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Temperature-Programmed Desorption and Infrared Study of CO and H_2 Adsorption on Cu/ZnO Catalysts

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We have characterized a series of Cu/ZnO catalysts prepared by several methods, using a combination of adsorbate uptake measurements, temperature-programmed desorption, and FTIR spectroscopy applied to CO, H_2, and O_2 adsorbates. Adsorbed CO is present on the reduced catalysts in several adsorption states which are distinguished by different vibrational frequencies in the range 2104–2067 cm^{-1}, and which desorb with apparent activation energies in the range 10–16 kcal/mol. When CO is adsorbed on oxidized catalysts, the frequencies shift to 2136–2110 cm^{-1} and the highest desorption energy increases to 19 kcal/mol. For H_2 adsorbed on reduced catalysts, a single desorption state which has an apparent activation energy of 20–21 kcal/mol is observed. When H_2 is adsorbed on oxidized catalysts, the desorption energy of this state increases to 26–27 kcal/mol. For the reduced catalysts, the amounts of reversible CO and H_2 adsorbed are found to correlate linearly with the amount of O_2 chemisorption measured at 98 K, with relative uptakes for CO, H_2, and O_2 in the ratio 9 : 2 : 10. These results are interpreted to suggest that Cu is present as metallic clusters which expose a large fraction of high-index surface planes and that the chemical behavior of these planes is significantly different from that of low-index single crystal planes.

INTRODUCTION

One of the major goals of catalyst research is to identify methods for measuring the concentration of active sites in a heterogeneous catalyst. In the case of the CH_3OH synthesis reaction on Cu/ZnO-based catalysts, such attempts have been hampered by disagreement about the identity of the active site itself; i.e., whether the reaction occurs primarily on the metallic Cu component of the catalysts (*1–11*) or at isolated Cu(I) cations dissolved in the ZnO lattice (*12, 13*).

Several techniques have been used to measure the surface area of the metallic copper component: N_2O decomposition in a conventional volumetric adsorption apparatus (*14*) or in a flow configuration (pulsed gas chromatographic method) (*15*), irreversible O_2 chemisorption at 77 K (*16*), reversible CO chemisorption at 300 K (*16*), and adsorption microcalorimetry (reaction of O_2 or N_2O with copper) (*17*). In contrast, only one method to date has been proposed to measure the surface concentration of dissolved Cu(I) species, namely to measure the amount of irreversible CO chemisorption at ambient temperature (*16*).

All of these methods have the common feature of providing only a single piece of information about the adsorption uptake, measured under a single set of conditions. In contrast, the temperature-programmed desorption technique is able to provide information about both the concentration of adsorption sites and also their adsorption energy. If the adsorbed species has an infrared-active vibrational mode, then it is also possible to directly monitor the condition of the adsorbate as adsorption or desorption proceeds.

In previous studies we have combined the TPD and IR techniques to obtain a de-

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tailed picture of the H_2 and CO adsorption sites on pure ZnO (*18, 19*) and also the kinetics of the CH_3OH decomposition reaction on these sites (*20*). We have also reported preliminary results for the desorption of H_2 and CO from coprecipitated Cu/ZnO catalysts (*21*). In this paper we report a more thorough study of the H_2 and CO adsorption behavior on a number of Cu/ZnO catalysts prepared using different methods, in both reduced and oxidized states. These results are also compared with the measured O_2 uptake at 98 K on the reduced catalysts.

EXPERIMENTAL

A total of six materials are compared in this study. Four samples were prepared using the precipitation method described by Herman *et al.* (*13*). This consisted of precipitation by dropwise addition of Na CO_3 solution to mixed $Zn(NO_3)_2$ and/or $Cu(NO_3)_2$ solutions, followed by filtering and drying of the precipitate, then calcining in air at 623 K for 16 h, and finally reducing in flowing H_2 (1 atm) at 483 K for 16 h. The four samples include pure ZnO, 33 wt% CuO/ZnO, 82 wt% CuO/ZnO, and pure CuO. The copper content of the mixed catalysts was confirmed using atomic absorption spectroscopy. The other two samples were prepared as supported metal catalysts: A 2 wt% CuO/ZnO catalyst was prepared by impregnating Kadox 25 ZnO (BET area 10 m^2/g, Gulf Western Natural Resources) with $Cu(NO_3)_2$ solution, drying, calcining, and reducing. A 1 wt% CuO/SiO_2 catalyst was prepared in a similar fashion using Aerosil 380 SiO_2 (BET area 380 m^2/g, Degussa).

