

FTIR studies of dynamic surface structural changes in Cu-based methanol synthesis catalysts¹

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Abstract

FTIR studies of CO adsorption have been carried out on Cu supported on ZnO, Al₂O₃, and SiO₂. The reducibility of Cu as well as the surface structures of the metallic Cu particles formed were found to differ on the various supports. The active state of copper was found to be metallic-like in all the systems. The relative ease of reduction of Cu and the specific methanol synthesis activity decrease according to: Cu/ZnO > Cu/Al₂O₃ ≫ Cu/SiO₂. Changes in the reduction potential of the gas result in reversible surface structural changes for Cu/ZnO but not for Cu/Al₂O₃ or Cu/SiO₂. Under moderate reducing condition, the CO adsorption results suggest that the Cu crystals on ZnO expose predominantly (110) facets. Under more severe reducing conditions, significant changes in the CO adsorption were observed and these cannot solely be explained by changes in the relative distribution of Cu surface planes. Instead, the IR transmission and CO adsorption results suggest that the higher reducing potential will lead to an increased number of oxygen vacancies at the ZnO surface and increased spreading of the Cu crystallites. Moreover, the large downward shifts in the CO band observed under severe reduction conditions suggest migration of zinc onto the surface of the Cu particles resulting in the formation of a Cu–Zn surface alloy. The proposal is seen to be in accord with recent surface science and theoretical investigations. The tendency to form the Cu–Zn surface alloy depends critically on the reduction potential of the gas. It is suggested that the recent observations of dynamic changes in the structural and catalytic properties of methanol synthesis catalysts is influenced by reversible reaction involving formation and destruction of the surface alloy. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: FTIR studies; Cu catalysts; Methanol synthesis; Surface structure; Spreading; Strain; Surface alloys; CO adsorption

1. Introduction

Over the years, many different views have been proposed regarding the reaction mechanism and the nature of the surface active sites of

Cu-based catalysts for methanol synthesis reaction. Specifically, for the important Cu/ZnO based catalysts, different types of interactions between Cu and ZnO have been proposed, such as Cu⁺ in ZnO matrix [1], and Cu[−] at the so-called Schottky junction [2] between the metal and the semiconducting oxide support. The active state of copper has also been proposed to be present as Cu⁰ [3–7]. Regarding the

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latter, some authors have proposed that a high coverage of the metallic copper by oxygen is important for methanol synthesis [4–6], whereas others [7,8] more recently have provided evidence to the contrary. Cu–Zn alloys have also been considered [9]. In situ EXAFS studies [10] have directly revealed the presence of Cu⁰ in active methanol synthesis catalysts and these studies did not provide evidence for the presence of other Cu phases. In support of the importance of Cu⁰, it has been shown that a microkinetic model using surface science data from experiments on Cu single crystal surfaces may explain the observed kinetic results quite well [11–13]. There exists, however, controversies in the surface science studies on model catalysts as to the absolute activity of Cu(110) [8] and Cu(111) [14] but the studies have shown that the (111) surfaces are the least active. Recent in situ EXAFS results [15] have shown that ZnO has an important influence on the morphology of the Cu crystals and that dynamic changes in the morphology may take place depending on the reaction conditions. It was furthermore shown [11,16] that these effects and the structure sensitivity of the reaction must be taken into account when explaining many steady state and transient catalytic phenomena. This was done by developing a dynamic microkinetic model [11]. It is noteworthy that large morphological changes were not observed for SiO₂ and Al₂O₃ supported Cu catalysts [15,16].

Recently, several infrared spectroscopic studies using CO adsorption on Cu based methanol synthesis catalysts have dealt with the morphology of Cu [17–19]. Most of these and earlier infrared studies [20–22] have based their assignment of CO vibrational bands on the extensive work of Pritchard et. al. [23]. In view of the above mentioned dynamic changes occurring in the Cu/ZnO catalysts [15,16], we have in the present study carried out FTIR studies using CO as the probe molecule to elucidate the types of Cu crystal planes exposed on different support materials under various reaction conditions. In particular, we have investigated further the dy-

namic aspects of the Cu/ZnO system as compared to the Cu/Al₂O₃ and Cu/SiO₂ systems.

