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# Spectroscopic evidence for adsorption sites located at Cu/ZnO interfaces

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FTIR spectra are reported of CO and formic acid adsorption on a series of $Cu/ZnO/SiO_2$ catalysts. Peaks due to linear CO adsorbed on copper diminished in intensity as the loading of ZnO was increased. This behaviour was explained in terms of ZnO island growth on the copper surface. Similarly, reduction of the copper concentration while maintaining a constant ZnO loading also resulted in further attenuation in bands ascribed to CO chemisorbed on copper. Formic acid exposure to a $Cu/SiO_2$ sample produced a formate species displaying a $\nu_{as}(COO)$ mode at 1585 $cm^{-1}$. Addition of a small quantity of ZnO to the catalyst resulted in substantial promotion of formate growth, which was accompanied by a shift (and broadening) of the $\nu_{as}(COO)$ vibration to 1660–1600 $cm^{-1}$. Since further ZnO incorporation poisoned formate creation it was concluded that formate species bonded to Cu and Zn sites located at interfacial positions had been formed. The role of such species in methanol synthesis is discussed.

**Keywords:** $Cu/ZnO/SiO_2$ catalysts; IR adsorbed CO; adsorbed formate

## 1. Introduction

Catalysts consisting of Cu/ZnO have been used successfully for the past three decades to synthesise methanol from a $CO/CO_2/H_2$ feedstock. Although detailed mechanisms have been presented to explain the synthetic pathway on copper [1–3], considerable debate surrounds the effect of the oxide support. Chinchen et al. [4,5] demonstrated that a linear relationship existed between the methanol synthesis activity and the total copper surface area, irrespective of the oxide support used. In contrast, Burch et al. [6–9] reinforce the idea that the catalyst activity is

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related to copper surface area but suggest that the nature of the support is critical. Possible explanations for this effect could invoke either the ability of the support to stabilise copper in a non-equilibrium state [10] or hydrogen spillover between the support and copper [8].

Alternatively, Klier [11] proposed that $Cu^+$ ions substituted in the oxide lattice were the centres of catalytic activity. Moreover, it was argued that methanol was formed from the CO component of the feedstock, and that the role of $CO_2$ was to keep the catalyst in the required oxidised state [11]. This hypothesis has, however, been discredited by isotopic labelling studies which demonstrate that $CO_2$ is the species hydrogenated to methanol [4].

Frost [12] has speculated that the effect of copper was to alter the electronic properties of the oxide in such a way as to increase the concentration of surface oxygen-ion vacancies [12]. Furthermore, it was shown that the methanol synthesis activity of the catalysts examined correlated with the calculated number of oxygen-ion defects.

Recently, evidence has been provided which indicates that special adsorption sites may be present at the interface between copper and zinc oxide [13–15]. In order to characterise these sites in more detail, FTIR spectroscopy has been used to identify adsorbates formed following CO and formic acid exposure to several Cu/ZnO catalysts of various composition.

## 2. Experimental

The preparation of a 5 wt% $Cu/SiO_2$ catalyst has been detailed elsewhere [16]. This procedure was adapted in the following manner for the production of $Cu/ZnO/SiO_2$ catalysts.

Silica (Cab-O-Sil M5, 200 $m^2\ g^{-1}$) was co-impregnated with an aqueous solution containing copper(II) acetate monohydrate (BDH AnalaR grade, >99%) and zinc(II) acetate (BDH AnalaR grade, >99.5%). After drying in air at 383 K for 5 h, a self-supporting disc was placed in a conventional vacuum line and then subjected to calcination in oxygen (50 $cm^3\ min^{-1}$) at 623 K for 1 h. Subsequently, the catalyst was reduced in hydrogen at 623 K for 18 h and then evacuated at 623 K for 1 h.

By varying the concentration of the precursors in the impregnating solution catalysts of differing composition were made. A brief notation is used to describe the loading of each catalyst, for example, a reduced catalyst containing 5 wt% Cu and a quantity of ZnO equivalent to 29 mol% of the copper loading is designated Cu/ZnO(5, 29). In every case the amount of ZnO present is given as a percentage of a 5 wt% Cu standard, and the quantity of Cu as a weight percentage of the $SiO_2$.

Infrared spectra were recorded using a PE-681 infrared spectrophotometer operating at 4 $cm^{-1}$ resolution [16]. Formic acid (BDH AnalaR grade) was further purified by a series of freeze–pump–thaw cycles.