Experiments were performed using the TPD/IR vacuum cell and gas handling system described previously (*22*). Typically a 50-mg sample of the catalyst in its calcined state was deposited from an aqueous slurry onto the front face of the cell mirror. The catalyst was then reduced *in situ*. The TPD experiments were performed using a heating rate of 0.3 K/s, while monitoring the flux of desorbing species with a quadruple mass spectrometer (Spectramass 800A) with computer-controlled multiple peak scanning. Infrared spectra were obtained using a Nicolet 60-SX FTIR spectrometer equipped with an MCT detector at a scan rate of 1–2 s^{-1} and a resolution of 4 cm^{-1}. For spectra that were recorded before starting the TPD warm-up, we used as many as 1000 scans; for spectra recorded during a TPD experiment we used 130 scans/spectrum.

Different adsorption procedures were used for each adsorbate because of the difference in sticking coefficient and/or adsorption energy of each molecule. For CO adsorption, a small excess of CO was admitted to the sample at 300 K, then the sample was cooled to about 150 K, and the residual CO in the gas phase was pumped away. For H_2 adsorption it was necessary to admit 40 Torr H_2 at 300 K for 10 min, then cool the sample to 150 K, and finally pump away the gas phase H_2. For O_2 chemisorption uptake measurements, two steps were needed: In the first step we admitted 10 Torr O_2 to the reduced catalyst at 98 K and volumetrically measured the total O_2 uptake (i.e., physisorbed plus chemisorbed). The physisorbed component was then removed by evacuating at 98 K for 2.5 h, warming to 300 K over a 40-min period, and then outgassing for an additional hour at 300 K. The O_2 adsorption step was then repeated, and the difference in O_2 uptake was taken to be the amount of chemisorbed O_2.

RESULTS

H_2 adsorption. The TPD spectra of 40 Torr H_2 adsorbed on the six freshly reduced samples are shown in Fig. 1. The spectra are drawn normalized to the same peak height; the amount of H_2 adsorbed (μmol H_2/g catalyst) is shown beside each spectrum. The latter quantity is determined by integrating the area under each TPD spectrum and multiplying by the system calibration factor for H_2 (measured daily).

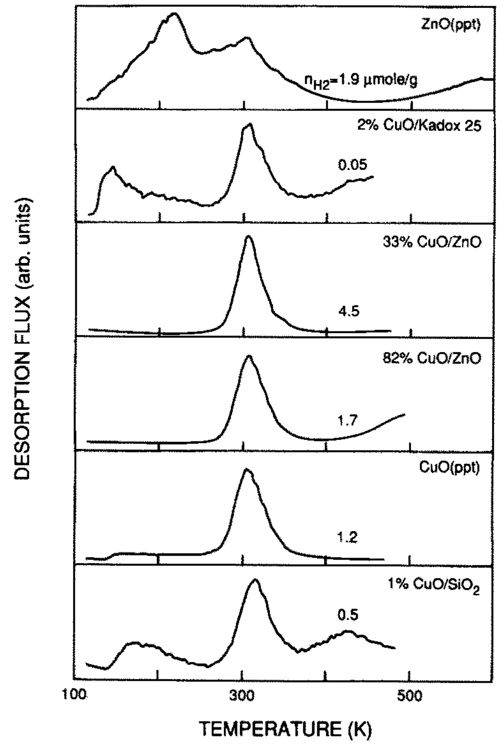

FIG. 1. TPD spectra of 40 Torr H_2 adsorbed on reduced Cu catalysts.

With the exception of the ZnO sample shown at the top of the figure, all of these results were obtained after the catalysts had been reduced at 483 K. To obtain any H_2 adsorption on pure ZnO, it was necessary to heat this sample to 673 K to remove the H_2O species which block the Type I H_2 adsorption sites. The resulting TPD spectrum for ZnO shows the multiple peaks at 215 and 305 K, structures that are characteristic of Type I adsorption sites (*19*). This confirms that Type I sites exist on precipitated ZnO as well as on Kadox 25. The increase in the desorption signal above 500 K is attributed to H_2 desorbing from non-Type I ZnO sites (*23*, *24*).

