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Methanol Synthesis Activity of Cu/ZnO Catalysts

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We have measured the rate of CH_3OH synthesis on a series of Cu/ZnO and related catalysts prepared by different techniques. Under reaction conditions of 523 K, 50 atm, and $H_2/CO/CO_2$ = 70/24/6, the CH_3OH rate varies approximately linearly with Cu surface area. The specific activity is 0.03 g CH_3OH/m^2 Cu/hr, in reasonable agreement with the results of other laboratories. Temperature-programmed desorption experiments using CO and H_2, together with the results of previous IR studies, appear to deny the existence of any unique Cu surface sites beyond those associated with metallic Cu clusters that contain a mixture of high- and low-Miller-index crystal planes.

INTRODUCTION

The CH_3OH synthesis reaction using copper-containing catalysts has received considerable attention in recent years, both because of methanol's present importance as a commercial chemical and because of its potential market as a liquid fuel or fuel additive. Understanding this highly selective synthesis reaction is also an important test of our fundamental knowledge of heterogeneous catalysis.

Several authors since 1979 have reported that the rate of CH_3OH formation on Cu-containing catalysts varies linearly with Cu surface area (*1–4*). Chinchen *et al.* (*1*) reported sp act 0.03 g CH_3OH/m^2 Cu/hr for a series of Cu catalysts prepared on different supports (e.g., ZnO, ZnO + Al_2O_3, SiO_2, Al_2O_3, MgO, and MnO). Hoppener *et al.* (*2*) obtained sp act 0.06 g CH_3OH/m^2 Cu/hr for a wide range of $Cu/ZnO/Al_2O_3$ catalysts which had Cu surface areas from 10 to 25 m^2/g. Bridgewater *et al.* (*3*) reported that both supported Cu catalysts and metallic Raney CuZn catalysts have comparable specific activities of around 0.02 g CH_3OH/m^2 Cu/hr.

In contrast, Klier and co-workers (*5–7*) have argued consistently that CH_3OH activity is not linearly correlated with Cu surface area. In a series of papers that contributed greatly to the current level of interest in the CH_3OH reaction in the open literature, these authors argued instead that CH_3OH synthesis occurs primarily at isolated Cu(I) cations on the surface of the ZnO support. The existence of these isolated Cu cations was documented by a variety of *bulk* characterization techniques.

Attempts to determine the *surface* composition of these catalysts have focused on adsorption measurements to determine the Cu surface area. The status of these measurements is summarized in two recent papers. Chinchen *et al.* (*1*) describe a dynamic N_2O adsorption technique based on the principle of reactive frontal chromatography (*8, 9*). The technique and apparatus are especially well-suited to sequential measurements of a catalyst sample that is to be

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exposed to a series of different reaction conditions. Parris and Klier (*7*) describe static adsorption measurements using irreversible O_2 adsorption at 78 K and reversible CO adsorption at 293 K. The two measurements gave similar results for the metallic Cu surface area. In the same paper, these authors also reported that a small fraction of the CO was adsorbed irreversibly. They attributed this fraction to CO adsorbed on isolated Cu cations on the ZnO support.

We recently reported a temperature-programed desorption (TPD) and IR spectroscopic study of CO and H_2 adsorption on a series of Cu/ZnO, Cu/SiO_2, and bulk Cu catalysts that had low Cu surface areas (*10*). The purpose of applying the TPD technique is to obtain information about the energetics of the adsorption sites, as well as their concentration. Our results showed that metallic Cu was present with a majority fraction of high-Miller-index surface planes and that the adsorption energy of both adsorbates increases when the surface is oxidized. In the present paper we extend the TPD experiments to high Cu surface area catalysts and include activity measurements for both groups of catalysts.

EXPERIMENTAL

All of the new samples were prepared by coprecipitation using starting solutions of 1.0 *M* $Zn(NO_3)_2$ and 1.0 *M* $Cu(NO_3)_2$ that were mixed to give the desired Cu/Zn ratio and then precipitated with 1.0 *M* Na_2CO_3. Following the lead of Courty and Marcilly (*12*), we tested the effect of three precipitation sequences: (i) addition of $NaCO_3$ to the mixed nitrates, as described by Herman *et al.* (*5*), (ii) addition of the mixed nitrate solution into the Na_2CO_3 solution, and (iii) addition of both solutions simultaneously into H_2O. The different procedures cause precipitation to occur at low, high, and neutral pH, respectively (*9, 10*). The resulting precipitates were filtered, dried, and calcined in air at 623 K for 16 hr. Individual samples were then loaded into the reactor and reduced in flowing H_2 (1 atm) at 483 K for 16 hr.