2. Experimental

The catalysts studied were 2.5% Cu/Al₂O₃, 1% Cu/SiO₂, 1 and 5% Cu/ZnO. The support materials and pure CuO were also studied. The 2.5% Cu/Al₂O₃ was prepared by impregnating the alumina support with an aqueous solution containing Cu-nitrate, whereas the 1% and 5% Cu/ZnO were prepared by coprecipitation of an aqueous solution of Cu- and Zn-nitrates [24]. The Cu/SiO₂ catalyst was prepared according to [25]. The Cu surface areas of the 2.5% Cu/Al₂O₃ and 1% Cu/ZnO were determined by the N₂O frontal chromatography method to be 0.8 and 0.3 m² Cu g⁻¹ catalysts, respectively. A total of 100 mg of each sample was pressed into self-supporting wafers and mounted into the in situ IR cell, where the adsorption and reaction experiments took place. Spectra were recorded on a Digilab FTS80 FTIR spectrometer equipped with a liquid nitrogen cooled MCT (Mercury–Cadmium–Telluride) detector.

Reduction was carried out in a flow (100 N ml min⁻¹) of reduction gas mixture consisting of 0.5% CO, 4% CO₂, 4% H₂ and balanced Ar for 16 h at temperatures of 220, 260 or 300°C. In all cases, the samples were then evacuated for 1 h without changing the temperature and subsequently cooled to room temperature (RT) at which temperature the CO adsorption took place.

Adsorption was performed by exposing the pretreated sample with 2.5 Torr of CO at RT for 1 h. This was followed by desorption under conditions where the CO pressure was progressively lowered at RT and subsequently at elevated temperatures. The surface adsorbed species were monitored by recording IR spectra at the various stages of adsorption/desorption.

The samples were also studied in situ during exposure to a methanol synthesis gas mixture consisting of 4.6% CO, 4.7% CO₂, 87.6% H₂

and balanced Ar. A gas flow of 100 N ml min^{-1} was used at reaction temperatures ranging from 220 to 300°C. The reactants and the reaction products were monitored on-line by a Balzers QMG 420 quadrupole mass spectrometer.

3. Results

In order to be able to discriminate between the adsorption properties of the surface Cu atoms and the support materials, CO adsorption was studied first on pure ZnO, SiO₂ and Al₂O₃ following the same pretreatments as used for the catalysts. Fig. 1 shows the room temperature IR spectra of CO in contact with the pure ZnO which was reduced at 220°C, and after removal of CO by brief evacuation. Only the characteristic gas phase CO spectrum is observed, and this disappears readily upon evacuation. No indication of any significant adsorption of CO on ZnO can be seen in this spectral region. Similar CO adsorption results were obtained on a ZnO sample previously subjected to an oxidation treatment. Furthermore, identical set of spectra (which will not be shown here) were obtained on SiO₂ and Al₂O₃ indicating that CO also does not adsorb on the supports after any of the treatments used presently.

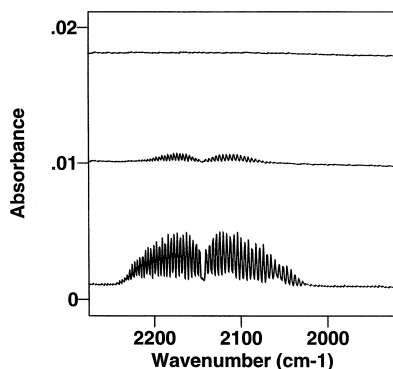


Fig. 1. IR spectra of CO adsorbed at RT on ZnO after reduction at 220°C. The spectra from bottom to top are obtained with CO gas, after evacuation for 2 and 15 min, respectively.

Fig. 2a, b, c and d show the IR spectra of CO adsorbed at RT after reduction at 220°C on 1% Cu/ZnO, 5% Cu/ZnO, 2.5% Cu/Al₂O₃, and 1% Cu/SiO₂, respectively. Mainly one CO band at 2085 cm^{-1} is seen on the 1% Cu/ZnO (Fig. 2a), whereas a band at 2096 cm^{-1} with a lower frequency shoulder at around 2080 cm^{-1} is seen for the 5% Cu/ZnO (Fig. 2b). In both cases, the absorption bands are readily removed upon brief evacuation at RT (the lower spectra in the figures) signifying weakly adsorbed CO. The CO adsorption behavior is quite different for Cu/Al₂O₃ (Fig. 2c). An intense band at 2094 cm^{-1} with a high frequency shoulder at 2139 cm^{-1} is seen here. When CO was desorbed from the alumina supported sample (lower spectra in Fig. 2c), the lower frequency band at 2094 cm^{-1} is seen to be removed much more readily than the higher frequency band at 2139 cm^{-1} and an additional CO band at 2117 cm^{-1} can also now be resolved. On Cu/SiO₂ (Fig. 2d), three CO absorption bands at 2155, 2139 and 2103 cm^{-1} are observed initially. Similar to the behavior seen for Cu/Al₂O₃, the lowest frequency CO band (2103 cm^{-1}) is also the most readily removed one of the three bands upon desorption.

