

An FTIR Study of the Adsorption of Methanol and Methyl Formate on Potassium-Promoted Cu/SiO₂ Catalysts

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FTIR spectra are reported for methanol and methyl formate on silica-supported potassium, potassium-promoted reduced copper/silica, and a potassium-promoted copper/silica catalyst which had been reoxidised by nitrous oxide. Adsorption of methanol on potassium/silica resulted in the formation of methoxy species on potassium. The corresponding adsorption of methanol on potassium-promoted reduced copper/silica catalyst produced copper methoxy groups in addition to K-OMe groups. Reoxidation of the copper component enhanced the quantity of methoxy species formed on copper. The concentration of potassium methoxy species was apparently unaffected. Adsorption of methyl formate on potassium/silica gave formate and methoxy species on potassium. The addition of copper caused a noticeable decrease in the amount of formate and methoxy groups on potassium. Furthermore, bridging formate was detected on the copper surface. Reoxidation of the copper component enhanced the quantity of formate species on potassium. An explanation is given in terms of adsorption of methyl formate at special sites located at the copper/potassium oxide interface. © 1993 Academic Press, Inc.

INTRODUCTION

Recent evidence suggests that the addition of alkali metals to copper-based catalysts can significantly enhance the rates of both methanol synthesis and the water-gas shift reaction (1–6). However, the nature of this promoting effect is not precisely known. Although the adsorption of molecules such as CO and H₂O on alkali-metal doped copper single crystals has been extensively studied (7–14), there have been few investigations of corresponding crystalline copper systems.

The addition of potassium to a polycrystalline copper catalyst causes a pronounced red shift in the vibrational wavenumber of adsorbed carbon monoxide on copper (15). Furthermore, the addition of CO₂ (15), or the interaction of CO and adsorbed oxygen (15), resulted in the formation of two distinct carboxylate structures. One of these was created at a special site located at the interface between copper and potassium oxide.

The adsorption on polycrystalline copper surfaces of more complex molecules asso-

ciated with methanol synthesis, such as formic acid (16), methanol (17), methyl formate (18), and formaldehyde (18), has been characterised previously using FTIR spectroscopy. It is of subsequent interest to examine the effect which potassium addition to polycrystalline copper has on the adsorption of these molecules. The absence of reported studies of these systems has therefore led to the present FTIR study of methyl formate and methanol adsorption on reduced and oxidised potassium-promoted Cu/SiO₂ catalysts.

EXPERIMENTAL

Catalyst preparation has been described in detail elsewhere (15). Briefly, silica (Cab-O-Sil M5, 200 m² g⁻¹) was coimpregnated with an aqueous solution containing copper(II) acetate monohydrate (B.D.H., AnalaR grade) and potassium acetate (B.D.H., AnalaR grade) and subsequently dried in air at 383 K for 5 h. A self-supporting disc was calcined in oxygen (50 cm³ min⁻¹) at 623 K for 1 h, and then reduced at 623 K in hydrogen for 18 h. The reduced

catalyst contained 5 wt% copper plus 29 mol% potassium, calculated as $(100 \times \text{mol K})/(\text{mol Cu} + \text{mol K})$. Reoxidation of the copper component to surface Cu_2O species was achieved using ca. 13 kPa of N_2O (B.D.H., 99.6%) at 348 K for 15 min. Methyl formate (Aldrich, 99%) and methanol (B.D.H., AnalaR grade) were purified by a series of freeze-thaw cycles under vacuum to remove dissolved gases.

A catalyst consisting of potassium and silica was prepared in an analogous manner, the only difference being the omission of copper(II) acetate monohydrate precursor from the initial impregnating solution.

Catalyst discs were at ambient temperature in the spectrometer beam during spectroscopic recording using a Perkin-Elmer 1720X FTIR spectrometer.

The copper surface area in reduced catalyst was $136 \text{ m}^2 \text{ g}^{-1}$ (measured by reactive frontal chromatography involving N_2O adsorption), which corresponds to a Cu^0 particle size of less than about 5 nm diameter. No XRD pattern for Cu crystallites could be detected. The copper surface contained both Cu^0 low index planes and Cu^0 stepped sites (as shown by IR spectra of adsorbed CO (15)), the proportion of stepped sites being 14% of the total (determined by TPD

of CO). A small amount of residual oxygen remained on the copper surface after reduction (15). Potassium existed in the catalyst partially as SiO^-K^+ on the silica surface and partially as potassium oxide (15). The intimacy of the Cu^0 and K_2O in the reduced catalyst was confirmed by the general red shift $\Delta\nu_{\text{CO}}$ in the IR band positions for adsorbed CO induced by the addition of potassium to Cu/SiO_2 catalysts (15).

