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An FTIR Study of the Adsorption of Formic Acid and Formaldehyde on Potassium-Promoted Cu/SiO$_2$ Catalysts

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FT-IR spectra are reported for formic acid and formaldehyde adsorbed on a reduced Cu/SiO$_2$ catalyst with and without the addition of potassium promoter. Catalysts partially oxidised by treatment with nitrous oxide have also been studied. Formic acid on potassium-promoted Cu/SiO$_2$ produced a formate species on "potassium" and bidentate copper formate. More of the former was generated in the presence of Cu than for a reduced potassium/SiO$_2$ catalyst without copper, suggesting that either the formate species formed initially on the copper surface subsequently spilled over onto potassium sites, or that the morphology of potassium oxide was influenced by the presence of copper. Adsorption of formaldehyde on a potassium/silica catalyst resulted in the formation of unidentate formate and physisorbed formaldehyde on potassium. Polymerised formaldehyde structures were also observed. Formaldehyde on a reduced potassium-promoted copper/silica catalyst gave not only bidentate formate species formed on copper but also a substantial increase in the quantity of unidentate formate species on potassium. This result suggested that new adsorption sites at interfaces between copper and potassium oxide were created, which facilitated formate production. © 1995 Academic Press, Inc.

INTRODUCTION

Recent studies (1, 2) of the effect of potassium addition to Cu/SiO$_2$ catalysts were stimulated by evidence suggesting that the addition of alkali metals to copper-containing catalysts could enhance the rates of both methanol synthesis and the water–gas shift reaction (3–8). Added potassium was found not only to cause a significant red-shift in the frequency of adsorbed carbon monoxide on copper, but also to produce surface species arising from a direct interaction between CO and potassium (1). Furthermore, exposure of carbon dioxide to these promoted catalysts resulted in the formation of CO_2^- species (1). It was demonstrated that activation of carbon dioxide was achieved by electron transfer from potassium oxide. The CO_2^- radical anions produced could then either adsorb on the copper surface to form carboxylate species or disproportionate to bidentate carbonate and adsorbed CO on potassium. Subsequent reaction of hydrogen with carboxylate species on copper resulted in the formation of formate species on potassium. More complex molecules which could be intermediates in the methanol synthesis reaction have also been studied. The adsorption of methanol on potassium-promoted copper catalysts produced physisorbed methanol on potassium in addition to methoxy species on copper (2). Methyl formate adsorption resulted in the formation of methoxy species, as well as bidentate formate on copper and formate on potassium (2). To complement these studies we report on an infrared investigation of formic acid and formaldehyde adsorbed on reduced and reoxidised potassium-promoted Cu/SiO$_2$ catalysts.

EXPERIMENTAL

The catalyst preparation procedure used comprised coimpregnation of silica (Cab-O-Sil M5, 200 m^2 g^{-1}) with an aqueous solution containing copper(II) acetate monohydrate (B.D.H., AnalaR grade) and potassium acetate (B.D.H., AnalaR grade) followed by subsequent drying in air at 383 K for 5 h. A self-supporting disc was calcined in oxygen (50 cm^3 min^{-1}) at 623 K for 1 h, and then reduced at 623 K in hydrogen for 18 h, which ensured effectively complete reduction of copper to Cu^0 with only a trace of residual surface oxygen (1). Finally, the catalyst was evacuated at 623 K for 1 h in order to desorb residual hydrogen and water. The reduced catalyst consisted of 5 wt% copper and 1.26 wt% potassium on silica, which corresponds to a K/Cu ratio of 0.29/1. The copper surface area in the reduced catalyst (measured by reactive frontal chromatography involving N$_2$O adsorption) was 136 m^2 g^{-1}. Reoxidation of the catalyst to a stoichiometric Cu$_2$O surface was achieved by contacting the catalyst with ca. 13 kPa of N$_2$O (B.D.H., 99.6%) at 348 K for 15 min with subsequent evacuation at 348 K for 5 min. This treatment ensures oxidation of surface copper sites to Cu$^+$ (1, 9). A

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more detailed description of the apparatus used to record infrared spectra and the catalyst preparation utilised has been presented elsewhere (9). A catalyst containing potassium on silica was prepared using a procedure analogous to that for the copper-containing catalyst. The only difference was the omission of copper(II) acetate from the impregnating solution. Formic acid (98–100% G.P.R.) was purified by a series of freeze–thaw cycles under vacuum to remove dissolved gases. Formaldehyde was prepared by heating paraformaldehyde (Aldrich, 95%) at 333 K.