Two other samples with compositions of 2 wt% CuO/ZnO and 1 wt% CuO/SiO_2 were prepared by impregnating $Cu(NO_3)_2$ into the support materials (Kadox 25 ZnO, Gulf Western Natural Resources, BET area 10 m^2/g; and Aerosil 380 SiO_2, Degussa, BET area 380 m^2/g). The same calcining and reduction procedures as those for the coprecipitated materials were followed for these samples.

Kinetic studies were performed in a high-pressure plug-flow tubular reactor operated at 50 atm. The other reaction conditions were $T = 523$ K and $H_2/CO/CO_2 = 70/24/6$. Methanol concentration in the product stream was determined by gas chromatography (Hewlett–Packard 5890 GC and 3393A integrator; Porapak T column at 413 K; thermal conductivity detector). The CH_3OH yield was measured at a series of different flow rates for each catalyst, and the rate under the inlet conditions was determined by extrapolating to $W/F = 0$.

The TPD experiments were done using our previously described apparatus and procedures (*10*). The samples were reduced in the TPD cell using the same time–temperature sequence as that for samples in the reactor studies. Carbon monoxide was adsorbed by admitting a small excess of CO to the cell at 300 K, cooling to 150 K, and pumping away the residual gas. Hydrogen was adsorbed by admitting up to 400 Torr of H_2 to the cell at 300 K, cooling to 150 K, and pumping away the residual gas. We also used this apparatus to measure the irreversible O_2 adsorption at 78 K on samples with low Cu surface areas (see below). This was done by making two successive uptake measurements, as described in our previous paper (*10*).

We performed BET measurements of the high surface area catalysts using a flow adsorption apparatus based on the design of Nelson and Eggerston (*11*). Specific areas were determined by N_2 adsorption at 98 K,

TABLE 1

CH_3OH Synthesis Activity of Low Cu Area Catalysts

Composition (mol%)	Copper area[a] (m^2/g)	CH_3OH rate (g/g/hr)	Specific activity (g/m^2 Cu/hr)
2 Cu/98 ZnO	0.08	0.0009	0.011
1 Cu/99 SiO_2	0.5	0.008	0.016
100 Cu[b]	1.2	0.004	0.003

[a] Based on CO adsorption.

[b] Reduced CuO.

as measured by integrating the decrease (increase) in N_2 concentration in an N_2/He mixture flowing continuously over the catalyst as the sample is cooled (warmed) between 300 and 98 K. Calibration experiments using materials with known surface areas (Kadox 25 ZnO, 10 m^2/g; Degussa P-25 TiO_2, 45 M^2/g; manufacturer's data) showed that the flow adsorption procedure gives results that are about 20% below values obtained by static adsorption. The corrected values are used below.

We also used the flow apparatus to measure Cu surface areas, using irreversible O_2 adsorption at 98 K. This was done by admitting pulses of O_2 from a sampling loop and measuring the decrease in the height of the first few pulses. Calibration experiments using static uptake measurements of duplicate samples in the TPD cell as described above suggest that the O_2 uptakes determined in the pulsed flow adsorption procedure are also about 20% low. The corrected values are used below.

RESULTS

Activity of low-area catalysts. The results for the two catalysts prepared by impregnation are shown in Table 1. Because of their low values, the Cu surface areas of these two materials had to be determined by O_2 chemisorption using the TPD cell. The specific activities are also included. Although there is considerable uncertainty associated with all of these numbers because of their small values, we note that the specific activity of the Cu/SiO_2 catalyst is larger than that of the Cu/ZnO sample. This suggests that ZnO does not play any exceptional role in determining the specific activity of the impregnated Cu catalysts.

Activity of bulk Cu. We also measured the CH_3OH activity of a bulk Cu catalyst prepared by reduction of precipitated CuO. This measurement is complicated by a rapid loss of activity while the sample is exposed to reaction conditions. Figure 1 is a semilogarithmic plot of the rate of CH_3OH formation on the reduced CuO sample as a function of time on stream. We were not equipped to measure the CO uptake of this sample after exposure to reaction conditions, but separate measurements of CO uptake on a progressively reduced CuO sample showed that surface area is lost rapidly under reducing conditions. This suggests that the activity decay is caused by loss of Cu surface area due to sintering.