For all of the samples which contain Cu, the main feature in the spectrum is a well-resolved desorption peak with a temperature maximum in the region of 308–318 K. Smaller features (note the absolute amounts adsorbed) are observed near 150 K in the spectra of the 2 wt% Cu/ZnO and 1 wt% Cu/SiO_2 samples, which may be due to a small amount of weakly bound molecular H_2. The high-temperature shoulder near 430 K in the spectrum of the 1 wt% CuO/SiO_2 sample may be due to H_2 adsorbed on incompletely reduced copper (see below). Finally, the desorption increase above 400 K in the 2 wt% Cu/ZnO and the 82% Cu/ZnO samples may be assigned to H_2 desorbing from non-Type I sites on the ZnO component (*25*).

Four pieces of evidence indicate that the major H_2 desorption state at 308–318 K on the Cu-containing catalysts is *not* due to the high-temperature fraction of the Type I sites on the ZnO component. (1) As noted above, Type I sites are not activated at the reduction temperature used for the Cu/ZnO samples. (2) The peak is observed on pure CuO (reduced) and 1 wt% CuO/SiO_2, both of which contain no ZnO. (3) No vibrational bands characteristic of H_2 chemisorption of H_2 on ZnO were observed in the IR spectra of any of the Cu-containing samples. (4) The H_2 desorption peak shifts to higher temperatures when the Cu-containing samples are preoxidized, while no such shift occurs for preoxidized ZnO (see below).

The apparent activation energy for the 308–318 K H_2 desorption state is 20 kcal/mol. This is calculated using the Redhead equation with a preexponential factor of 10^{13} s^{-1} and assuming that readsorption can be neglected. The latter approximation is based on the presence of a significant barrier to H_2 adsorption on Cu (cf. the need to use a dosing pressure of 40 Torr during the H_2 adsorption step).

In order to test the effect of oxidation state on the H_2 adsorption properties of these catalysts, we repeated the above experiments after exposing each sample to 10 Torr O_2 at 483 K for 10 min. This caused a color change in the 33% CuO/ZnO and 82% CuO/ZnO samples (from maroon to gray), the CuO sample (from pink to gray), and the 1 wt% CuO/SiO_2 sample (from black to brown). One experiment was also per-

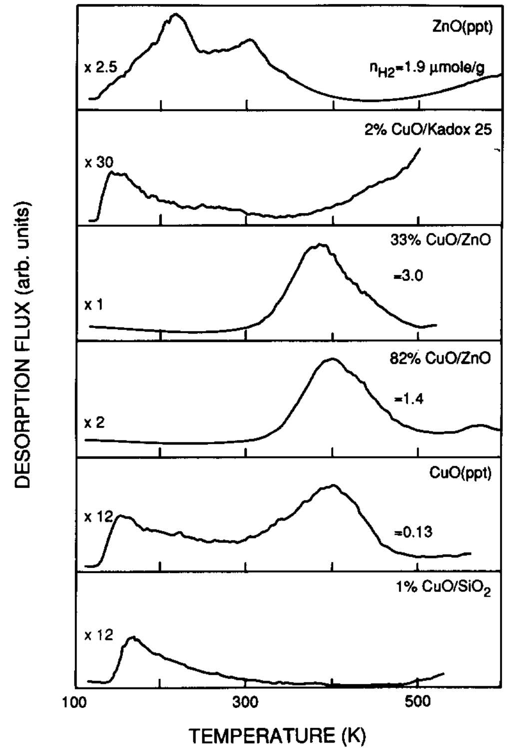

FIG. 2. TPD spectra of 40 Torr H_2 adsorbed on oxidized Cu catalysts.

formed using a calcined CuO sample that had not been reduced; this gave results similar to those of the CuO sample that had been reduced and then reoxidized.

We also note that the amount of O_2 consumed during this oxidation step (i.e., measured volumetrically) was many times greater than the amount of O_2 uptake at 98 K (see below). This confirms that the Cu component in these catalysts is present as multilayer clusters that are at least several layers thick, and that multilayer oxidation of these Cu clusters occurs readily at higher temperatures.

The TPD spectra of 40 Torr H_2 adsorbed on the preoxidized samples are shown in Fig. 2. Temperature maxima due to chemisorbed H_2 are observed in all the spectra, except for the case of the 2% CuO/Kadox 25 and 1% CuO/SiO$_2$ samples. For pure ZnO, the H_2 desorption peaks at 215 and 305 K are essentially unchanged from their positions for the reduced sample. In contrast, the H_2 desorption peak present on the 33% CuO/ZnO, 82% CuO/ZnO, and pure CuO samples has shifted to 387–403 K. This corresponds to an increased apparent activation energy of desorption of about 26 kcal/mol.