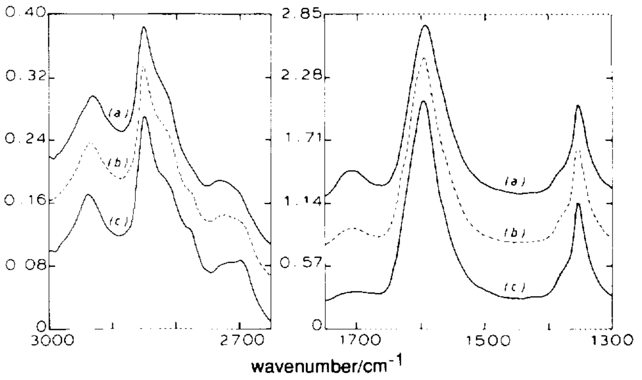


FIG. 2. Potassium-doped copper/silica catalyst (a) after exposure to formic acid at 295 K, followed by evacuation at 295 K for (b) 5 min, (c) 20 min.

RESULTS

Adsorption of Formic Acid on a Potassium-Promoted Reduced Cu/SiO$_2$ Catalyst

Figure 1 displays spectra of formic acid at increasing pressures on a potassium-promoted reduced copper catalyst at 295 K. Initially, bands appeared at 1696, 1597, and 1354 cm^{-1} in the 1750–1300 cm^{-1} spectral region. As the dosage was increased, additional peaks grew at 1718 and 1380(sh) cm^{-1} and the maxima at 1597 and 1354 cm^{-1} shifted to 1587 and 1353 cm^{-1}, respectively. Bands appearing in the CH-stretching region at low exposures of formic acid (Fig. 1b) were a broad maximum at ca. 2937 cm^{-1}, a peak at 2850 cm^{-1} with a low-frequency tail containing possibly two other bands at 2817 and 2775 cm^{-1}, and a small maximum at 2687 cm^{-1}. As the pressure was increased (Fig. 1g) the band at 2937 cm^{-1} shifted to 2924 cm^{-1}, and the peak at 2850 cm^{-1} grew steadily in intensity. A distinct shoulder at ca. 2817 cm^{-1} was discernible, and a new broad band centred at 2738 cm^{-1} was noted which obscured detection of peaks which were formerly present at 2775 and 2687 cm^{-1}. Prolonged evacuation at 295 K (Fig. 2) resulted in substantial removal of the band at 1717 cm^{-1}. Furthermore, the maximum at 2924 cm^{-1} shifted to 2938 $^{-1}$, the shoulder at 2817 cm^{-1} was attenuated, and bands became detectable at 2778(sh) and 2698 cm^{-1}. The peak at 2698 cm^{-1} also contained a broad band at ca. 2724 cm^{-1}.

Assignment of these bands was facilitated by examination of spectra obtained by contacting formic acid with a catalyst consisting of only potassium and silica (Fig. 3). It has previously been demonstrated that this catalyst contained SiO$^-$K$^+$ and K$_2$O species (1). Bands developed at 1597, 1376, and 1355 cm^{-1} initially in the 1750–1300 spectral region (Fig. 3a). As the dosage increased an intense maximum appeared at 1722 cm^{-1}, the band at 1597 cm^{-1} shifted to 1582 cm^{-1}, and the peak at 1376 cm^{-1} intensified remarkably. In the CH-stretching region of the spectrum maxima initially discerned at 2820, 2776, and 2692 cm^{-1} (Fig. 3c) gradually became obscured by the growth of bands at 2923, 2830, and ca. 2725 cm^{-1}. By analogy to results published by Kantschewa *et al.* (10) and by Solymosi and Knözinger (11) the present bands at 2776 [ν(CH)], ca. 1597 [ν_{as}(COO)], 1376 [δ(CH)], and 1355 [ν_s(COO)] cm^{-1} can be ascribed to potassium formate