The above results could suggest that after similar reduction treatment at 220°C, Cu atoms are not reduced to the same extent in the different samples. In view of this, higher reduction temperatures have been studied to follow the reduction process. The results are shown in Fig. 3. In general, reduction temperatures higher than 220°C do not give rise to increase in CO band intensity in any of the samples. Rather, a progressive intensity decrease is clearly seen for both the 1 and 5% Cu/ZnO (Fig. 3a and b). In both cases, beside a decrease in the intensity, the band position is seen to shift downwards. For the 1% Cu/ZnO catalyst, the band at 2085 cm^{-1} is shifted to 2083 cm^{-1} and subsequently to 2067 cm^{-1} as the reduction temperature was raised from 220 to 260°C and to 300°C (Fig. 3a). Similar frequency shifts from 2096 to 2088 cm^{-1} and to 2060 cm^{-1} are seen for the 5%

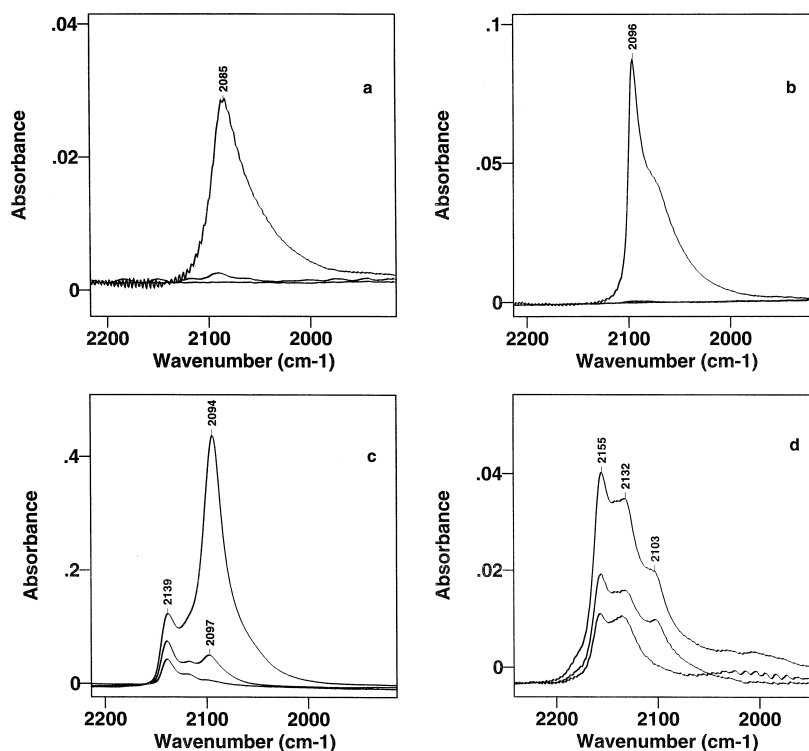


Fig. 2. IR spectra of CO adsorption followed by desorption at RT on (a) 1% Cu/ZnO, (b) 5% Cu/ZnO, and (c) 2.5% Cu/Al₂O₃, (d) 1% Cu/SiO₂ after reduction treatment at 220°C. The spectral conditions are: (top) with CO gas, (middle) evacuated for 2 min, (bottom) evacuated for 15 min.

Cu/ZnO (Fig. 3b). In contrast to Cu/ZnO, no band shifts to lower frequencies were observed for Cu supported on either Al₂O₃ or SiO₂. For Cu/Al₂O₃ (Fig. 3c), the higher frequency CO band at 2139 cm⁻¹ is seen to decrease initially when the reduction temperature was raised from 220 to 260°C, whereas the intensity of the 2093 cm⁻¹ band remains approximately constant. Upon increasing the reduction temperature further to 300°C, intensity of this latter band decreases while that of the higher frequency band stays unchanged. The changes seen in Cu/SiO₂ (Fig. 3d) with increasing reduction temperature are different from that of both the ZnO and Al₂O₃ supported catalysts. The lowest frequency CO band disappears completely after reduction at 300°C, where the highest frequency band is seen to dominate.