RESULTS

Adsorption of Methanol on a Potassium/Silica Catalyst

Figure 1(a) displays spectra obtained by dosing methanol at increasing pressures and at 295 K onto a sample disc containing only potassium and silica. It has been proposed that the potassium in the system was present as SiO^-K^+ and K_2O species, an opinion reinforced by the fact that no infrared bands were detected which could be ascribed to KOH or carbonate species (15). Bands developed at 2990(sh), 2954, 2917(sh), 2855, 2834, 1465, 1451, and ca. 1416(sh) cm^{-1} . Evacuation at 295 K (Figs. 1b–1e) resulted in the substantial removal of bands characteristic of methanol weakly adsorbed on silica (17). Maxima remained at 2994, 2958, 2856, and 1468 cm^{-1} which

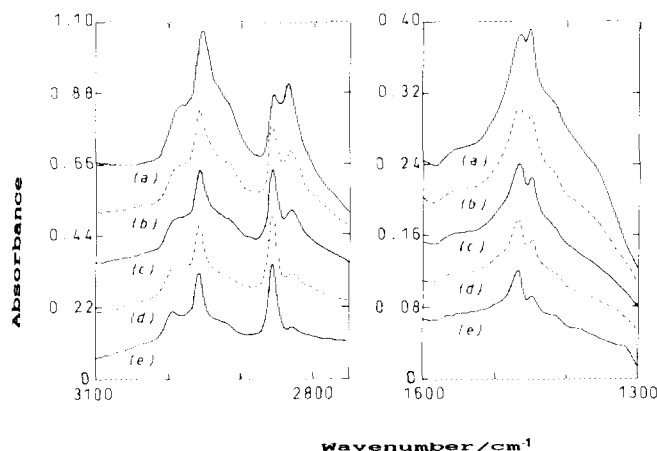


FIG. 1. Spectra of $\text{K}^+/\text{K}_2\text{O}/\text{SiO}_2$ exposed (a–d) to methanol at 295 K at (a) 0.63 kPa, followed by evacuation at 295 K for (b) 0.5, (c) 2, (d) 10, and (e) 40 min.

were typical of both strongly physisorbed methanol on silica and SiOMe species (17). In addition, peaks at ca. 2924, 2830, and 1448 cm⁻¹ were detected. By comparison with band positions for copper methoxy (17) and zinc methoxy groups (19, 20) these peaks were ascribed to vibrations of methoxy groups on potassium. It was also discovered that adsorption of methanol on catalysts containing greater quantities of potassium resulted in a significant shift of these vibrational frequencies to lower wavenumbers.

Adsorption of Methanol on a Reduced Cu/K₂O/SiO₂ Catalyst

A potassium-promoted reduced copper/silica catalyst was gradually exposed to methanol vapour at 295 K. The spectra obtained are shown in Fig. 2a. Maxima were observed at 2988(sh), 2952, 2917(sh), 2853, 2834, ca. 1625, 1463(sh), 1451, and 1413(sh). Following evacuation at 295 K (Figs. 2b–2e) bands were still evident at 2991, 2958, 2889, 2857, and 1466 cm⁻¹ which were attributed to a mixture of strongly physisorbed molecular methanol on silica and SiOMe groups (17). Furthermore peaks at 2922 and 2810 cm⁻¹ could be ascribed to the presence of methoxy groups on copper (17), and bands at 2833 and 1448

cm⁻¹ to vibrations of potassium methoxy species. Bands at 2922 and 1448 cm⁻¹ probably contain a contribution from both copper and potassium methoxy groups. Finally, maxima at 1670 and 1332 cm⁻¹ were comparable to bands obtained when CO was adsorbed on a potassium/silica catalyst (15). A few methoxy species had apparently decomposed to CO and H₂.

Adsorption of Methanol on a Reoxidised Cu/K₂O/SiO₂ Catalyst

Spectra in Fig. 3a resulted from addition of methanol to a potassium-promoted reduced copper catalyst, which had first been wholly reoxidised to surface Cu₂O species by contact with N₂O at 348 K. Infrared bands appeared at 2988, 2952, 2921(sh), 2853, 2834, 1620, 1463, 1451, and 1414(sh) cm⁻¹. The existence of a band at 1620 cm⁻¹ was indicative of molecular water physisorbed on silica (21). Upon evacuation at 295 K (Figs. 3b–3e) bands were still present at 2993, 2958, 2895(sh), 2857, 1466 cm⁻¹, all due to SiOMe groups and strongly physisorbed molecular methanol (17). Maxima at 2925 and 2814 cm⁻¹ typical of methoxy groups on potassium and copper were clearly more intense on the reoxidised catalyst relative to the reduced surface. This promoting effect by adsorbed oxygen on