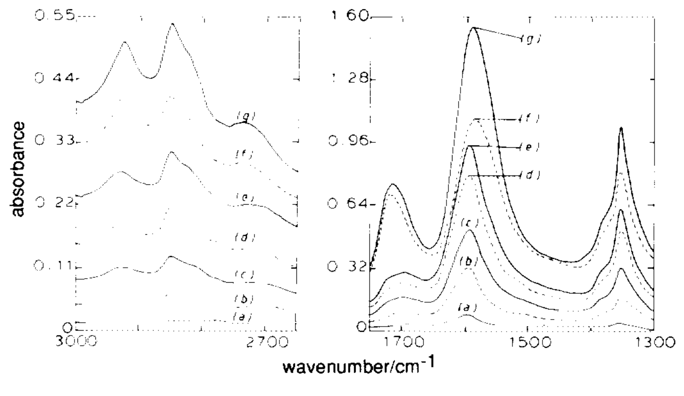


FIG. 1. Spectra of formic acid adsorbed on a potassium-promoted reduced Cu/SiO$_2$ catalyst at increasing surface coverages, (a)–(g). Spectrum (g) corresponds to an equilibrium formic acid pressure of 0.13 kPa.

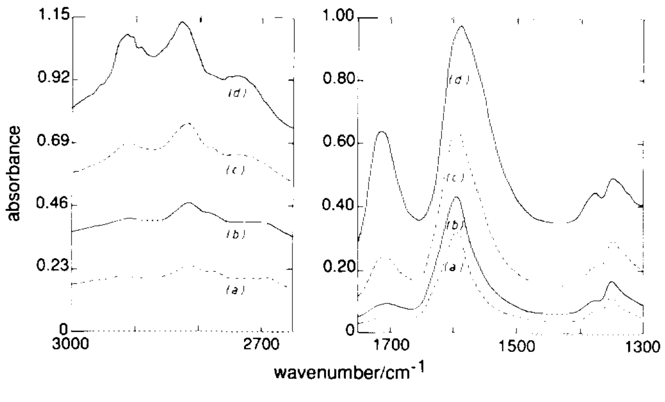


FIG. 3. Spectra of formic acid adsorbed on a potassium/SiO$_2$ catalyst at increasing surface coverages (a)–(d). Spectrum (d) corresponds to an equilibrium formic acid pressure of 0.13 kPa.

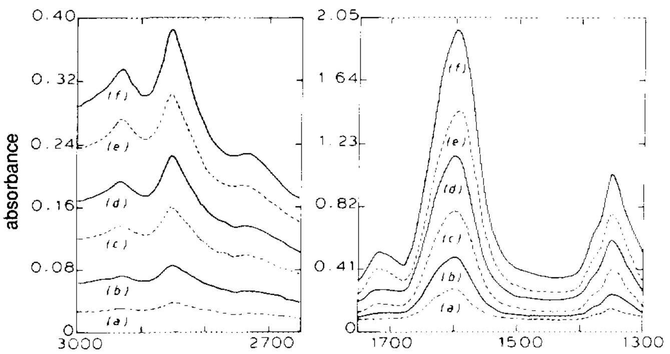


FIG. 4. Spectra of formic acid adsorbed on a reoxidised potassium-promoted Cu/SiO_2 catalyst at increasing surface coverages (a)–(f). Spectrum (f) corresponds to an equilibrium formic acid pressure of 0.13 kPa.

species. It has also been proposed that the peak noted at 2692 cm^{-1} (Fig. 3c) may be a vibration of potassium formate, possibly due to Fermi resonance between ν(CH) and an overtone of the ν_s(COO) mode (12). Remaining maxima at 2923 and 1722 cm^{-1} are ascribed to modes of strongly physisorbed formic acid on potassium/SiO_2 by comparison with previous spectra obtained after exposure of formic acid to silica (13). Bands at 2830 and and 2725 cm^{-1} cannot be clearly assigned; however, they may be due to formic acid molecules physisorbed at different phases of potassium oxide. The weak band at 1696 cm^{-1} for K-doped Cu/SiO_2 (Fig. 1a) but not observed for potassium/SiO_2 (Fig. 3) may be ascribed to adsorbed formic acid molecules ligated to the copper surface (13).