A large drop in sample transparency is observed for pure ZnO as it undergoes a reduction

treatment (dashed spectrum) as shown in Fig. 4 (spectra shown in absorbance scale for quantitative comparison). When Cu is present on ZnO, the sample transparency increases and furthermore, reduction treatment is seen to have only negligible effects on sample transparency (shown for 5% Cu/ZnO after reduction as dashed spectrum in Fig. 4). Such effects of Cu has also been reported by other authors [26]. It is seen in Fig. 5 that the IR transmittance (measured as throughput over the whole mid-IR region) varies significantly upon varying the temperatures in the synthesis gas. The sample becomes progressively more transparent as the synthesis temperature was increased from 220 to 260°C and to 300°C. The effect is seen to be reversible in that the sample loses and regains transmission as the synthesis temperature was lowered to 220°C and increased again. However, the overall transmittance drops in general

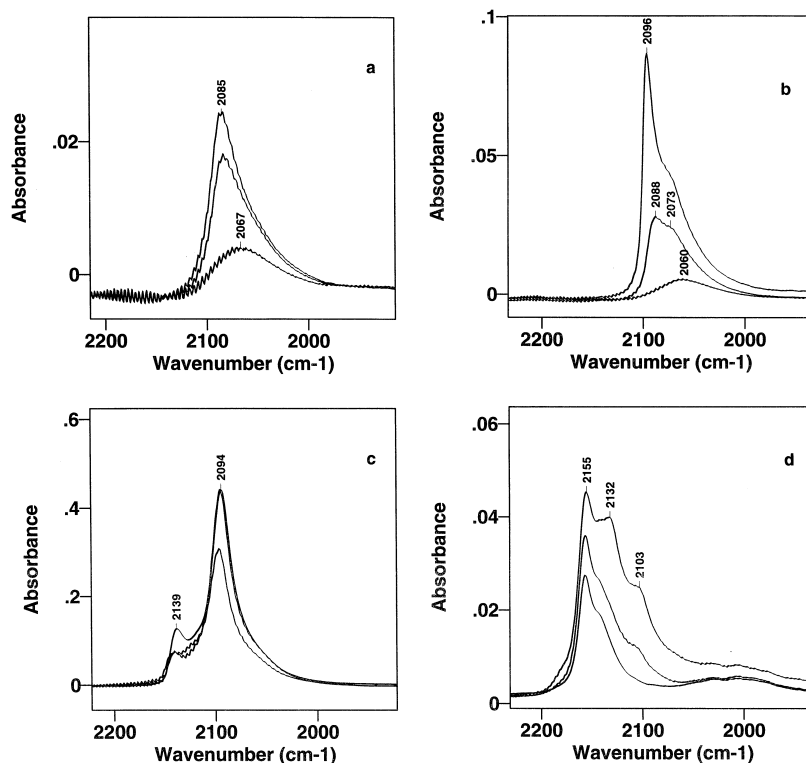


Fig. 3. IR spectra of CO adsorbed at RT on (a) 1% Cu/ZnO, (b) 5% Cu/ZnO, and (c) 2.5% Cu/Al₂O₃, (d) 1% Cu/SiO₂, after reduction treatment at 220°C (top), 260°C (middle) and 300°C (bottom). (Spectral contribution due to gas phase CO has been subtracted from all spectra.)

after each successive temperature variation sequence. In contrast to the behavior of the Cu/ZnO catalysts, no change of IR transmis-

sion is seen for the Cu/Al₂O₃ (as also shown in Fig. 5) and Cu/SiO₂, regardless of the tempera-

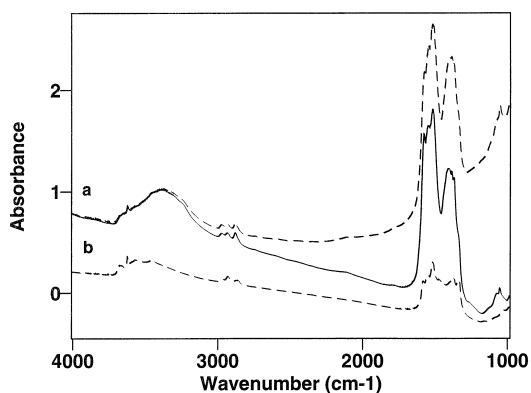


Fig. 4. The IR absorbance spectra of (a) ZnO after oxidation at RT (solid spectrum) and after reduction at 220°C (dashed spectrum), and (b) 5% Cu/ZnO after reduction at 220°C (dashed spectrum).

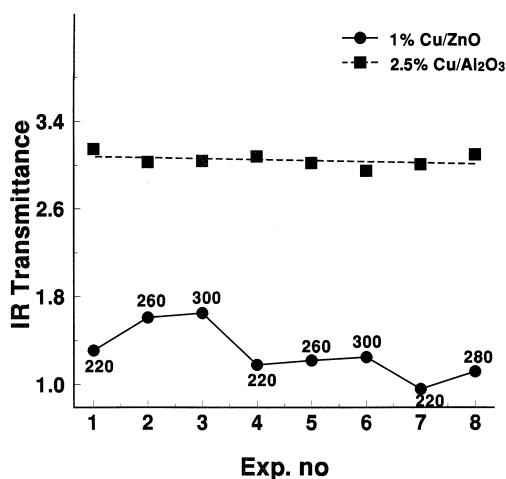


Fig. 5. The IR transmittance (measured as overall IR throughput in arbitrary unit) of 1% Cu/ZnO, and 2.5% Cu/Al₂O₃ under synthesis conditions at temperatures (°C) specified on plot.

ture and reduction potential of the gaseous surroundings.