## 3. Results and discussion

### 3.1. CO ADSORPTION ON Cu/SiO$_2$, ZnO/SiO$_2$ AND Cu/ZnO/SiO$_2$

Fig. 1a displays the spectrum obtained after CO exposure to a Cu/SiO$_2$ catalyst at 295 K. An intense peak was detected at 2115 cm$^{-1}$ with a broad band at 2169 cm$^{-1}$ due to gaseous CO. Previous studies [16] revealed that CO adsorbed on a fully reduced supported copper surface produced a band at ca. 2100 cm$^{-1}$, whereas CO present on a partially oxidised copper surface was characterised by a peak at ca. 2115 cm$^{-1}$. The present preparation therefore led to completely reduced copper particles with a partially oxidised copper surface [16]. A distinct shoulder was also evident at ca. 2070 cm$^{-1}$in fig. 1a which is typical of linear CO adsorption on low-index fully reduced copper crystal faces [16].

When CO was exposed to a copper catalyst containing a small quantity of ZnO [Cu/ZnO(5, 10)] a similar set of bands were observed (fig. 1b). However, there was an overall attenuation of peaks associated with CO adsorption on copper. This behaviour was further highlighted when CO was dosed on to a Cu/ZnO(5, 29) catalyst (fig. 1c). Again, it was apparent that increasing the concentration of ZnO resulted in a concomitant decrease in the number of copper sites available for chem-

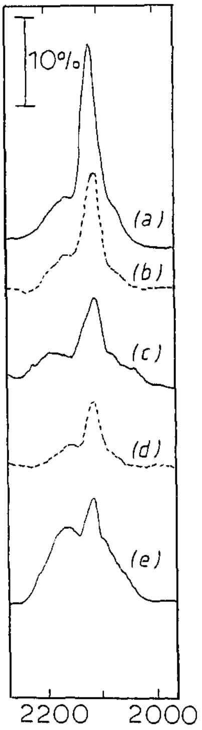

Fig. 1. Addition of CO (26.6 kN m$^{-2}$) at 295 K to (a) Cu/SiO$_2$, (b) Cu/ZnO/SiO$_2$(5, 10), (c) Cu/ZnO/SiO$_2$(5, 29), (d) Cu/ZnO/SiO$_2$(2.5, 29), and (e) Cu/ZnO/SiO$_2$(1, 29).

isorption of CO. Comparison of the copper surface areas measured for the $Cu/SiO_2$ and $Cu/ZnO/SiO_2$(5, 29) catalysts used in this study (136 $m^2$ ($g^{-1}$ Cu) and 70 $m^2$ ($g^{-1}$ Cu), respectively) with the intensities of the bands due to adsorbed CO (figs. 1a and 1c) suggests that the observed intensity of the peak at ca. 2115 $cm^{-1}$ approximately correlates with the copper surface area.

Two explanations satisfactorily rationalise the decrease in copper surface area with increased ZnO loading. Firstly, the morphology of the copper particles could substantially change as a consequence of epitaxial interaction with ZnO [10]. However, this theory is not supported by the CO spectra obtained for the various catalysts (figs. 1a–1c) since the CO profiles are similar in each case. Instead, it is appropriate to assume that the catalyst consisted of a copper surface decorated to varying extents with ZnO clusters (fig. 2).

The effect of reducing the copper content of the catalyst while maintaining a constant ZnO loading has been investigated. The infrared spectra displayed in figs. 1d and 1e show a decrease in the amount of adsorbed CO with decrease in copper loading. In the case of a Cu/ZnO(1, 29) catalyst (fig. 1e) only a relatively small band characteristic of adsorbed CO was distinguished above background features typical of gaseous CO at 2179 and 2115 $cm^{-1}$. These observations are consistent with the model presented in fig. 2. Tohji et al. [17] concluded from in situ EXAFS spectra that copper was present as a reasonably uniform distribution of small particles when supported on ZnO. This suggests that reduction of the copper loading will lead to a decrease in the number of copper clusters present and not a change in cluster size. A greater amount of ZnO is therefore available to cover the remaining particles. Implicit in this argument is the fact that there must be an attractive interaction between Cu and ZnO, otherwise the ZnO could simply disperse over the high area $SiO_2$ support. Klier [11] has advocated the possible importance of $Cu^+$ species in methanol synthesis catalysts, yet no spectroscopic evidence for their existence has been obtained [18]. However, this discrepancy can be resolved if it is postulated that $Cu^+$ sites were capable of initiating growth of ZnO islands upon the copper surface during catalyst formulation. An alternative rationalisation involved the formation of a surface brass species which could then subsequently oxidise to produce copper catalyst decorated by ZnO crystallites [19].