Reexamination of spectra for the copper-containing catalyst (Fig. 1) revealed that bands at 2937 cm^{-1} (which became obscured by a band at 2923 cm^{-1} due to physisorbed formic acid on potassium) and a peak at 2850 cm^{-1} are still unassigned. Exposure of a reduced copper/silica catalyst to formic acid at 300 K produced bands at 2937 [ν_{as}(COO) + δ(CH)], 2857 [ν(CH)], and 1358 [ν_s(COO)] cm^{-1}, ascribed to vibrations of bidentate formate on copper (13). It appears here that addition of formic acid to a potassium-promoted copper catalyst resulted in the formation of formate species on both copper and potassium sites.

Adsorption of Formic Acid on a Reoxidised Catalyst

A potassium-promoted reduced copper catalyst was contacted with nitrous oxide at 348 K in order to reoxidise the copper surface to Cu_2O species. Figure 4 displays spectra resulting from the gradual exposure of formic acid to a reoxidised catalyst at 295 K. Bands due to formate species at 1598, 1377(sh), and 1352 cm^{-1} grew steadily in intensity. The absorbance of these peaks was greater than that of the corresponding maxima for the reduced catalyst, thus suggesting that the quantity of formate species was higher. A shoulder at 1625 cm^{-1} was also observed which was characterisitc of physisorbed water on silica (14). Additionally, bands at 2918 and 1718 cm^{-1}, typical of physisorbed formic acid on potassium/silica, were remarkably less intense than those on the reduced catalyst (Fig. 1). Bands at 2937 and 2850 cm^{-1} which were present on the reduced catalyst (Fig. 1) were not present on the reoxidised catalyst, indicating that bidentate copper formate species were absent. Normally when formic acid is exposed to reoxidised Cu/SiO_2 catalyst, a substantial concentration of unidentate copper formate species are formed (13). However, the most intense band for this species was at ca. 1581 cm^{-1} and as this frequency is very similar to that for potassium formate, it is difficult to identify the presence of this structure unequivocally, although the observed increase in intensity of the maximum at ca. 1598 cm^{-1} is certainly consistent with the presence of copper formate species.

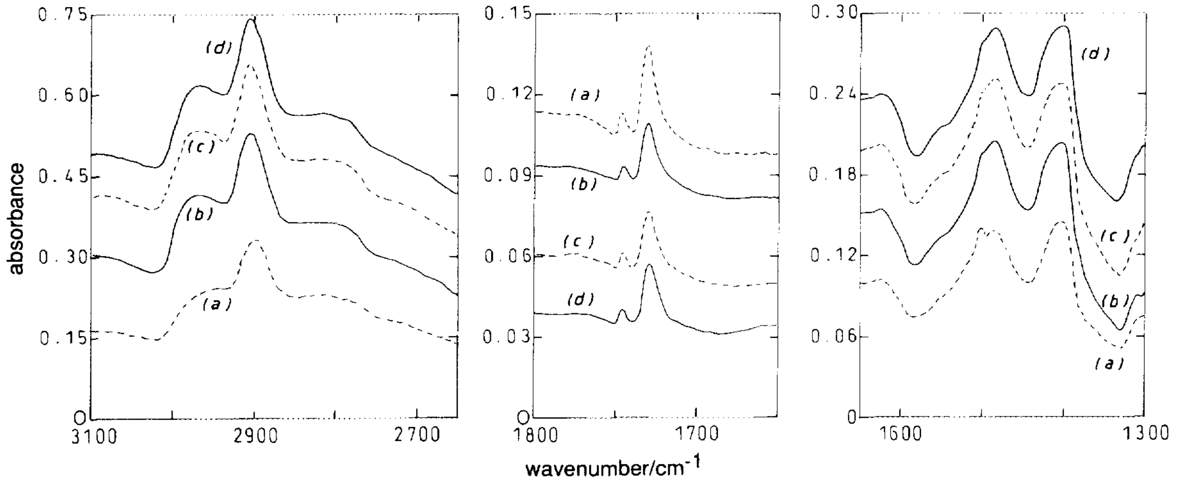


FIG. 5. Spectra of potassium/SiO_2 at 295 K in the presence of formaldehyde (333 Pa) for (a) ca. 45 s, (b) 2 min, (c) 10 min, and (d) 25 min.