CO adsorption. The TPD spectra of CO adsorbed at saturation coverage on the same set of catalysts in their reduced state are shown in Fig. 3. As was the case for Fig. 1, to obtain any CO adsorption on ZnO at 150 K it was necessary to heat the sample briefly to 673 K before the adsorption step to remove H_2O from the Type I sites. The surface coverages of CO shown in Fig. 3 have been computed for each sample by integrating the area under the TPD curve beginning at 150 K. At temperatures below 150 K, the contribution of condensed CO in the catalyst pore structure becomes significant (*19*).

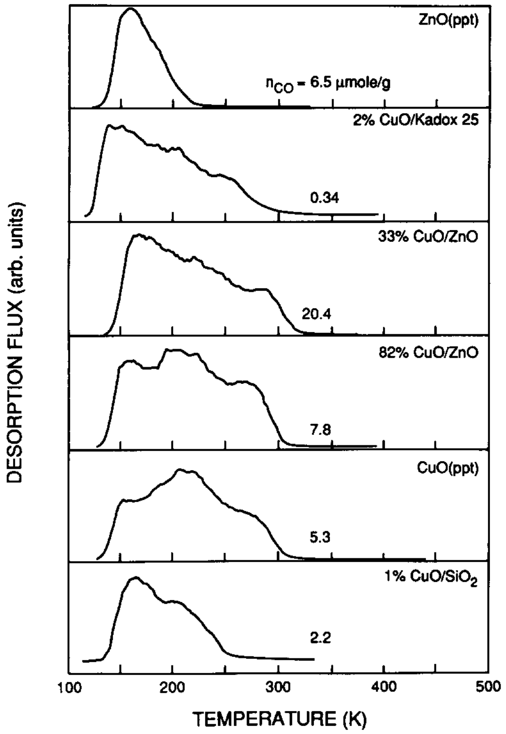

FIG. 3. TPD spectra of CO adsorbed on reduced Cu catalysts.

The spectrum for ZnO shows a weakly bound state with a temperature maximum at 160 K, which has previously been assigned to CO molecules adsorbed adjacent to Type I adsorption sites. For all of the Cu-containing samples, there is a significantly broader range of desorption states. The most weakly bound state appears to have a desorption maximum near 160–180 K, while the more strongly bound states appear to have maxima around 210 and 280 K. An exception is the 1 wt% Cu/SiO_2 catalyst, which does not appear to possess the 280 K desorption state. Despite the overlap in temperature with the spectrum for ZnO, we can conclude that the 160–180 K state on the Cu-containing catalysts is associated with the Cu component (see below).

The adsorption energies corresponding to the above temperature maxima have been calculated using a TPD equation which accounts for readsorption effects in porous samples (*26*). The need for this correction is indicated by experiments in which CO was admitted at 150 K instead of 300 K followed by cooling. There was no difference in the TPD spectra obtained after adsorption at the two temperatures, which indicates that the activation for CO adsorption is negligible in these experiments. The 160–180 K state corresponds to an apparent adsorption energy of 9–10 kcal/mol, while the 210 and 280 K states correspond to energies of 12 and 16 kcal/mol, respectively.

The results in Fig. 3 show no evidence for a CO adsorption state that would be irreversibly bound at room temperature. To test whether the oxidation state of the catalyst might affect this result, we repeated the above experiments after first exposing each sample to 10 Torr O_2 at 483 K for 10 min. The resulting TPD spectra are shown in Fig. 4. In general, the low-temperature desorption states appear to be unaffected. In particular, the desorption spectrum from ZnO is unchanged following the oxidation step. In contrast, the higher-temperature states on the Cu/ZnO samples have shifted upward, indicating that CO is more strongly bound to the oxidized Cu component. The apparent adsorption energies corresponding to the resolvable temperature maxima at 270 and 330 K are 15 and 19 kcal/mol, respectively. A smaller amount of CO_2 desorption was also observed around 370 K, but only on the pure CuO catalyst.