4. Discussions

4.1. Cu/ZnO: adsorption of CO

According to the literature [23,27], CO bands above 2000 cm^{-1} are attributed to linearly bonded CO molecules. Furthermore, CO bands lying below 2100 cm^{-1} are characteristic of CO adsorbed on metallic Cu, whereas those above 2100 cm^{-1} are generally assigned to CO adsorbed on oxidized forms of Cu. For more detailed interpretation of CO adsorbed on metallic Cu, many researchers have relied on the IR data from single crystal studies on different crystalline faces of Cu.

The very large variations in CO band frequencies observed in the different Cu/ZnO experiments indicate that the morphology, surface composition or surface structure of Cu may vary depending on the Cu loading, and the reduction conditions. It is also seen that the absorption band envelope ($< 2100\text{ cm}^{-1}$) due to CO adsorbed on Cu^0 does not lie at the same position for the different samples. This envelope may contain contributions from several CO bands as, for example, seen in the results for the high loading Cu/ZnO catalyst as well as in the spectral changes observed upon increasing the reduction temperature. The band at 2096 cm^{-1} which dominates in the 5% Cu/ZnO may, for example, according to [23] be assigned to CO adsorbed linearly on Cu(110) planes, whereas the lower frequency band seen for the 1% Cu/ZnO at around 2085 cm^{-1} may be assigned to CO adsorbed linearly on Cu(100) [23]. Following this interpretation, the IR results suggest that for mildly reduced catalysts, mainly Cu(100) surfaces are exposed in the 1% Cu/ZnO, whereas the 5% Cu/ZnO exposes predominantly the Cu(110). The additional low frequency shoulder at around 2080 cm^{-1} seen in the spectrum of the latter sample (Fig. 2b)

suggests, however, that significant amounts of other types of Cu surfaces may also be present in the high loading Cu/ZnO.

When both Cu/ZnO catalysts were reduced at progressively elevated temperatures, the CO band envelope generally shifts to lower frequencies suggesting some changes in the nature of the Cu surfaces. Below, we will discuss some different possible explanations for the very low band frequencies observed following reduction at the highest temperature for both the 1% (2067 cm^{-1}) and 5% Cu/ZnO (2060 cm^{-1}) catalysts. According to the CO band assignment for Cu single crystal faces [23], the observation of bands at such low frequencies could be taken as an indication of an increased relative concentration of Cu(111). Thus, the result shown in Fig. 6 may, for example, be interpreted as a continuous morphology change from Cu(110) to Cu(100) and finally to Cu(111) with increasing temperature in the reducing environment. This interpretation is, however, inconsistent with several other findings. For example, the almost complete absence of bands around 2085 and 2095 cm^{-1} in these samples would suggest that the Cu crystallites do not expose any appreciable amounts of either (110) or (100) surfaces.

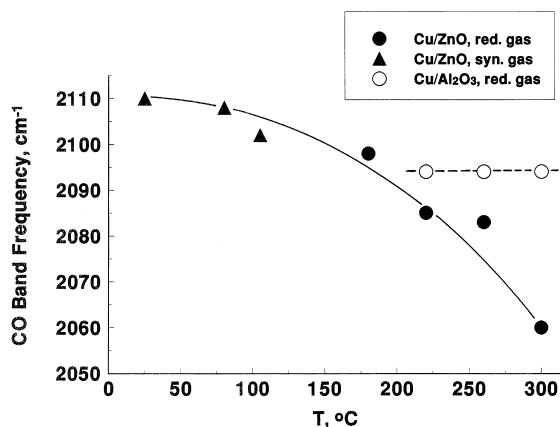


Fig. 6. CO band frequencies for CO adsorbed on Cu/ZnO as function of temperature in synthesis gas (\blacktriangle) and reduction gas (\bullet). The data points at 220, 260 and 300°C were obtained from RT CO adsorption after reduction at the given temperature. The corresponding data points (\circ) for CO adsorption on Cu/Al₂O₃ after reduction are also shown.

This situation is unlikely as indicated from recent Wulff constructions of small Cu particles [11,15]. Furthermore, a tendency to form more (111) surfaces is not in accordance with the observed activity changes (discussed below in a subsequent section). Recently [28], it has been suggested that the bands in the 2065–2078 cm^{-1} region may be due to CO adsorbed at the edges of small Cu particles, but for the same reasons given above this proposal cannot explain the complete disappearance of the higher frequency bands.