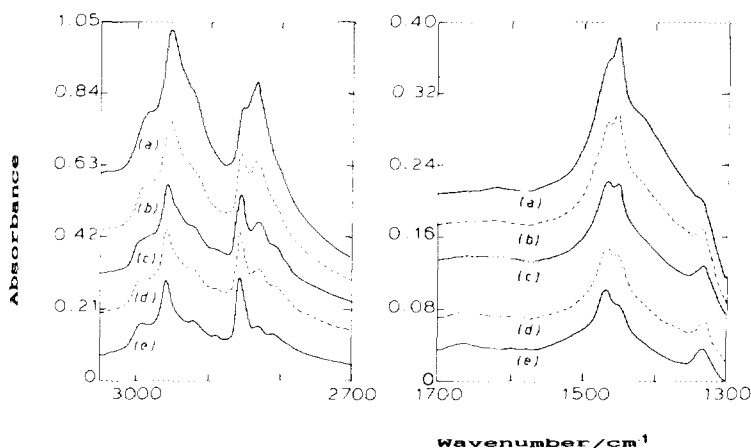


FIG. 2. Spectra of a potassium-promoted reduced Cu/SiO₂ catalyst exposed to methanol at 295 K at (a) 0.63 kPa, followed by evacuation at 295 K for (b) 0.5, (c) 2, (d) 5, and (e) 20 min.

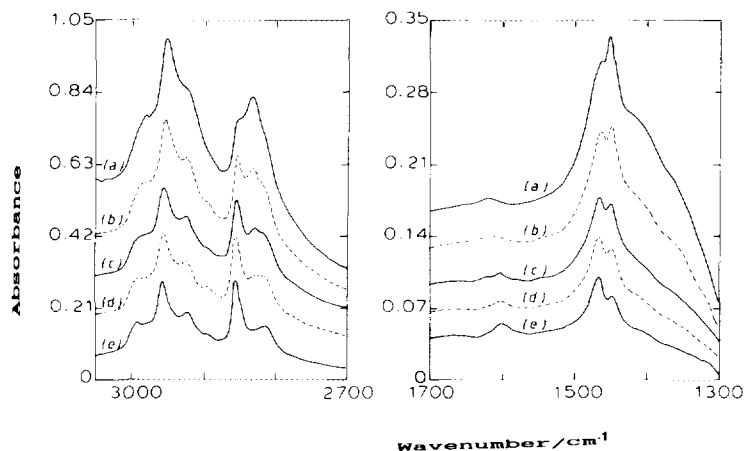


FIG. 3. Spectra of a nitrous oxide pretreated potassium-promoted Cu/SiO_2 catalyst exposed to methanol at 295 K at (a) 0.63 kPa, followed by evacuation at 295 K for (b) 0.5, (c) 2, (d) 5, and (e) 20 min.

methanol adsorption has been suggested by several authors (17, 22, 23). When methanol was exposed to a potassium/silica catalyst which had first been pretreated with nitrous oxide, spectra identical to those displayed in Fig. 1 were obtained (24). Therefore it can be concluded that the additional methoxy species detected on reoxidised $\text{Cu}/\text{K}_2\text{O}/\text{SiO}_2$ catalyst were formed on the copper component.

The interaction of formic acid with a potassium/silica catalyst produced a maximum at ca. 1600 cm^{-1} , which was assigned

to a vibration of unidentate formate on potassium (25). Consequently the presence of a band at 1603 cm^{-1} in this study implied that a small quantity of methoxy groups had been oxidised to give unidentate formate.

Adsorption of Methyl Formate on Potassium/Silica

Figure 4 shows spectra resulting from the addition of methyl formate at increasing pressures to a potassium/silica catalyst at 295 K. Bands which appeared at 3041, 3013, 2963, 2946(sh), 2899(sh), 2856, ca.

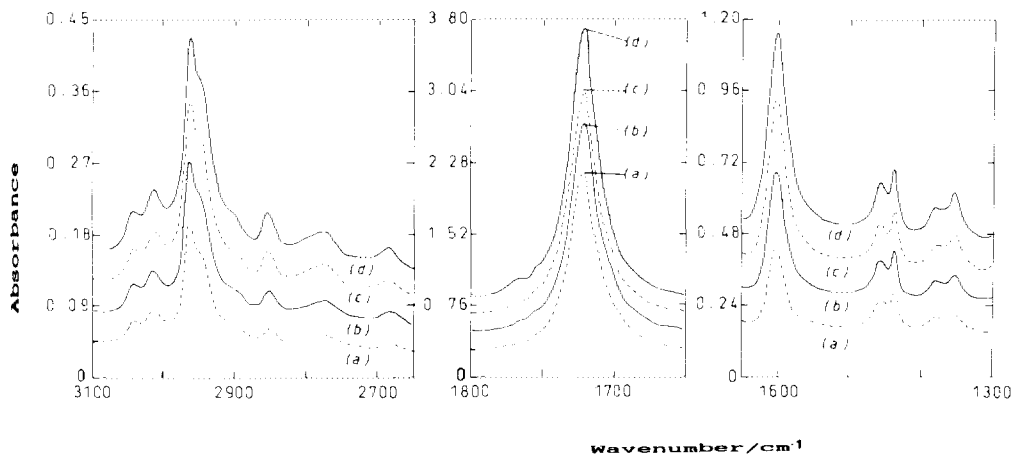


FIG. 4. Spectra of $\text{K}^+/\text{K}_2\text{O}/\text{SiO}_2$ exposed (a-d) to increasing pressures of methyl formate at 295 K up to (d) 0.4 kPa.