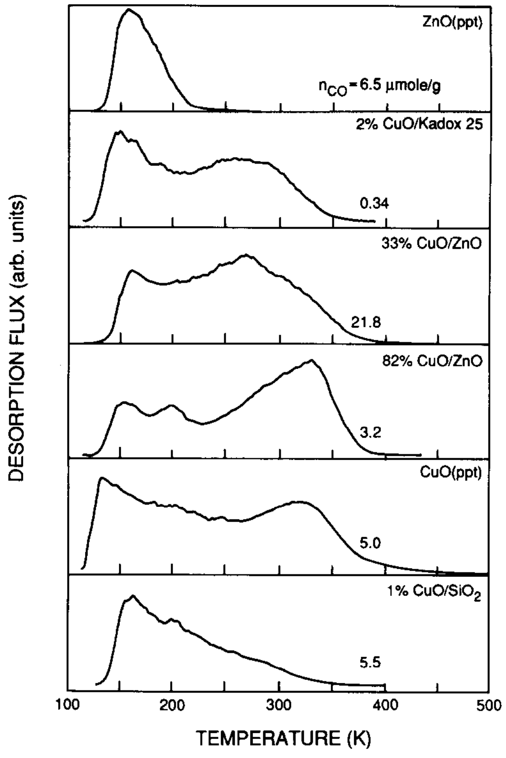

FIG. 4. TPD spectra of CO adsorbed on oxidized Cu catalysts.

CO vibrational spectra. The IR spectra recorded before starting each of the CO desorption experiments are shown in Figs. 5 and 6. The results are shown as difference spectra, obtained by subtracting the spectrum of each sample recorded before the CO adsorption step. The signal/noise level is low for these spectra, even though as many as 1000 scans were collected for each spectrum. We attribute this to severe absorbance and/or light scattering by the Cu-containing samples.

The spectrum on pure ZnO shows a single band at 2184 cm^{-1}, in agreement with our earlier studies of CO adsorbed adjacent

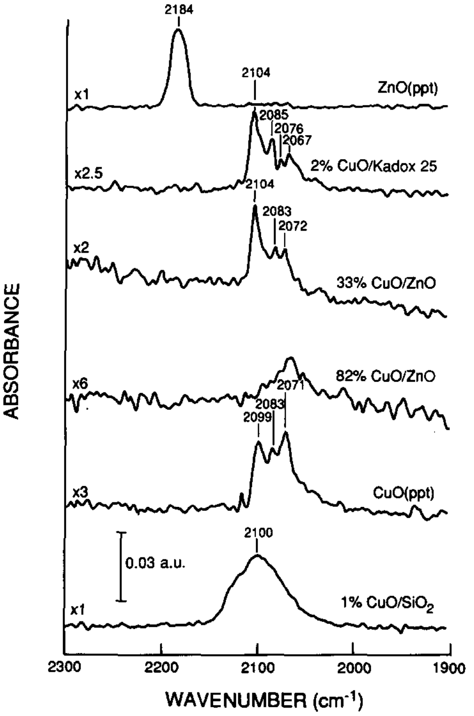

FIG. 5. Infrared spectra of CO adsorbed on reduced Cu catalysts (cf. Fig. 3).

to Type I ZnO sites (*19*). All of the Cu-containing samples show a distribution of bands between 2104 and 2071 cm^{-1}. Somewhat of an exception is seen for the 1 wt% Cu/SiO_2 sample, which appears to have vibrational bands as high as 2130 cm^{-1}. The bands in the region 2085–2067 cm^{-1} are characteristic of CO adsorbed on low-Miller-index planes of metallic copper (*27*), while the band(s) in the region 2104–2099 cm^{-1} is consistent with CO adsorbed on high-index planes (*27*). Since the band at 2184 cm^{-1} for CO adsorbed on ZnO does not appear in any of the Cu-containing catalysts, we conclude that the CO desorption spectra shown in curves 2–5 of Fig. 3 are due to CO adsorbed on only the copper component of the catalysts.

The IR spectra recorded for CO adsorbed on the oxidized samples are shown in Fig. 6. The band at 2184 cm^{-1} on pure ZnO is unchanged, while bands on all of the Cu-containing catalysts have shifted to the region 2136–2110 cm^{-1}. The detailed behavior of this shift is quite complex, as revealed by separate experiments in which the severity of the oxidation treatment was varied by changing the temperature at which the samples were exposed to O_2. These separate experiments showed that the bands at 2134–2123 cm^{-1} grow in at constant frequency, while simultaneously the bands at 2087–2065 cm^{-1} disappear at constant frequency. Thus it appears that the low-Miller-index planes of the metallic Cu phase are converted to Cu_2O in a manner resembling a first-order phase transformation. In contrast, the band at 2112 cm^{-1} reaches that position via a continuous shift of the 2104–2099 cm^{-1} band on the reduced catalyst, which suggests that a more continuous transformation of the high-index surface planes is taking place. Similar behavior has also been observed by Boccuzzi *et al.* (*28*) in their IR study of coprecipitated Cu/ZnO catalysts.