The results for the initial activity and surface area of the bulk Cu sample are included in Table 1. The specific activity is smaller than that of the impregnated catalysts. It is also smaller than the literature

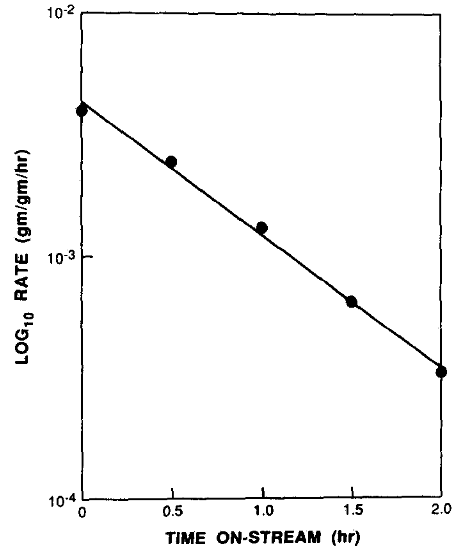

FIG. 1. Methanol synthesis rate as a function of time on-stream for unsupported CuO catalyst. Decay of initial activity (50 atm, 523 K, CO/H_2/CO_2 = 24/70/6).

TABLE 2

Influence of Preparation Method on CH_3OH Synthesis Activity of Cu/ZnO Catalysts

Composition (mol%)	Precipitation conditions	BET area (m^2/g)	Copper area (m^2/g)	CH_3OH rate (g/g/hr)
33 Cu/67 ZnO	Low pH	18	1.1	0.1
30 Cu/70 ZnO	High pH	59	33	0.8
30 Cu/70 ZnO	Neutral pH	65	60	1.9

values for coprecipitated catalysts listed in the Introduction. The specific activities of both impregnated catalysts are two to four times lower than these values. These results confirm that the choice of preparation method has a strong influence on catalyst activity.

Influence of precipitation conditions. In Table 2 we list the surface areas and CH_3OH activities of three catalysts with roughly equal Cu/ZnO ratios that were prepared using the three precipitation sequences described in the procedure section. The BET area, Cu surface area, and CH_3OH activity all increase in the order low pH $\leqslant$ high pH $<$ neutral pH.

Influence of composition. In Table 3 we list the surface areas and CH_3OH activities of a series of catalysts with different Cu/ZnO ratios, all prepared by precipitation at neutral pH. These results are also presented graphically in Fig. 2. All three measured quantities reach their maximum values in the composition range between 20 and 40 mol% Cu. For compositions greater than 30 mol% Cu, the Cu surface area is quite close to the measured BET surface area. This suggests that the Cu component may actually "coat" the ZnO component of these catalysts (see below).

TABLE 3

Influence of Composition on CH_3OH Synthesis Activity of Cu/ZnO Catalysis Precipitated at Neutral pH

Composition (mol%)	BET area (m^2/g)	Copper area (m^2/g)	CH_3OH rate (g/g/hr)
20 Cu/80 ZnO	83	41	1.0
30 Cu/70 ZnO	65	60	1.9
40 Cu/60 ZnO	63	61	1.6
50 Cu/50 ZnO	61	45	1.6
66 Cu/34 ZnO	43	36	1.3
80 Cu/20 ZnO	31	30	0.7

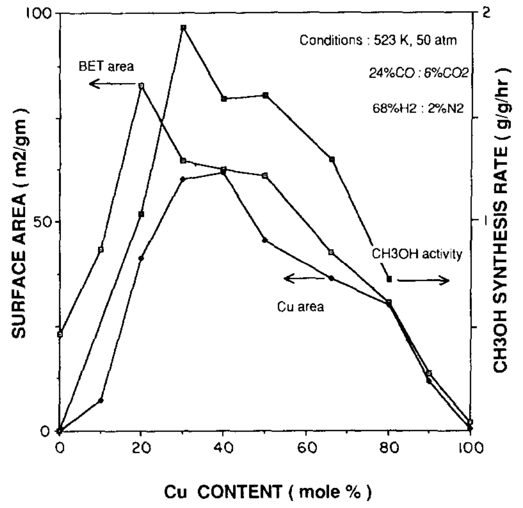

FIG. 2. BET surface area, Cu surface area, and CH_3OH synthesis activity of Cu/ZnO catalysts prepared by simultaneous coprecipitation as a function of calculated Cu content. Influence of Cu/Zn ratio.