Alternatively, two other possible explanations for the appearance of the low frequency band will be proposed and discussed below. Both proposals take into consideration the recent observations [11,15,16] of morphological changes in Cu/ZnO catalysts. In these studies, it was suggested that under very reducing atmospheres oxygen vacancies are formed at the surface of ZnO. This leads to an increased interaction between Cu and Zn as also evidenced by the IR transmission results discussed below. It is thus expected that the concentration of the peripheral Cu sites at the Cu–ZnO interface will increase. These peripheral Cu atoms may resemble those in a Cu–Zn alloy and they are expected to adsorb CO differently from normal Cu metal atoms. It is, however, not likely that spectra of the reduced catalysts which exhibit exclusively low frequency CO bands can be explained by adsorption only on these sites, since again one cannot satisfactorily explain the lack of band contributions at higher frequencies associated with CO adsorbed on other Cu surfaces. Thus, it is proposed that at the most severe reduction conditions, reduced zinc species may start to migrate from the interface to the Cu surfaces. Consequently, the Cu atoms at the surface of the Cu particles will have properties resembling those of a surface Cu–Zn alloy. It is proposed that the alloy formation is restricted to the surface of the Cu particles since at these reduction conditions bulk Cu–Zn alloys have not been observed in previous experiments [5,15,24]. The observed downward frequency shift suggests

that the Cu surface alloy and periphery sites have an increased relatively higher electron density.

The previous model [11,15] for the structural changes occurring in Cu/ZnO catalysts may be expanded to incorporate the idea of surface alloy formation under very reducing conditions. Also, the observation that the structural changes are reversible [15] upon changing the reduction potential of the gas is also consistent with the idea of surface alloy formation, since upon re-exposure to more oxidizing conditions, surface Zn will reoxidize to ZnO, and the surface Cu atoms will again behave like normal metallic Cu atoms. The proposed picture of formation of surface alloy is also consistent with the observed activity changes as discussed in a separate section below.

In view of the present findings, it is noteworthy that recent DFT calculations performed on different Cu surfaces including Cu surface alloys containing zinc [29] show that the presence of the metallic Cu surfaces stabilizes reduced Zn species (by about 60 kJ mol^{-1}). Thus, we may expect to encounter Cu–Zn surface alloys under conditions where reduced Zn itself is not favored. Furthermore, the calculations suggest, in agreement with the present results, that a downward shift of the CO band frequency would be expected for adsorption on the Cu surface alloy atoms.

Below, we would like to discuss one other possible explanation for the appearance of the new low frequency CO band. This is also based on the enhanced interaction between the Cu and the ZnO under more severe reducing conditions. This interaction may lead to strain in the Cu overlayer and this is expected to affect the CO adsorption properties. Indeed, Kampshoff et al. [30] have recently studied the CO adsorption on strained overlayers of Cu on different substrates and observed very significant band shifts. In view of these authors' results, the downward frequency shift observed presently would indicate that the resulting Cu atoms are subjected to compressive strain and have higher electron

density. This explanation could also account for the presence of reversible changes since the strain is expected to decrease under more oxidizing conditions where the support interaction decreases. Nevertheless, if strain is assumed to be the origin of the frequency changes, the data of Kampshoff et al. [30] indicate that several percent changes in the lattice constant of Cu must occur. So far, EXAFS results [15,24] have not given evidence for such changes. Thus, it is concluded that the major origin of the CO shifts observed presently is surface alloy formation.

4.2. Cu/ZnO: transmittance studies

The presence of the Cu–ZnO interactions discussed above are also reflected by the change in IR transmittance when the catalyst is exposed to the reducing environment at different temperatures. In particular, the transmittance changes for Cu/ZnO are different from those seen for the pure ZnO under similar reduction conditions (as shown in Fig. 4). This further supports that Cu, when in close contact with ZnO, can modify the defect structure of the ZnO support as discussed below.