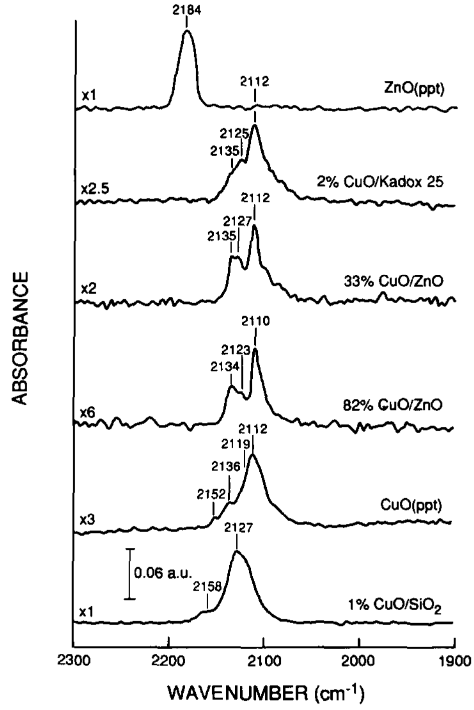

FIG. 6. Infrared spectra of CO adsorbed on oxidized Cu catalysts (cf. Fig. 4).

With the exception of the 1 wt% Cu/SiO_2, the effects of the oxidizing treatment were reversed upon reducing the catalysts in H_2 at 483 K. For the Cu/SiO_2 catalyst, attempts to reduce the sample at temperatures as high as 600 K were unable to shift the band of subsequently adsorbed CO by more than a few wavenumbers from its fully oxidized position at 2127 cm^{-1}. Thus it appears that oxidation of the Cu/SiO_2 sample *after the initial reduction step* causes an irreversible change in the morphology of the Cu component. This may be consistent with reports (*29*) of the existence of a distinct copper–silica phase for similar high-area CuO/SiO_2 samples with low copper loadings.

O_2 adsorption at 98 K. The amount of O_2 that can be adsorbed irreversibly at 98 K was determined for the three samples with the highest copper surface areas, i.e., 33 wt% CuO/ZnO, 82 wt% CuO/ZnO, and pure CuO. The O_2 uptakes for these samples were 21.3, 9.8, and 5.9 μmol/g, respectively, which corresponds to Cu surface areas of 4.3, 2.0, and 1.2 m^2/g (*16*). These areas are low, relative to other catalysts reported in the literature (*12*), a result we attribute to the precipitation method used for this group of catalysts. The Cu surface areas of the other three samples studied here were below the sensitivity limit of the O_2 adsorption procedure.

DISCUSSION

Comparison of uptake measurements. Determining the amounts of H_2 and CO adsorbed on the catalyst samples by measuring the area under their TPD curves can provide two alternate methods for determining the concentration of Cu adsorption sites in Cu-based methanol catalysts. The correlation between these two measurements is shown in Fig. 7, which plots the amount of CO adsorbed above 150 K (cf. Fig. 3) against the amount of H_2 adsorbed starting at 300 K with a dosing pressure of 40 Torr (cf. Fig. 1). The observed correlation is linear, which strongly suggests that measurements are detecting the same sites. This was confirmed by performing coadsorption experiments in which H_2 was adsorbed on the surface first, followed by CO. The effect of the preadsorbed H_2 was to reduced the intensity of the CO vibrational bands and decrease the amount of CO measured under the CO TPD curve, thus confirming that the adsorbed H_2 was blocking the CO adsorption sites.