The correlation between activity and Cu surface area is demonstrated in Fig. 3, which contains the results of Tables 2 and 3. The results are correlated by a line with a

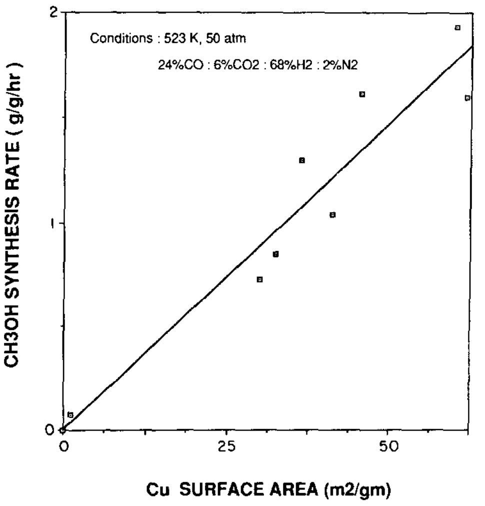

FIG. 3. Methanol synthesis activity of Cu/ZnO catalysts. Correlation of CH_3OH synthesis activity with Cu surface area.

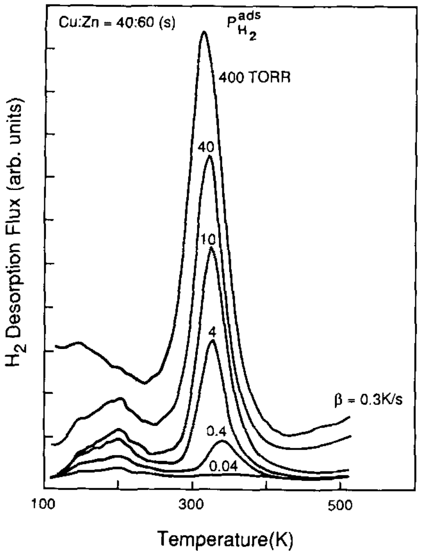

FIG. 4. Temperature-programmed desorption spectra of H_2 on a 40 Cu/60 ZnO catalyst, showing the influence of initial H_2 coverage.

slope of 0.030 g CH_3OH/m^2 Cu/hr and correlation coefficient of 0.94. This slope lies within the range of values for other Cu catalysts listed in the Introduction, i.e., 0.02–0.06 g/m^2 Cu/hr (*1–3*).

Adsorption studies. Figure 4 shows the TPD spectra of H_2 from the 40 Cu/60 ZnO catalyst. The six curves that are presented were obtained using different H_2 pressures for the adsorption step. All of the curves produce a single peak at around 320 ± 10 K, which agrees with the peak temperatures we observed previously for both supported and unsupported Cu samples (*10*). The desorption peaks are relatively narrow, which suggests that all of the H_2 is desorbing from a single type of adsorption site. The peak temperature decreases slightly with increasing coverage, as expected for second-order desorption kinetics. The amount of H_2 adsorbed increases as the H_2 pressure during the adsorption step is increased, which suggests that the adsorption step obeys Elovich kinetics.

The TPD spectra for three different initial coverages of CO are shown in Fig. 5. At low coverage all of the CO appears to desorb from a single state with a desorption peak around 290 K. At higher coverage, this state saturates and additional desorption occurs from lower temperature states. This behavior is in agreement with our previous results for several low surface area Cu/ZnO catalysts and is indicative of CO adsorbed on different crystal planes of metallic Cu (*11*). There is no CO desorption at temperatures above 350 K, which argues against the presence of a strongly bound CO state associated with Cu sites.

DISCUSSION

Our results support the theory that CH_3OH synthesis activity is associated primarily with the metallic Cu component in these catalysts. The choice of support has little effect on the specific activity of the Cu surface (cf. Table 1). In contrast, the method of preparation has a significant effect, even for catalysts with similar overall chemical composition (cf. Table 2).