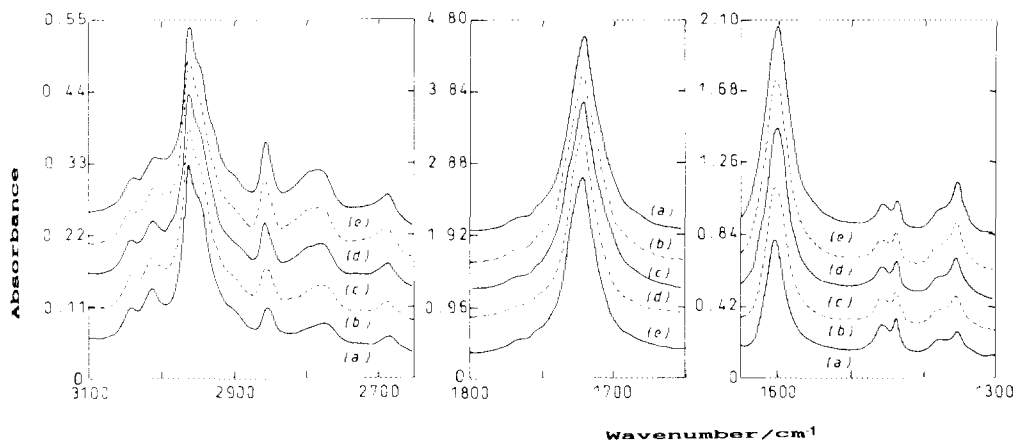


FIG. 5. Spectra obtained by leaving K⁺/K₂O/SiO₂ in contact with methyl formate (0.5 kPa) at 295 K for (a) 1, (b) 5, (c) 15, (d) 30, and (e) 50 min.

1721, 1457, 1437, and 1381 cm⁻¹ resembled those due to physisorbed methyl formate on silica (18). However, the intensities of these peaks for potassium/silica were clearly greater than those noted for methyl formate on silica alone, even though the addition of potassium reduced the number of SiOH groups available for hydrogen bonding with weakly adsorbed molecules (15). This implies that nondissociative adsorption of methyl formate must also have occurred on the potassium component of the system. Bands attributed to gaseous methyl formate were also detected at 1765 and 1753

cm⁻¹ (18). Maxima which were discerned at 2776, 2685, 1601, and 1354 cm⁻¹ were characteristic of unidentate formate species on potassium (25).

Methyl formate was allowed to remain in contact with the catalyst at 295 K for an extended period of time. Bands associated with physisorbed methyl formate diminished in intensity and concomitant to this, peaks at 2858, 2775, 2688, 1600, and 1354 cm⁻¹ developed significantly (Fig. 5). A shoulder was also detected at ca. 2930 cm⁻¹

Evacuation at 295 K (Fig. 6) removed all maxima attributed to physisorbed methyl

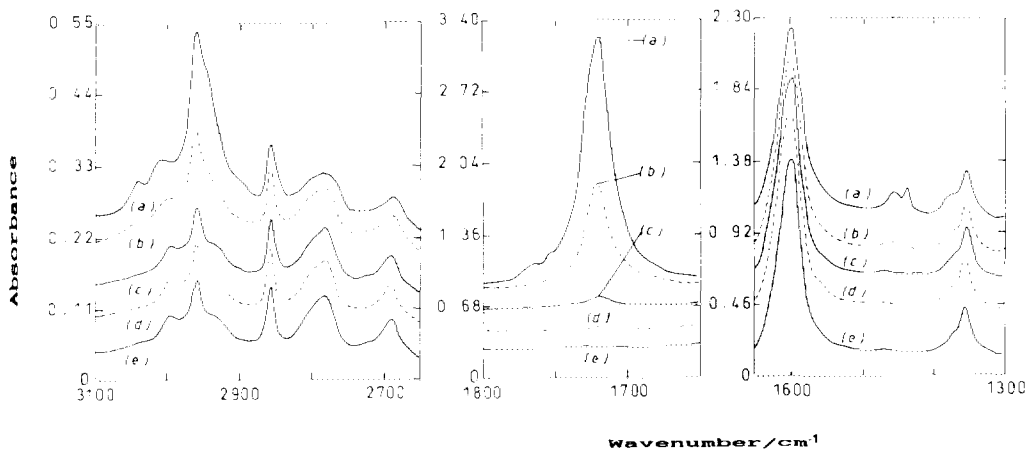


FIG. 6. (a) Same as Fig. 5d followed by evacuation at 295 K for (b) 0.5, (c) 5, (d) 10, and (e) 40 min.