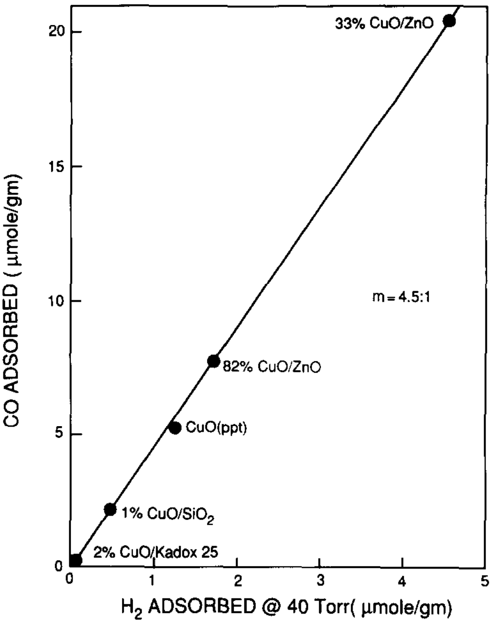

FIG. 7. Adsorption capacity of reduced Cu catalysts: CO vs H_2.

The correlation between the amount of CO adsorbed at 150 K and the amount of irreversibly adsorbed O_2 adsorbed at 98 K is shown in Fig. 8. In addition to the three samples described above, the figure also includes results for a reduced CuO sample prepared by direct calcination of solid $Cu(NO_3)_2$. A nearly linear correlation is observed, which together with the results in Fig. 7 suggests that all three adsorption techniques are sensitive to the same adsorption sites.

Information about the adsorption stoichiometry of these sites is provided by the slopes of the lines in Figs. 7 and 8. The slope in Fig. 8 is 0.9, which suggests a

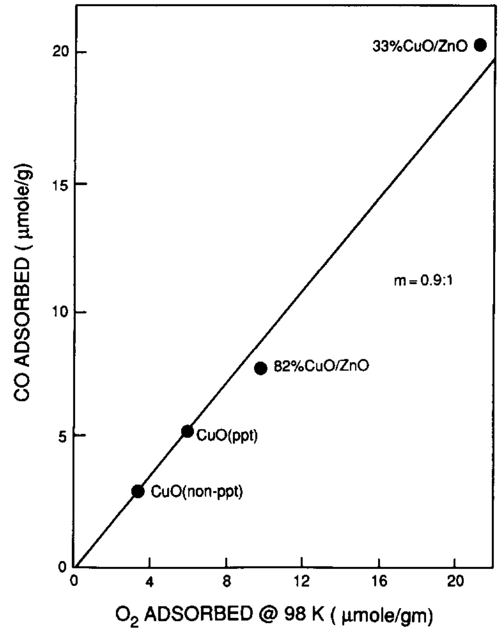

FIG. 8. Adsorption capacity of reduced Cu catalysts: reversible CO vs irreversible O_2 (98 K).

$CO:O_2$ adsorption stoichiometry of 1:1. Since earlier studies have concluded that the adsorption stoichiometry of O_2 *on low-index planes* of Cu is one $O_{(a)}$ atom for every two $Cu_{(s)}$ atoms, this would imply an adsorption stoichiometry of one $CO_{(a)}$ for every four $Cu_{(s)}$ atoms. This would be consistent with earlier reports that the saturation coverage at 195 K on Cu powders and films corresponds to an absolute fractional coverage of $\Theta_{CO} = 0.25$. This agreement must be observed with some caution, however, since the IR results shown above have already indicated that much of the CO is adsorbed on *high-index Cu planes*.

The slope of the line in Fig. 7 is 4.5. This implies that although both H_2 and O_2 are adsorbing on the same sites, the adsorption stoichiometry for H_2 is much smaller than that for CO. If the value for O_2 adsorption on low-index planes is retained, the present results suggest that one $H_{(a)}$ atom is adsorbed for every *nine* $Cu_{(s)}$ atoms. It seems unlikely that steric interaction between neighboring $H_{(a)}$ atoms could be the cause of this limited adsorption stoichiometry. Instead, we suggest repulsive interactions which serve to prevent $H_{(a)}$ atoms from existing on every Cu site. These repulsive interactions may be partially responsible for the barrier to H_2 adsorption noted above.

Nature of Cu/ZnO adsorption sites. The results show that Type I ZnO sites are *not* present on Cu/ZnO catalysts. The control experiment with precipitated ZnO showed that Type I sites are present on the pure component, although it is necessary to heat the sample above the temperature used in the usual reduction treatment in order to desorb the H_2O which blocks these sites. In contrast, we were never able to observe *any* evidence for H_2 or CO adsorption at Type I sites on *any* of the Cu/ZnO catalysts, even after heating to the higher temperature needed to activate the sites on pure ZnO. Much of the available evidence suggests that Type I sites are associated with Zn cation vacancies on ZnO(0001) crystal surfaces (*18–20*). This leads us to suggest that stable Cu cations may be replacing these cation vacancies, as a possible explanation for the absence of Type I sites in Cu/ZnO catalysts. Regardless of the reason for their absence, we conclude that Type I sites do not play a significant role in the CH_3OH synthesis reaction on Cu/ZnO catalysts.