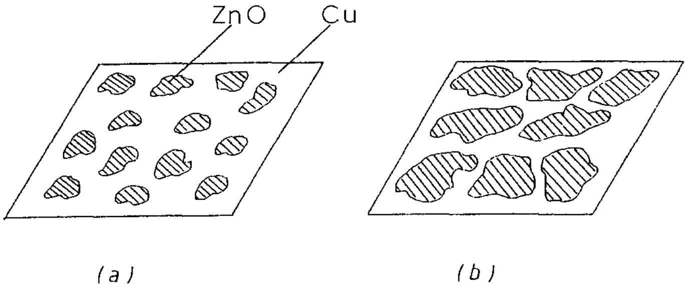

Fig. 2. Model of Cu/ZnO catalyst; (a) low concentration of ZnO, (b) high concentration of ZnO.

Finally, CO was exposed at 295 K to a $ZnO/SiO_2$ sample, and in accordance with the study of Scarano et al. [20] no bands due to adsorbed species were observed when CO was admitted to $ZnO/SiO_2$ at 295 K.

### 3.2. ADSORPTION OF FORMIC ACID

When formic acid was exposed to a $Cu/SiO_2$ catalyst at 295 K bands appeared at 2945, 1732 and in part 1363 $cm^{-1}$ which were typical of physisorbed formic acid on $SiO_2$ [21]. Evacuation at 295 K revealed peaks due to chemisorbed species at 2976, 2892, 1585 and 1360 $cm^{-1}$ (fig. 3a). A similar set of bands were obtained after formic acid adsorption on a partially oxidised copper surface [21] and these were ascribed to vibrations of a unidentate formate species on copper. Of particular interest is the $\nu_{as}(COO)$ mode at 1585 $cm^{-1}$ since this vibration should be sensitive to the exact orientation of the formate ion and also reflect the character of the adsorption site [22].

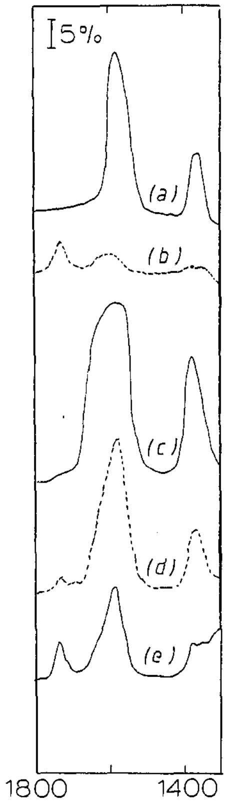

Fig. 3. Infrared spectra obtained after exposure of formic acid (2.66 kN $m^{-2}$) at 295 K and evacuation at 295 K for 30 min. (a) $Cu/SiO_2$, (b) $ZnO/SiO_2$, (c) $Cu/ZnO/SiO_2(5, 10)$, (d) $Cu/ZnO/SiO_2(5, 29)$ and (e) $Cu/ZnO/SiO_2(1, 29)$.

Formic acid adsorption and desorption on $ZnO/SiO_2$ (fig. 3b) gave a substantially smaller band at ca. 1600 $cm^{-1}$ (relative to the copper catalyst) and an accompanying peak at ca. 1360 $cm^{-1}$. These bands may be assigned to the $\nu_{as}$(COO) and $\nu_s$(COO) modes of bidentate formate on ZnO [14]. The peak at 1732 $cm^{-1}$ was caused by residual formic acid physisorption on $SiO_2$.

The structure of Cu/ZnO catalysts is here probed via the effect of changing the catalyst composition upon the profile of the $\nu_{as}$(COO) infrared band. The $\nu_{as}$(COO) band obtained by formic acid addition to Cu/ZnO(5, 10) was approximately twice as broad (fig. 3c) as the peak detected for a $Cu/SiO_2$ catalyst (fig. 3a), but was of comparable absorbance at the band maximum. Upon increasing the ZnO loading (fig. 3d) the $\nu_{as}$(COO) mode narrowed substantially and the peak position shifted to ca. 1590 $cm^{-1}$.