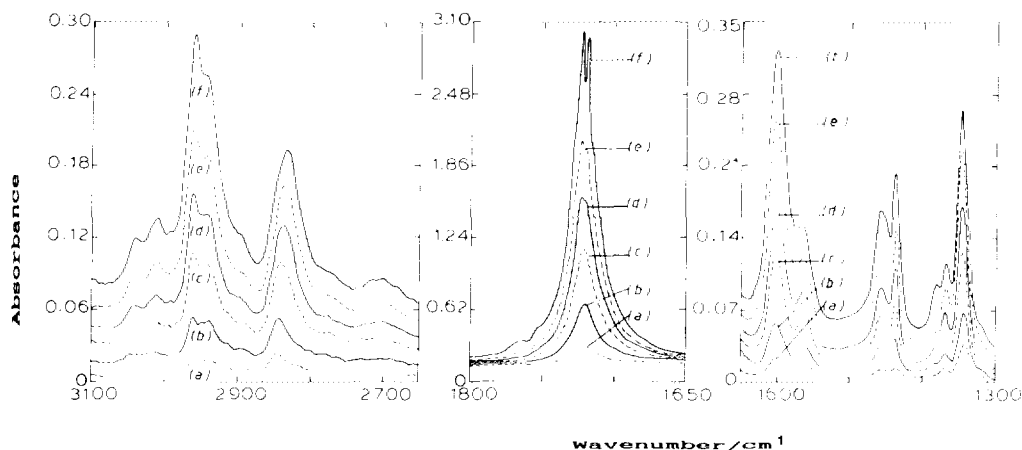


Fig. 7. Spectra of a potassium-promoted reduced Cu/SiO_2 catalyst exposed to increasing pressures of methyl formate at 295 K up to (f) 0.4 kPa.

formate. Bands were noted at 2782, 2691, 1598, 1370(sh), and 1355 cm^{-1} which were typical of unidentate formate species on potassium (25). Furthermore, peaks were present at 2996, 2960, 2859 and 1465 cm^{-1} which were characteristic of strongly physisorbed molecular methanol on silica (17). The remaining shoulder at 2931 cm^{-1} was similar to a band at 2924 cm^{-1} (Fig. 1e) which was ascribed to a vibration of potassium methoxy species.

Adsorption of Methyl Formate on Reduced $\text{Cu}/\text{K}_2\text{O}/\text{SiO}_2$

Figure 7 shows spectra obtained by dosing methyl formate onto a potassium-promoted reduced copper catalyst at 295 K. Bands were again discerned at 3041, 3010, 2961, 2944(sh), ca. 1721, 1457, 1437, and 1380 cm^{-1} characteristic of methyl formate physisorbed on potassium and silica. Weak bands at 1766 and 1753 cm^{-1} due to gaseous methyl formate (18) were also visible. Maxima at 2833, 1567, and 1347 cm^{-1} are ascribed to bridging formate species on copper (16).

When methyl formate was left in contact with a potassium-promoted reduced copper catalyst at 295 K (Fig. 8), bands at 2778(sh), 2687, 1599, 1367(sh), and 1352 cm^{-1} due to

unidentate formate on potassium (25) increased in intensity. Furthermore, peaks at 2995, 2951, and 2855 cm^{-1} attributed to methoxy groups on silica (17) and strongly physisorbed methanol (17) also intensified. A peak at 2926 cm^{-1} and a shoulder at 2842 cm^{-1} both grew in size; this represented production of methoxy (17) and bidentate formate (16) species on copper, respectively. Concomitant with this there was considerable attenuation of a band at 1720 cm^{-1} , ascribed to physisorbed methyl formate.

After evacuation (Fig. 9) bands remained at 2779(sh), 2691, 1599, 1368(sh), and 1351 cm^{-1} which were attributed to unidentate potassium formate (25). Peaks were also evident at 2995, 2959, and 2854 cm^{-1} which were characteristic of strongly physisorbed methanol and SiOMe groups (17). The identification of bridging formate on copper (16) was inferred from the presence of bands at 2938(sh), 2843, and 1560 cm^{-1} and a peak at ca. 1351 cm^{-1} which was superimposed upon a similar maximum assigned to a vibration of unidentate formate on potassium. As discussed previously (16), the appearance of the shoulder at 1560 cm^{-1} , due to the $\nu_{\text{as}}(\text{COO})$ vibration of bidentate copper formate, which is normally