Upon reduction, the IR transmittance of pure ZnO drops drastically (Fig. 4). This phenomenon has also been observed by Taylor and Amberg [31]. These authors also noticed a simultaneous increase in electrical conductivity. Similar effects have later been discussed by Bocuzzi et al. [26]. The loss of transmission in ZnO is not originated from molecular vibration but is associated with IR photoionization of V_O^+ donor centers (monoionized oxygen vacancies) [26] created during reduction. When Cu is present on the ZnO, only negligible effect on the IR transmission is seen under similar reduction conditions. This shows that the presence of Cu modifies the electronic properties of ZnO. This effect has been explained in terms of the semi-conducting nature of the system and electron transfer between the Cu and ZnO at the interface where the two phases are in good contact [26]. The extent of such an effect is therefore

expected to depend on the extent of the Cu–ZnO interface. The observation that a progressive increase in the IR transmittance occurs when the temperature was increased from 220 to 300°C in synthesis gas (Fig. 5) can thus be taken as an indication of a change in the morphology of the Cu particles such that the amount of the contact surface between Cu and ZnO is increased. In other words, these results provide independent support for an increased ‘spreading’ of Cu on ZnO surface under more reducing conditions. The drop in the IR transmittance observed upon lowering the temperature again suggests some ‘non-spreading’ or agglomeration of Cu. The spreading/non-spreading behavior therefore appears to be largely reversible. Similar morphological changes have also been observed in V_2O_5/TiO_2 [32] and other systems [33]. The general decrease in transmittance level following several successive cycles of changing conditions indicates that some sintering of the Cu particle takes place.

It is noteworthy that all these results are in good agreement with the recent EXAFS findings on similar Cu/ZnO catalysts [15]. Reversible spreading/agglomeration processes were suggested based on reversible changes in the Cu–Cu coordination numbers upon changing the reduction potential of the synthesis gas. The results suggested that the largest degree of wetting of the ZnO support occurs for the most reducing conditions. The present FTIR results have provided more direct information about the amount of this Cu–ZnO interface and the extent of spreading. In agreement with the present results, the EXAFS results [15] also showed some sintering of the Cu particles upon several reduction–oxidation cycles.

4.3. Cu/Al₂O₃

An intense band at 2094 cm^{-1} attributed to CO adsorbed linearly on Cu(110) is observed for reduced Cu/Al₂O₃ catalyst. Besides this, a higher frequency band at 2139 cm^{-1} which can be attributed to CO adsorbed on Cu⁺ species

[21,27] is also seen. Thus, in contrast to Cu/ZnO, some of the Cu atoms are still found in an oxidized environment in Cu/Al₂O₃. This is also supported by the desorption behavior which is different from that of Cu/ZnO. For the ZnO supported Cu catalysts (Fig. 2), the adsorbed CO is removed readily, whereas for Cu/Al₂O₃ the higher frequency CO band disappears much slower with additional band resolved at 2117 cm⁻¹. This observation agrees with the band assignment of the lower frequency band to CO on Cu⁰ and the higher frequency bands to CO on oxidized Cu (e.g., Cu⁺ in different surface surroundings). Previous temperature-programmed desorption studies [22] have also shown that CO adsorbs stronger on oxidized than reduced Cu/ZnO. Thus, it can be concluded from the IR results that the reducibility of Cu is lower for Cu/Al₂O₃ than for Cu/ZnO catalysts.

Unlike Cu/ZnO, there is no shift in CO band frequency in Cu/Al₂O₃ upon increasing the reduction temperature and the main change is some band intensity decrease at the highest temperature. This suggests that only some further reduction (decrease in 2139 cm⁻¹ band) and sintering occurs at more severe reduction conditions but the morphology of Cu on Al₂O₃ remains essentially unchanged exposing predominately (110) surfaces (Fig. 3c). The fact that the high frequency band at 2139 cm⁻¹ persists even at reduction temperature of 300°C indicates the presence of some very stable Cu⁺ species associated with the surface of the Al₂O₃ support.

Also, in contrast to pure ZnO and Cu/ZnO, no significant IR transmittance change is seen for the Cu/Al₂O₃ catalysts under changing reduction and synthesis conditions (Fig. 5). This result shows that similar 'electronic effects' as seen for Cu/ZnO do not, as expected, occur in Cu/Al₂O₃. Thus, in view of the above and the remarkable constant CO band position observed after reduction of different severity (Fig. 6), no change in the spreading of Cu over Al₂O₃ is apparent under the various reduction and syn-

thesis conditions studied here. This finding is in agreement with other recent results [16].

4.4. Cu/SiO₂

The surface properties Cu/SiO₂ are quite different from Cu supported on the two other supports. The very high frequency band at 2155 cm⁻¹ may be assigned to CO adsorbed on Cu²⁺ [22,27]. The band lying at 2132 cm⁻¹ is, as was the case for Cu/Al₂O₃, attributed to the presence of Cu⁺. The origin of the 2103 cm⁻¹ band is not completely clear. It could be due to CO bonded to a coordinatively unsaturated Cu⁺ ions associated with the surface of the SiO₂ support. No significant amount of exposed metallic copper atoms is evidenced for the present Cu/SiO₂ sample under the reduction conditions used here. For example, the 2103 cm⁻¹ band disappears entirely without the formation of any low frequency CO bands characteristic of Cu metal. This behavior is different from that of Cu/Al₂O₃ and it may reflect that although Cu metal is formed during reduction (as observed by EXAFS [16]) at higher reduction temperatures, silica may migrate over the metal surface and render the Cu inaccessible for adsorption and catalysis (see below). Evidence for such encapsulation effects has been presented for other SiO₂ supported systems [34]. The absence of large reversible changes in the IR transmittance throughout the reduction and synthesis sequences also shows that these catalysts behave very differently from Cu/ZnO in accord with recent studies [15].