The $\nu_{as}$(COO) profile observed for a Cu/ZnO(1, 29) catalyst at 1585 $cm^{-1}$ also contained a weak shoulder at ca. 1610 $cm^{-1}$ (fig. 3e). The intensity of the 1585 $cm^{-1}$ peak was less than half of the absorbance of the comparable band for a $Cu/SiO_2$ sample (fig. 3a). This observation is in accordance with the CO adsorption data (fig. 1) which indicates that the available copper surface was considerably less when ZnO was present and the copper loading was reduced. The shoulder at 1610 $cm^{-1}$ is ascribed to formate adsorbed on ZnO (fig. 3b).

The effect of ZnO addition upon the shape of the $\nu_{as}$(COO) formate profile was informative. At relatively low concentrations ZnO promoted formate production (fig. 3c), yet when the amount of ZnO was further increased (fig. 3d) a diminished quantity of formate was detected. This behaviour is intriguing since the copper area is known to substantially decrease as the ZnO loading is increased (fig. 1). It is therefore implausible to assign the extra formate formation on the Cu/ZnO(5, 10) catalyst to formate species on copper. This conclusion is also supported by the fact that the wavenumber of the new formate species (ca. 1660–1600 $cm^{-1}$) is significantly higher than the values normally associated with formate on copper [21]. It is also unreasonable to assign the extra formate production to formate species on ZnO, because when the ZnO loading was further increased (fig. 3d) the $\nu_{as}$(COO) profile not only decreased in absorbance but shifted in position to resemble formate formation on copper.

These observations can be resolved by consideration of the model derived from CO studies, concerning the structure of Cu/ZnO catalysts (fig. 2). At low ZnO loadings (fig. 2a) the copper surface is decorated with relatively small ZnO islands, and consequently there will be a large number of interfacial sites between copper and ZnO. In contrast, the presence of greater ZnO concentrations results in amalgamation of ZnO islands to create much larger clusters (fig. 2b). Considerably fewer interfacial sites will therefore be present on the catalyst of higher ZnO loading.

If formate species were formed at interfacial sites the following predictions could be made. On a $Cu/SiO_2$ catalyst only a band due to formate on copper would be expected, whereas on a Cu/ZnO(5, 10) sample, in addition to formate on cop-

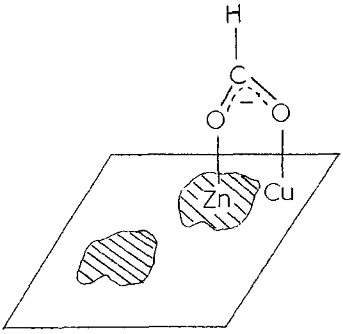

Fig. 4. Diagrammatic representation of the unique bridging formate species situated at special sites located at the copper–zinc oxide interface.

per, bands characteristic of interfacial formate should also be observed (fig. 4). With regard to the expected vibrational position the analysis of Busca and Lorenzelli [22] shows increased splitting of the $\nu_{as}(COO)$ and $\nu_s(COO)$ modes for formate species bonded to inequivalent sites. This theory is in accordance with the observation that the $\nu_{as}(COO)$ vibration shifted towards higher wavenumbers in the current study (fig. 3c).

Furthermore, as the number of interfacial sites diminished with enhanced ZnO concentration, the infrared spectrum should again resemble that of formate on copper (fig. 3d). The spectrum in fig. 3e for formate adsorbed on Cu/ZnO(1, 29) catalyst is practically a combination of formate on copper (fig. 3a) and formate on ZnO (fig. 3b). This is not surprising as this catalyst is expected to comprise of copper particles almost entirely encapsulated by ZnO islands. Therefore, only very few interfacial sites would be present. It is pertinent to emphasise here that the formate species could either be bound to "ZnO" or maybe to Zn atoms which have been postulated to be present at the periphery of ZnO particles [23]. Previous studies regarding brass formation in copper/zinc oxide catalysts may also be of relevance to this argument [19].

In summary, the adsorption data in this investigation can only be rationalised if the formation of interfacial formate structures is invoked. The role of such species in the synthesis of methanol will be a function of the catalyst morphology. As already indicated [13] in conventional $Cu/ZnO/Al_2O_3$ systems their importance may not be substantial. However, rare-earth metal/copper alloy catalysts which contain very small copper clusters in intimate contact with the oxide, exhibit a very high proportion of interfacial sites [24–26]. Consequently, interfacial formate species could play a significant role in the synthesis mechanism.

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