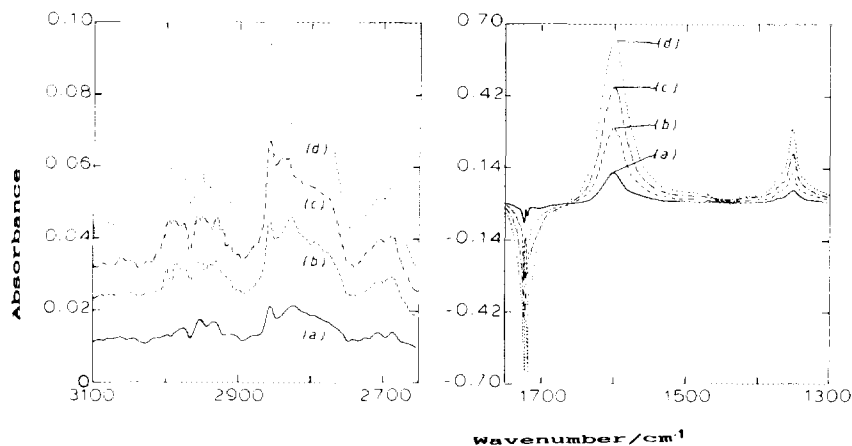


FIG. 8. Changes induced in Fig. 7f induced by leaving methyl formate (0.4 kPa) in contact with potassium-promoted reduced Cu/SiO₂ catalyst at 295 K for (a) 3, (b) 10, (c) 22, and (d) 50 min.

a forbidden infrared vibration, was present as a result of the "surface roughness" of the copper catalyst.

Adsorption of Methyl Formate on a Reoxidised Cu/K₂O/SiO₂ Catalyst

Methyl formate was contacted with a potassium-promoted reduced copper catalyst which had first been reoxidised to surface Cu₂O species by exposure to N₂O at 348 K. Bands developed at 3040, 3010, 2961,

1945(sh), 2855(sh), 1721, 1457, 1437, and 1380(sh) cm⁻¹ due to methyl formate physisorbed to potassium and silica (Fig. 10). A shoulder was observed at 2825 cm⁻¹ which could be assigned to methoxy groups on either copper (17) or potassium. Furthermore peaks were apparent at 2773(sh), 2683, 1601, 1366(sh), and 1352 cm⁻¹ typical of unidentate formate species on potassium (25). A shoulder at 1570 cm⁻¹ was also noted and this was similar to a peak at 1583

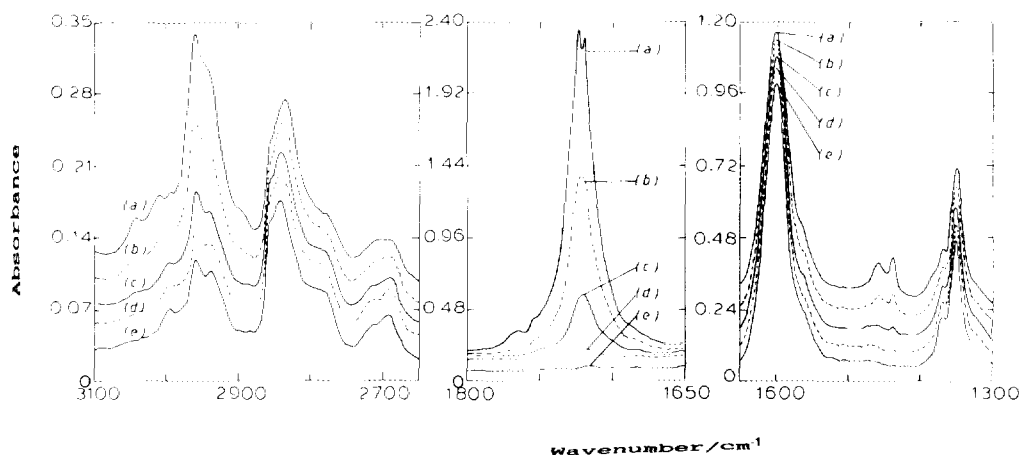


FIG. 9. (a) Spectrum after methyl formate (0.4 kPa) was left in contact with catalyst for 50 min at 295 K followed by evacuation at 295 K for (b) 0.5, (c) 2, (d) 10, and (e) 20 min.

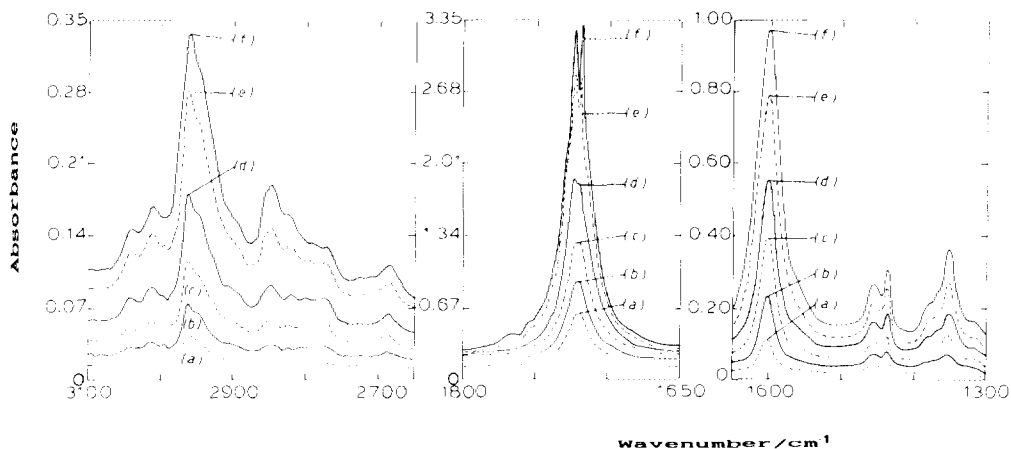


FIG. 10. Spectra of a nitrous oxide pretreated potassium-promoted Cu/SiO_2 catalyst exposed (a-f) to increasing pressures of methyl formate up to (f) 0.5 kPa.