4.5. Catalytic implications of the changes in surface structures

In situ IR/reactivity studies of the present samples show a higher methanol synthesis activity at 220°C for the Cu/ZnO (0.105 μmol methanol produced/m² Cu) than for the Cu/Al₂O₃ (0.03 μmol/methanol produced/m² Cu), whereas hardly any measurable activity is found for Cu/SiO₂. These results show that the

presence of exposed metallic-like copper atoms are essential for methanol synthesis. The lack of methanol synthesis activity for the present Cu/SiO₂ samples appears to be related to the encapsulation described above.

The activity results for Cu/Al₂O₃ and Cu/ZnO suggest that although metallic-like copper are important for methanol synthesis, differences in activity may be observed depending on the nature of the support. Previous results have shown that the reduction potential of the gaseous environment also influences the activity of Cu/ZnO catalyst [11]. The activity differences between Cu/Al₂O₃ and Cu/ZnO may be related to the different types of Cu sites which dominate in the two systems. The result, that despite a lower Cu surface area for Cu/ZnO as compared to Cu/Al₂O₃, the specific activity for the Cu/ZnO catalyst is significantly higher, suggests that the Cu/ZnO system exposes special surface sites. Indeed, the CO adsorption results show that this is the case and different models for the nature of the surface sites have been considered above. The likelihood of each of these will be discussed below in relation to the activity results.

The simplest model considers that the main difference between catalyst systems is in the relative distribution of different Cu surface planes. The comparison with CO adsorption data from single crystal studies would suggest that Cu(110) surfaces dominate in all Cu/Al₂O₃ catalysts and mildly reduced Cu/ZnO catalysts, while Cu(111) surfaces dominate in Cu/ZnO after more severe reduction. In view of the low activity reported for (111) surfaces, we would expect that this treatment should result in an activity decrease, which is in fact opposite of what we have observed for the present catalysts [35]. Thus, it is concluded that the changes occurring at more severe reduction conditions are not simply due to changes in the distribution of different Cu surface planes. Based on this and the CO adsorption results discussed above, we favor the formation of surface Cu–Zn alloys. It is furthermore suggested that the ten-

dency to form these structures increases with the reduction potential of the gas and the resulting changes give rise to increases in the catalytic activity. Regarding the surface alloy model, it is interesting that Nakamura et al. [9] recently have observed activity increases upon doping Cu(111) single crystal surfaces with Zn. It should be noted that the reduction conditions employed presently to produce the surface alloys are probably more severe than those encountered in the recent kinetic study [11]. In view of this, we are presently examining the issue as to what extent surface alloys may also be formed under typical methanol synthesis conditions.

5. Conclusions

Infrared studies of CO adsorption and transmission properties have provided evidence for the nature of surface species in Cu/Al₂O₃, Cu/ZnO and Cu/SiO₂ catalysts. All the results suggest that the active copper species present during methanol synthesis is metallic-like. The differences in catalytic activities are attributed to Cu located in different crystalline faces and in different surface structures. Cu(110) surfaces which are seen to dominate in the Cu/Al₂O₃ catalyst are observed to have lower specific activities than the Cu surfaces exposed in Cu/ZnO catalysts. The nature of the exposed Cu surfaces in Cu/ZnO catalysts are seen to change reversibly with changing reduction conditions and simple changes in the relative abundance of different crystallographic Cu metal planes cannot account for all the observations. The results suggest that the Cu exposes predominantly (110) surfaces under mild reduction conditions. At higher reduction potential, formation of strong bonds with the ZnO support occurs leading to increased spreading of the Cu. Reversible changes in spreading have been observed upon decreasing the reduction potential of the gas. The results also suggest that under severe reduction conditions, reduced Zn species

may migrate onto the Cu surfaces forming surface Cu–Zn alloy structures with high activity. Recent theoretical calculations [29] support the presence of such structures and, moreover, recent surface science experiments [9] also suggest that surface alloys may yield structures with high activity. The very low activity of Cu/SiO₂ catalysts appear to be due to encapsulation of the metallic Cu by SiO₂.

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