We are also unable to identify any definitive evidence for adsorption on isolated Cu(I) cations on the ZnO surface. For example, we cannot resolve any new Cu–H vibrational band in the spectra of the oxidized or reduced catalysts. The H_2 TPD spectra are consistent with the behavior of high-index planes of metallic Cu, and similar spectra are observed on both Cu/SiO_2 and Cu/ZnO catalysts. The CO vibrational spectra are again consistent with the behavior of high-index metallic Cu planes, and not with the vibrational frequency that would be expected for $CO_{(a)}$ adsorbed on a Cu cation. Finally, the CO TPD spectra show a range of desorption states, which would be expected for a sample which contains a distribution of Cu crystal planes. In addition, none of these desorption states occur significantly above room temperature, which prevents us from classifying them as being strongly chemisorbed.

Instead, all of our evidence is consistent with a model in which the Cu component is present as metallic clusters which expose a large fraction of high-Miller-index crystal planes. The vibrational bands of CO chemisorbed on the low-index (111), (100), and (110) faces of Cu at saturation coverage at 77 K have been reported at 2070, 2088, and 2094 cm^{-1}, respectively (*27, 30*). In contrast, bands on the higher-index (211), (311), and (755) faces under the same conditions have been observed at 2110, 2103, and 2016, respectively (*30*). Those authors also studied various polycrystalline copper samples and concluded that low-index faces are rarely found with evaporated films or with supported copper catalysts. The fact that the majority of the adsorbed CO on the present catalysts has a frequency in the range 2104–2099 cm^{-1} supports the model that the Cu component is present with high-Miller-index crystal planes.

Additional support for this conclusion comes from the H_2 adsorption behavior. The present work clearly indicates the existence of an activated adsorption state for H_2 on Cu/ZnO catalysts. In contrast, negligible H_2 adsorption has been reported for the low-index planes of Cu single crystals. Exposure of Cu(100), (111), and (110) to H_2 at room temperature and pressures up to 1 Torr has resulted in no measurable change of surface potential (*30*), implying little adsorption of H_2. A molecular beam study (*31*) has also shown that the majority of incident H_2 molecules are not adsorbed on the (100) and (110) crystal faces of copper. In these and other studies (*32*), researchers have concluded that there are substantial energy barriers to H_2 adsorption on copper (approximately 5 kcal/mol).

There are, however, several reports regarding H_2 adsorption on higher-index planes. Marked negative surface potentials, indicating the adsorption of H_2, were measured for the (211), (311), and (755) faces after exposure to 1–3 Torr H_2 at room temperature (*30*). In the molecular beam study (*31*) nearly identical results were obtained for (110) and stepped (310) faces, which was taken to imply that the open surface structure of higher-index planes rather than ledge defects on stepped surfaces is responsible for H_2 adsorption. Consideration of these results leads us to conclude that H_2 is adsorbing on the high-index faces of copper present in our samples.

Reported heats of adsorption for H_2 on copper single crystals and evaporated films range from 9 to 12 kcal/mol for Cu(111) (*33*), Cu(311) (*30*), and evaporated Cu films (*34*). Similar values have been reported for Cu powders (*35–38*). Since our TPD results gave a value of 20 kcal/mol for the apparent desorption energy of H_2, this is consistent with the presence of an activation energy barrier for *adsorption* of the order of 10 kcal/mol.

The fact that the CO and H_2 uptakes are proportional to the low-temperature O_2 uptake suggests that simple uptake measurements of the former molecules may not provide any additional insight for correlating the CH_3OH synthesis activity of different catalysts. Using either of the two molecules as an alternative to O_2 chemisorption measurements may provide improved sensitivity for measuring the concentration of adsorption sites. It is possible that the distribution of CO vibrational frequencies and adsorption energies may provide information that can lead to a better correlation of CH_3OH synthesis activity than is provided by uptake measurements alone. Additional work should be performed to test for such a correlation and also to develop methods for performing these adsorption measurements directly on samples whose CH_3OH synthesis activity has been measured.

ACKNOWLEDGMENT

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