cm^{-1} assigned to a unidentate formate species on copper (16). However, an important aspect of this study was the relative weak intensity of this band, in relation to the comparable study of methyl formate interaction with a reoxidised Cu/SiO_2 catalyst.

Following evacuation at 295 K (Fig. 11) maxima remained at 2780, 2691, 1599, 1367(sh), and 1353 cm^{-1} due to unidentate

formate on potassium (25). In addition bands at 2997, 2959, 2891(sh), and 2856 cm^{-1} ascribed to SiOMe groups and strongly physisorbed methanol were detected. A peak at $2933(\text{sh}) \text{ cm}^{-1}$ due to a combination band of bridging copper formate (16) and a shoulder at 2906 cm^{-1} tentatively ascribed to a vibrational mode of unidentate formate on copper (16) were also present.

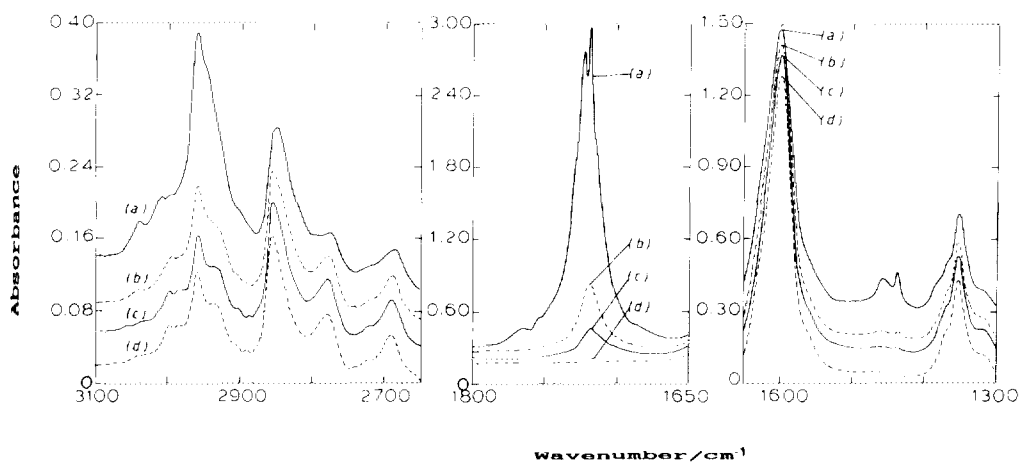


FIG. 11. (a) Spectrum after a nitrous oxide pretreated potassium-promoted Cu/SiO_2 catalyst was left with methyl formate (0.5 kPa) at 295 K for 50 min followed by evacuation at 295 K for (b) 2, (c) 5, and (d) 20 min.

DISCUSSION

Berkó *et al.* (26) concluded from a combined TPD and UPS study of methanol adsorption on a potassium-doped Rh(111) single crystal that potassium methoxide species were formed. The EELS spectra presented by DePaola *et al.* (27) for methanol interaction with a potassium-promoted Ru(001) surface appeared to support the hypothesis for potassium methoxide formation. The assignment of bands at 2924, 2830, and 1448 cm⁻¹ (Fig. 1e) to methoxy groups on potassium oxide was therefore plausible. This deduction was given credence by the fact that upon an increase in the quantity of potassium in the system, the frequencies shifted to lower wavenumbers. This was consistent with the methoxy species on potassium oxide being anionic in nature. Hence this should give CH₃-stretching vibrations at wavenumbers much lower than those of species such as CuOMe. An important aspect of this study was that the vibrational frequency detected was highly dependent upon the quantity of potassium present.

On reduced Cu/K₂O/SiO₂, the frequencies of the CH-stretching vibrations for copper methoxy species were shifted to lower wavenumber by ca. 5 cm⁻¹ relative to unpromoted Cu/SiO₂ catalyst. A possible explanation was in terms of charge transfer from methoxy groups on copper to potassium ions in the near vicinity. Similar behaviour was observed when CO was adsorbed on a potassium-promoted copper/silica catalyst (15).