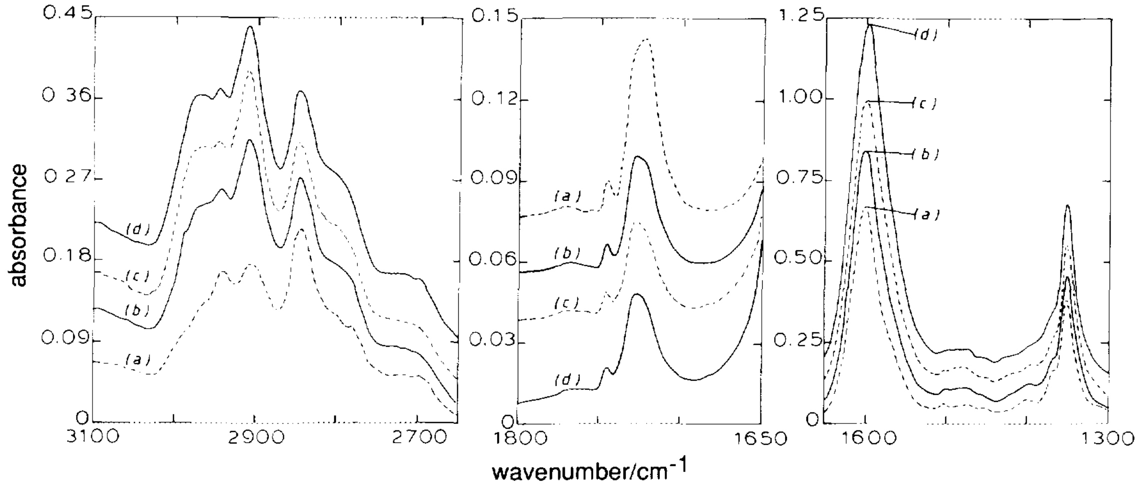


FIG. 6. Spectra of potassium-promoted reduced Cu/SiO$_2$ catalyst at 295 K in the presence of formaldehyde (333 Pa) for (a) 45 s, (b) 105 s, (c) 6 min, and (d) 25 min.

Adsorption of Formaldehyde on a Potassium/Silica Catalyst

Figure 5 displays spectra obtained from a time-dependence study of formaldehyde addition to a potassium/silica catalyst at 295 K. As time elapsed, bands at 2975, 2908, 1485, and ca. 1400 cm^{-1} grew in intensity, and these can be ascribed to vibrations of polymeric formaldehyde species (15). However, there were several differences in the band structure for these species compared to the corresponding polymerisation over silica alone (15). Maxima at 2982 and 1426 cm^{-1} observed on silica diminished substantially on potassium/silica catalyst. As these vibrations are most probably assigned to modes of trioxane or other comparable short-chain structures of polymerised formaldehyde (15), it can be concluded that the presence of potassium increased the molecular weight of the polymers formed.

Concomitant to the formation of polymeric structures, maxima at 1745, 1723, and 1501 cm^{-1} attributable to gaseous and physisorbed formaldehyde were gradually attenuated (16). A broad band at ca. 2807 cm^{-1} also became more pronounced as the reaction time extended; this band can be assigned to polymeric formaldehyde (15).