We propose to account for the results in Table 2 as follows: Campbell (*13*) showed that the solution pH strongly affects the relative rate of precipitation of the Zn and Cu

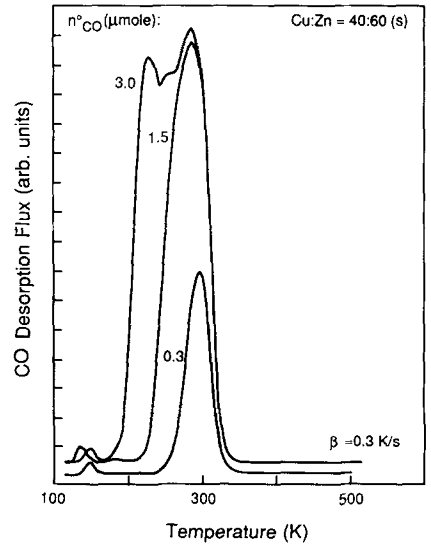

FIG. 5. Temperature-programmed desorption spectra of CO on a 40 Cu/60 ZnO catalyst, showing the influence of initial CO coverage.

cations, with the Cu component being removed from solution faster at low pH. Other workers (*2, 12*) have shown that the catalyst precursors formed during the precipitation step can include the single-cation compounds $Cu_2(OH)_3NO_3$ (gerhardite) and $Zn_5(OH)_6(CO_3)_2$ (hydrozincite), as well as the binary compounds $(Cu,Zn)_2(OH)_2CO_3$ (rosasite) and possibly $(Cu_{5-x},Zn_x)(OH)_6(CO_3)_2$ (aurichalcite). We have not performed X-ray diffraction to confirm that these phases exist in the present catalysts. However, it seems reasonable to postulate that sequential precipitation of Cu and Zn cations will favor the formation of the single-cation gerhardite and hydrozincite phases, while simultaneous precipitation will favor formation of the mixed cation precursor phases.

The fact that the Cu surface areas are almost as large as the BET areas for catalysts with Cu content greater than 30 mol% (cf. Fig. 2) may be related to the formation of a mixed cation phase in the precipitated precursor. Our reasoning is that the Cu atoms formed during the reduction of this phase may diffuse to the surface to form a highly uniform layer that covers a majority of the surface of the remaining ZnO phase. This model is consistent with thin film experiments we have performed, in which a Zn layer is deposited on a Cu_2O substrate and heated to produce ZnO (*14*). During the heating process, the Cu atoms that are released as Zn reacts with the Cu_2O substrate diffuse through the growing ZnO layer and appear at the surface. At intermediate temperatures during the warm-up this Cu layer can completely cover the surface, before eventually breaking up into segregated cu clusters at higher temperatures.

As shown in Fig. 2, the CH_3OH synthesis activity of all catalysts correlates reasonably well with the initial Cu surface area measured by pulsed-flow O_2 chemisorption technique. The specific activity is 0.03 g CH_3OH/m^2 Cu/hr, which lies within the range reported by other workers (*1–3*). We note that if the catalyst activities reported by Herman *et al.* (*5, 6*) are correlated with Cu surface area, sp act 0.052 g/m^2 Cu/hr is obtained with a correlation coefficient of 0.78. The latter measurements were made at 75 atm total pressure, which may account for part of the difference.

The TPD spectra of H_2 and CO also fail to provide evidence for any unique adsorption sites with properties different from those expected for metallic copper. The results are similar to those of our earlier study of low Cu surface area catalysts, which showed that both molecules behave as if adsorbed on high-Miller-index planes of metallic Cu (*10*). The calculated desorption energy for H_2 is 21 kcal/mol, based on second-order desorption kinetics with a preexponential factor of 10^{-2} cm^2/molecule/sec and a saturation site density of 10^{15} cm^{-2}, and neglecting readsorption effects because of the barrier for adsorption noted above. The calculated desorption energy for CO is 17 kcal/mol, based on the assumptions of equilibrated readsorption during the warm-up and parameter values listed previously (*15*).

SUMMARY

The Cu surface area and CH_3OH synthesis activity of coprecipitated Cu/ZnO catalysts are very sensitive to the method of preparation. For the catalysts studied here, the primary correlating factor for CH_3OH activity is the metallic Cu surface area. There is no evidence in the kinetic or adsorption experiments to support a major role for unique, atomically dispersed Cu species in the CH_3OH reaction. The choice of ZnO as the usual support material in Cu-based CH_3OH synthesis catalysts may therefore reflect its ability to coprecipitate to form precursor compound(s) that can be calcined and reduced to yield stable, high dispersions of Cu.

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