The enhancement in the concentration of methoxy species formed on copper, observed when methanol was exposed to reoxidised Cu/K₂O/SiO₂ catalyst, was in agreement with previous investigations (17, 22, 23). Preadsorbed oxygen on the copper component promotes the removal of hydroxyl protons from methanol molecules and hence increases the quantity of methoxy groups produced. An optimum surface coverage of 0.5 oxygen monolayers

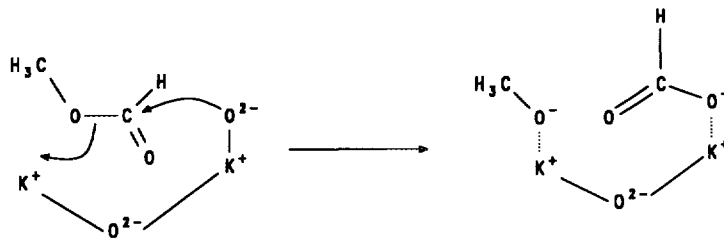


SCHEME 1

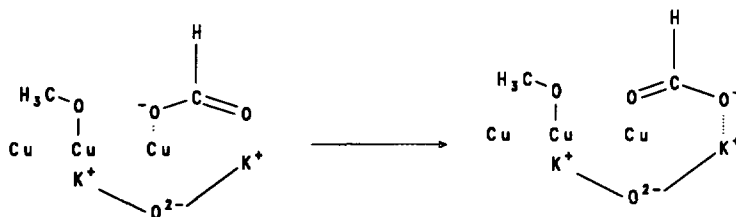
has been deduced (28). This implied that the mode of adsorption involved methanol initially ligating to a copper metal site adjacent to an adsorbed oxygen species. Subsequent nucleophilic attack by oxygen removed the hydroxyl proton to give methoxy and hydroxyl species on copper (Scheme 1).

Methyl formate interacted with potassium oxide/silica catalyst (Fig. 6) to produce unidentate formate and methoxy structures on potassium oxide in addition to strongly physisorbed methanol and SiOMe groups on silica. The detection of the latter species on silica suggests that a quantity of the methoxy groups on potassium oxide were destabilised to such an extent that they recombined with adsorbed hydrogen (present either on the silica surface, in the form of hydroxyl groups, or possibly in the potassium oxide lattice) to give molecular methanol. This effect has also been observed on ZnO-based catalysts (29). It is proposed that the mechanism of methyl formate interaction with a potassium oxide surface can be represented by Scheme 2.

The same reaction on a potassium-promoted reduced copper/silica catalyst interestingly produced a diminished quantity of formate species on the potassium component. The absorbance of the band at ca. 1599 cm⁻¹ ascribed to a vibration of unidentate potassium formate was 0.93 units (Fig. 9) compared to 1.26 units for potassium/silica catalyst (Fig. 6). Similar behaviour was noted when methyl formate interacted with ZnO/SiO₂ and reduced Cu/ZnO/SiO₂ catalyst (29). This was attributed to the presence of small copper clusters on the zinc oxide surface which blocked the active site for methyl formate adsorption. Therefore it appears appropriate to infer that a similar effect occurred in the present system.



SCHEME 2



SCHEME 3

Reaction of methyl formate with a catalyst in which the copper surface had been reoxidised produced an enhanced quantity of formate species on potassium oxide, relative to a potassium-promoted reduced copper catalyst (1.25 compared to 0.93 absorbance units). The interaction of methyl formate with a catalyst surface to give formate and methoxy species required an adsorbed oxygen moiety on the surface (18). Therefore, increasing the oxygen coverage on a copper surface would favour the formation of these structures. However, nitrous oxide treatment did not oxidise potassium oxide; hence formate species may have migrated from the copper component to the potassium oxide surface. When methyl formate reacts with an oxidised copper surface, unidentate copper formate species are initially formed. It is proposed that if these were located on a copper atom at an interfacial site between copper and potassium oxide, the migration of this structure to potassium oxide was possible (Scheme 3).

CONCLUSIONS

(a) The adsorption of methanol on potassium-promoted Cu/SiO_2 leads to the forma-

tion of methoxy groups ligated to potassium and also of methoxy groups ligated to copper. Partial oxidation of reduced copper promotes proton transfer from methanol molecules to surface oxygen anions and hence also enhances the formation of adsorbed methoxy groups on copper.

(b) Methyl formate adsorbs on silica-supported potassium oxide to give SiOMe groups on silica and unidentate formate, methoxy groups and methanol molecules on potassium oxide. The formation of the formate and methoxy groups ligated to K^+ sites required the involvement of a surface oxide anion for each methyl formate molecule.

(c) The adsorption of methyl formate on potassium oxide was partially inhibited by the presence of copper, suggesting that the dispersed potassium oxide surface may have been decorated with small site-blocking clusters of copper atoms.

(d) Partial preoxidation of $\text{Cu}/\text{K}_2\text{O}/\text{SiO}_2$ allows reaction between methyl formate and oxide sites on copper. This leads to formate species which spill over to the potassium oxide catalyst component, possibly via the involvement of junction sites be-

tween exposed potassium oxide and islands of oxidised copper.

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