Adsorption of Formaldehyde on a Reduced Catalyst

Figure 6 displays spectra obtained from a time-dependence study of formaldehyde adsorption on a potassium-doped reduced copper catalyst at 295 K. Initially (Fig. 6a) bands at 2778(sh), 2696(sh), 1600, 1368, and 1351 cm^{-1} appeared which were characteristic of formate species on potassium. The ratio of the intensity of the band at 1600 cm^{-1} to that at 1351 cm^{-1} was smaller than the corresponding ratio of comparable bands due purely to formate species on potassium (Fig. 3). Therefore, the presence of a bidentate formate structure on copper possessing a ν_s(COO)band at ca. 1351 cm^{-1} can be identified (13). This deduction was reinforced by the appearance of bands at 2942 and 2846 cm^{-1} in the CH-stretching region. Maxima due to gaseous formaldehyde at 1745 and 1502 cm^{-1} were also discerned as well as a band at 1723 cm^{-1} which contained a shoulder at 1728 cm^{-1} due to formaldehyde physisorbed on potassium/silica. Only comparatively weak bands attributable to polymerised formaldehyde were detectable at 2980(sh), 2907, 1485, and 1398 cm^{-1}. Increasing the contact time (Fig. 6d) caused all bands to intensify apart from those ascribed to gaseous and physisorbed formaldehyde, which decreased in size.

An important conclusion from this investigation was that the quantity of unidentate formate species formed on potassium dramatically increased in the presence of copper, as compared with the amount produced on the potassium/silica catalyst (Fig. 5).

Adsorption of Formaldehyde on a Reoxidised Catalyst

Figure 7 shows spectra obtained from a time-dependence study of formaldehyde adsorption on a potassium-doped reduced copper catalyst which had first been reoxidised to surface Cu$_2$O species by exposure to N$_2$O at 348 K. Maxima at 2780(sh), 2690, 1598, 1368, and 1353 cm^{-1} attributed to formate on potassium grew in intensity as the contact time was increased. Bands at 2848 and ca. 1353 cm^{-1} due to bidentate formate on copper were less intense than those on the reduced copper surface, as expected from inspection of previous data concerning formic acid exposure to copper/silica catalysts (13). A peak at 2942 cm^{-1}, ascribed to a combination band of bidentate formate (15), was not detected for the oxidised catalyst.

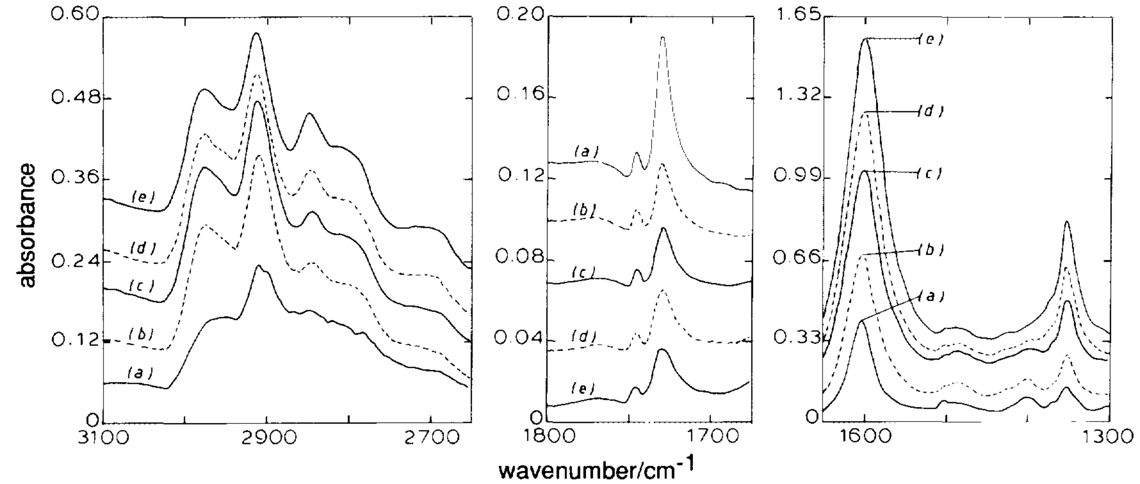


FIG. 7. Spectra of reoxidised potassiusm-promoted Cu/SiO$_2$ catalyst at 295 K in the presence of formaldehyde (333 Pa) for (a) 45 s, (b) 165 s, (c) 8 min, (d) 18 min, and (e) 40 min.

