JOURNAL OF CATALYSIS **100,** 17–27 (1986)

Hydrogenolysis of Methyl Formate over Copper on Silica

I. Study of Surface Species by *in Situ* Infrared Spectroscopy

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Received July 9, 1985; revised January 6, 1986

The hydrogenolysis of methyl formate to methanol over silica-supported copper has been studied using *in situ* infrared spectroscopy coupled with simultaneous determination of rate. Under flow reaction conditions two forms of adsorbed methyl formate exist. One has a carbonyl absorption at 1726 cm^{-1} and is bound to the support by hydrogen bonding with a heat of adsorption of 65 kJ mol^{-1}. The second absorbs at 1666 cm^{-1} and is bound to copper with an approximate heat of adsorption of 140 kJ mol^{-1}. At 457 K the hydrogenolysis rate is directly proportional to the band intensity of the latter and hence it, or another species in equilibrium with it, is involved in the rate-determining step. Adsorption of CO from CO/H_2 mixtures gives rise to a single infrared band at 2117 cm^{-1}, the corresponding heat of adsorption being 60 kJ mol^{-1}. Competitive measurements under hydrogenolysis conditions show that methyl formate will partially displace adsorbed CO and not vice versa. Nonetheless CO does reversibly inhibit the rate and this is attributed to its adsorption displacing hydrogen from the surface. The lower concentration of surface hydrogen also reduces the rate of hydrogenation of a formaldehyde intermediate leading to its deposition as a polymer as revealed by infrared bands at 1483 and 1375 cm^{-1}. The same polymer accretes more rapidly during the reverse methanol to methyl formate reaction for which CO is a substantial by-product and hydrogen pressures are much lower than used for hydrogenolysis. Continuous deactivation of the catalyst is then observed.

INTRODUCTION

Copper-based catalysts have been identified as outstandingly effective for the hydrogenolysis of aliphatic esters to the corresponding alcohols (*1*). Among the copper catalysts, copper chromite is widely used (*2*), but Raney copper and various supported copper catalysts have also been considered (*3*). Catalyst stability is good with acetates (*3*) and higher formates (*4*).

Only recently, the hydrogenolysis of methyl formate $CH_3OCHO + 2H_2 \rightarrow 2CH_3OH$ has been reinvestigated (*4*) because of its importance in a long-known two-stage production route for methanol (*5, 6*). This process comprises the carbonylation of methanol to methyl formate as a first stage followed by the hydrogenolysis of this compound, to double the amount of methanol, in a second stage. It has been claimed that substantial energy savings could be achieved if this route proved to be feasible (*7, 8*). Studies of the hydrogenolysis of methyl formate in the gas phase over a variety of copper-based catalysts, including Raney copper and copper chromite, resulted in significant catalyst deactivation (*8*). Similar behavior is known for the reverse dehydrogenation of methanol to methyl formate (*9, 10*) and is particularly pronounced with Raney copper (*9*). In that case it was argued that the formation of polymers of formaldehyde was facilitated by the continuous copper surface whereas well-dispersed copper would not be so affected.

In recent work (*11*) we have shown that finely dispersed copper on silica, prepared by ion exchange, shows no signs of deactivation for methyl formate hydrogenolysis. Sodesawa (*10*) has also reported good stability for methanol dehydrogenation over a

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similar catalyst. In our work (*11*) deactivation occurred only if substantial additional carbon monoxide was included in the feed stream and it was suggested that stable activity might be characteristic of catalysts which minimize formation of this by-product which originates by decarbonylation of methyl formate $CH_3OCHO \rightarrow CH_3OH + CO$ (*2*).

In this work we have used infrared spectroscopy to identify surface species adsorbed on copper on silica under conditions of methyl formate hydrogenolysis and methanol dehydrogenation. Particular attention has been paid to species forming under actual reaction conditions with carbon monoxide present.

EXPERIMENTAL

The copper catalyst was prepared by ion exchange of an aerosil-type silica (Aerosil 200, Degussa AG) following the procedure described by Kobayashi *et al.* (*12*). The details of the preparation method have been reported elsewhere (*11*). Some properties of the reduced catalyst are: BET surface area by nitrogen adsorption: 190 m^2/g; copper content by atomic absorption spectroscopy: 6.6 wt%; apparent copper surface area by nitrous oxide decomposition using a pulse chromatographic method (*13*): 5 m^2/g. The corresponding particle size would be 8.8 nm if uniform spheres are assumed. Blank experiments were carried out using a sample of the support material which had been subjected to a procedure similar to the one used for the preparation of the catalyst but omitting copper. Samples of each were finely ground and pressed into 3.2-cm-diameter pellets using a pressure of 60 MPa for 5 min. Disks of 1.9 cm diameter weighing about 65 mg were cut from each pellet. The catalyst disks were pressed from material prereduced at 570 K and further reduced in the infrared cell at 520 K.

The infrared cell/flow reactor was identical to that described by Hicks *et al.* (*14*). Its optical path length between the windows was 2.4 mm with an internal cell volume of 0.4 cm^3. Because of this low value, residence times of 1 s or less could be achieved even with flow rates as low as 25 cm^3 min^{-1}. The temperature of the cell was maintained constant to within ±0.5 K by a temperature controller connected to the thermocouple located inside the reactor.

The cell/reactor was connected to a supply system comprising calibrated rotameters for high-purity H_2, He and a mixture of 20% CO in H_2 (CIG, Australia) and three saturators containing methyl formate, methanol (Ajax Chemicals Co.), and methanol-d_4 (Merck, Sharp & Dohme, Canada). These were maintained in ice baths at 273 K. The feed stream from the supply system was directed to the inlet sample loop of a heated Valco 10-port valve, to the reactor, and then back to a matched product sample loop of the same valve. This arrangement allowed alternate injections of the feed and product streams into an on-line gas chromatograph (Packard, Model 427, United Technologies Inc.) and an easy determination of changes in composition of the inlet and outlet gas streams.

Separation of the carbon monoxide (CO), methanol (MeOH), and methyl formate (MeF) was performed on a 2 m × 6 mm o.d. column of Porapak N maintained at 420 K. Hydrogen was used as carrier gas at a flow rate of 50 cm^3/min when the hydrogenolysis of methyl formate was investigated. In the cases where methanol was fed as a reactant, He at the same flow rate was used instead.

Infrared spectra were recorded with a Perkin–Elmer Model 580 ratio-recording spectrometer operated with a spectral slitwidth of 3.5 cm^{-1} which was sufficiently small to avoid bandshape distortion. The spectrometer was linked to a Perkin–Elmer Model 3600 infrared data station which enabled the acquisition and storage of digitized spectra and data processing. