations of Al₂O₃ or ZrO₂. Thus, most BET areas appear to originate from the supports. The copper area S_{Cu} measured by N₂O 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 CO₂ conversions and methanol selectivity in methanol synthesis from CO₂/H₂ at 230°C and 20 bar. Improved selectivity was due to suppressed formation of CO and CH₄. In general, as will be discussed shortly, ZnO was more effective than ZrO₂ 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>Fe₂O₃>SiO₂>Al₂O₃>ZrO₂>TiO₂. Correlation between S_{BET} and S_{Cu} is weak. The reactivity of catalysts also showed a marked support effect in methanol synthesis from CO₂/H₂ at 230°C and 30 bar. The Cu/Fe₂O₃ catalyst produced 35.2% hydrocarbons (>C₂) and Cu/Al₂O₃ yielded 2.0% dimethylether. Both of these products could be formed on supports. Other catalysts produced only CH₃OH, CO, and CH₄ as shown in Table 2. Figure 4 shows graphically CO₂ conversion and methanol selectivity for this series of two component catalysts. The supports were lined up in the order of increasing surface copper areas. CO₂ conversion decreased as ZnO>Fe₂O₃>SiO₂>ZrO₂>Al₂O₃>TiO₂. 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 Al₂O₃>ZnO>TiO₂>ZrO₂>Fe₂O₃>SiO₂.

Compared to TPR results in Fig. 2, it appears that active and selective supports Al₂O₃ and ZnO are the ones which showed low temperature reduction peaks in TPR. In contrast, SiO₂ and TiO₂ which showed high temperature reduction peaks showed poor selectivity. It is interesting to note that Al₂O₃ and ZnO, components of commercial Cu/ZnO/Al₂O₃, perform the best individually as well in both activity and selectivity.

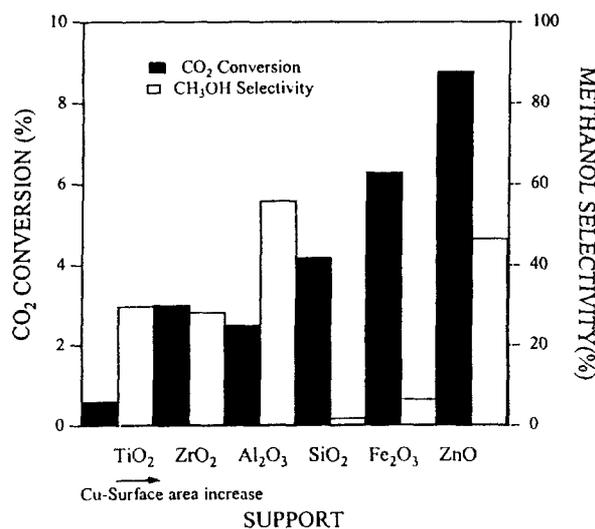


Fig. 4. Comparison of catalytic performance for two component catalysts containing 24 wt% copper in methanol synthesis from CO₂/H₂ at 230°C and 30 bar. H₂/CO₂=3. GHSV=6000 h⁻¹.

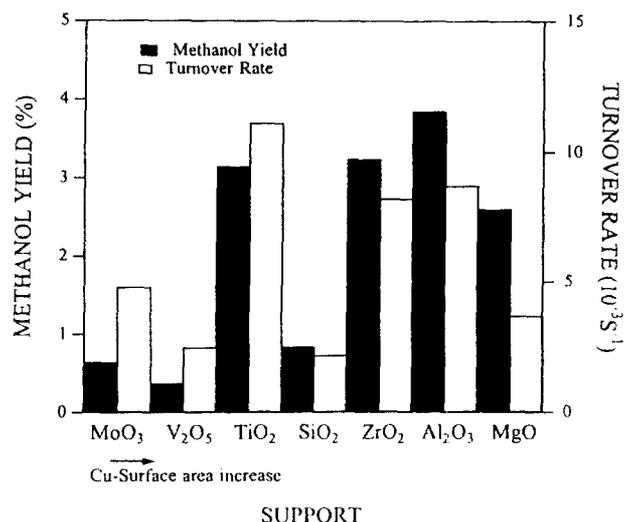


Fig. 5. Comparison of catalytic performance for three component catalysts containing 24 wt% copper in methanol synthesis from CO₂/H₂ at 230°C and 30 bar. H₂/CO₂=3. GHSV=6000 h⁻¹.

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>Al₂O₃>ZrO₂>SiO₂>TiO₂>V₂O₅>MoO₃. 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 (CO₂ conversion x methanol selectivity) and turnover rate (rate of CO₂ conversion per second per surface copper atom titrated by N₂O) are shown in Fig. 5. Cu/ZnO/Al₂O₃ containing the same components as commercial catalysts showed the highest methanol yield. TiO₂ and ZrO₂ were found to be almost as effective. The effectiveness of Al₂O₃ and ZrO₂ as supports of Cu/ZnO has also been reported [Xu et al., 1991]. In particular, Cu/ZnO/TiO₂ showed a higher turnover rate than Cu/ZnO/Al₂O₃, 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/TiO₂, 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/V₂O₅ 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, SiO₂ support showed relatively high S_{Cu} values, yet very poor methanol yield. Cu/SiO₂ showed high selectivity to CO and Cu/ZnO/SiO₂ showed a poor activity of CO₂ conversion. Similar effect has been observed by Ramarosan et al. [1982]. Since Chinchin et al. [1986] reported that Cu/SiO₂ showed a turnover rate similar to that of Cu/ZnO/Al₂O₃ in methanol synthesis from CO/H₂ containing ca. 5% CO₂, 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/CO₂/H₂ [Höppener et al., 1986].

4. Correlation between Copper Surface Area and Catalytic

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

Support	S_{BET} (m ² g ⁻¹)	S_{Cu} (m ² g ⁻¹)	N_s/N_T^b (%)	CO ₂ conversion (%)	Selectivity (%)			Turnover rate ^c (10 ⁻³ s ⁻¹)
					CH ₃ OH	CO	CH ₄	
Al ₂ O 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 ₂ O ₅	15.9	3.8	3.0	1.3	28.4	70.3	1.3	2.5

^aReaction conditions: 230°C, 20 bar, H₂/CO₂=3, GHSV=6000 h⁻¹.

^b% surface copper atom relative to total copper.

^cThe rate of CO₂ conversion per second per surface copper atom measured by N₂O titration.

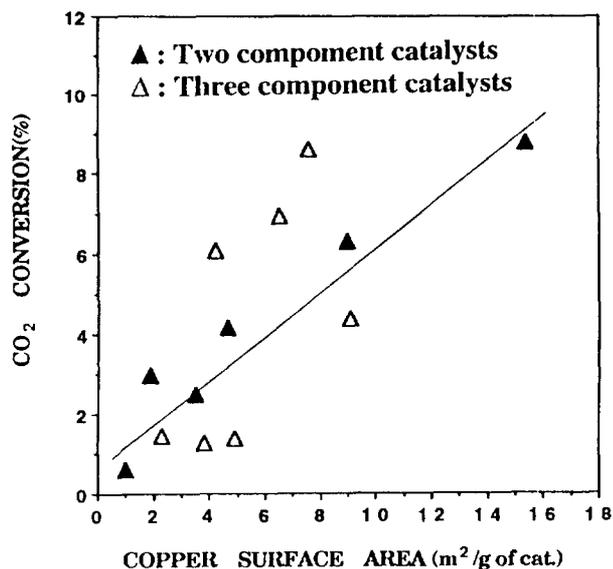


Fig. 6. Dependence of CO_2 conversion on copper surface area in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $\text{H}_2/\text{CO}_2=3$. $\text{GHSV}=6000 \text{ h}^{-1}$.

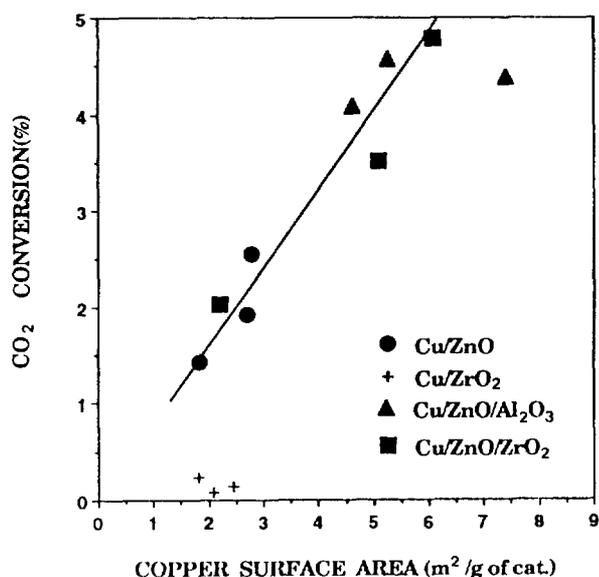


Fig. 7. Dependence of CO_2 conversion on copper surface area for catalysts with different copper loading in methanol synthesis from CO_2/H_2 at 230°C and 30 bar. $\text{H}_2/\text{CO}_2=3$. $\text{GHSV}=9600 \text{ h}^{-1}$.

Activity

Despite a long experience of commercial operations and extensive studies on the fundamental aspects of the process, the active copper species in $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ or $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ is still under debate [Bart and Sneed, 1987]. Chinchin et al. [1986] proposed metallic copper Cu^0 based on their observation that methanol synthesis activity from $\text{CO}/\text{CO}_2/\text{H}_2$ is proportional to copper metal area titrated by N_2O for $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, Cu/SiO_2 , $\text{Cu}/\text{Al}_2\text{O}_3$, 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 cor-

relation 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 $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$. 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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