However, the increased absorbance value of the band at 1598 cm^{-1} suggested that a greater amount of formate species was formed, albeit at a slower rate than on the reduced copper surface. The rate of polymerisation of formaldehyde on a reoxidised copper/silica catalyst was also slower than on the comparable reduced catalyst (15). This result suggested that reduced copper was more efficient than oxidised copper sites at weakening the carbonyl bond of formaldehyde, in agreement with previous studies (15).

Bands also appeared at 2976, 2913, 1484, and 1402 cm^{-1} due to polymerised formaldehyde, and peaks at 1746,

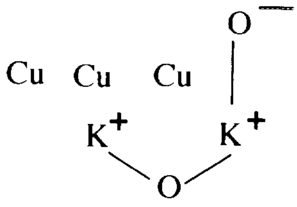
TABLE 1

Infrared Band Positions (in cm^{-1})

Formic acid			Formaldehyde			
K/SiO$_2$	Reduced K/Cu/SiO$_2$	Oxidised K/Cu/SiO$_2$	K/SiO$_2$	Reduced K/Cu/SiO$_2$	Oxidised K/Cu/SiO$_2$	Assignment
2923	2924	2918				Physisorbed HCOOH
1722	1718	1718				
			1745	1745	1746	HCHO(g)
			1501	1502	1503	
			1723	1723	1730	Physisorbed HCHO
			2975	2980	2976	(HCHO)$_n$
			2908	2907	2913	
			2807			
			1485	1485	1484	
			1400	1398	1402	
2776				2778	2780	HCOO$^-$K$^+$
2692				2696	2690	
1597	1597	1598		1600	1598	
1376	1380	1377		1368	1368	
1355	1354	1352		1351	1353	
	2937			2942		Bidentate formate on Cu
	2850			2846	2848	
	1358			*ca*1351	*ca*1353	
		1581(?)				Unidate formate on Cu

1730, and 1503 cm^{-1} caused by gaseous and physisorbed formaldehyde gradually lost intensity as the contact time increased.

Table 1 contains positions and assignments of the main infrared bands described here. Similar tabulations for related studies are given elsewhere (1, 13, 15).



SCHEME 1

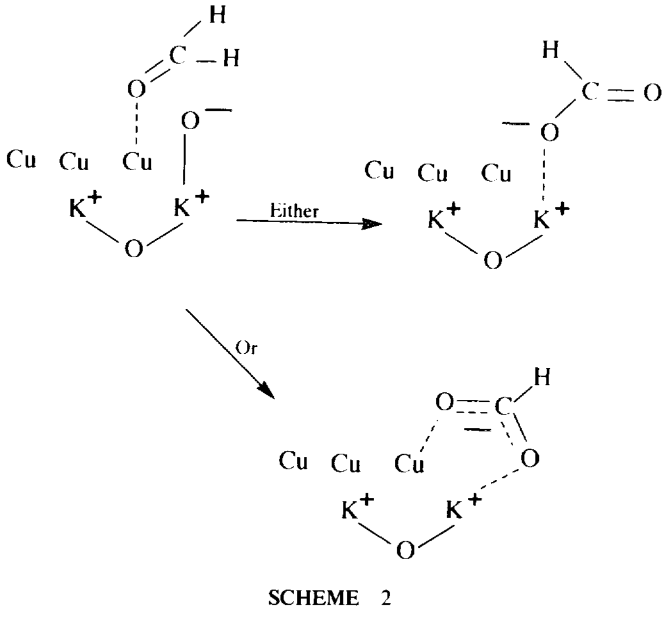
DISCUSSION

Not unexpectedly (17, 18), the exposure of formic acid to potassium/silica catalyst produced potassium formate species (Fig. 3). Furthermore, adsorption of formic acid on potassium-doped reduced copper/silica catalyst (Fig. 1) resulted in the formation of bridging formate species on copper and potassium formate structures. However, a significant difference was noted between these two sets of spectra. The quantity of potassium formate observed in Fig. 1 was remarkably greater than that in Fig. 3. This was curious as it had been shown that the surface area of potassium oxide did not substantially increase in the presence of copper metal (2). Previous studies have suggested that a formate species present on a copper atom at an interfacial site between copper and potassium oxide may either migrate to the potassium oxide component (2) or become bonded to both copper and potassium sites. The latter proposal is the more reasonable explanation of the present data. However, one caveat is that the presence of copper species may have altered the composition of potassium oxide species present in such a way as to favour potassium formate formation, although the nature of this reconstruction is not obvious. Regardless of any ambiguity surrounding the exact reason for the observed increase in formate concentration, it is important to note that the present evidence shows that the catalyst components do not act independently of each other.

Exposure of formic acid to a doped catalyst which had initially been treated with nitrous oxide (Fig. 4) gave an increased quantity of formate species. When formic acid was contacted with a nitrous-oxide-pretreated Cu/SiO$_2$ catalyst at 295 K, unidentate copper formate species were detected (13). These could be identified by their characteristic strong maximum at ca. 1583 cm^{-1}. From Fig. 4 we can deduce that the oxidation treatment did in fact cause a reduction in the concentration of bridging copper formate structures, as evidenced by the attenuation of bands at 2937, 2850, and 1353 cm^{-1}. Since potassium formate and unidentate copper formate both exhibit intense absorption around 1585 cm^{-1} it was not clear if unidentate copper formate species were present, although on the basis of previous data (13) the additional formate formation on reoxidised catalyst can be sensibly assigned to unidentate formate species on copper.

Interaction of formaldehyde with potassium/silica catalyst at 295 K (Fig. 5) only produced polymeric species and a very small quantity of formate species (ca. 1610 cm^{-1}). The addition of copper to this sytem resulted in an extremely large enhancement in the amount of formate species associated with potassium (Fig. 6). One argument is that the increase in formate species may be correlated with a corresponding increase in potassium ion defects which could be perceived as sites capable of producing formate species (19). This does not appear to be appropriate because contacting a metal with a metal oxide normally results in increased oxygen ion vacancies in the oxide structure, and not cation vacancies (20). However, investigations of methyl formate on potassium-promoted copper catalysts (2) have suggested that small islands of copper decorate the potassium oxide surface, and as a consequence, the sites depicted in Scheme 1 were present. If formaldehyde were to adsorb on the copper atom at the interfacial site, its carbonyl bond would be weakened significantly. This activated formaldehyde molecule would then be able to react with adsorbed oxygen on the potassium oxide surface to produce formate species (Scheme 2) either located solely on the potassium component or bonded to both copper and potassium sites.

If the copper adlayer was not present, no reaction between formaldehyde and adsorbed oxygen would occur



SCHEME 2

because of the excessive distance between neighbouring cations on this surface.

Any arguments based on the assumption that copper species extensively modified the morphology of potassium oxide structures present in the system are not supported by the formic acid adsorption studies. Comparison of the spectra in Figs. 1 and 3 does suggest that a small change in the orientation of potassium oxide species may have occurred since slightly more formate species associated with potassium sites were observed than would initially be anticipated. However, the changes detected do not appear substantial enough to explain the dramatic growth of formate species associated with potassium sites when formaldehyde was exposed to a potassium-doped copper catalyst (Fig. 6).

Finally, oxidation of the potassium-doped Cu/SiO_2 catalyst before exposure to formaldehyde (Fig. 7) promoted the enhanced formation of unidentate formate species at the expense of bidentate copper formate, as expected (12). Thus the band at 1598 cm^{-1} due to unidentate formate was more intense for the oxidised (Fig. 7) than for the reduced (Fig. 6) catalyst, whereas bands at 2848 and 2942 cm^{-1} for bidentate formate on copper were weaker for the oxidised catalyst.

In summary, the addition of potassium to a copper catalyst results in some interesting observations. The different components of the catalyst do not always act independently of each other. At the very least, the orientation of potassium oxide structures is modified slightly in the presence of copper. It also appears that adsorption sites could be created at interfacial locations. Furthermore, it is apparent that alkali metals do not act simply as electronic promoters; indeed direct bonding to possible reaction intermediates occurs. Therefore it can be concluded that the system studied here offers potentially important catalytic functions.

ACKNOWLEDGMENTS

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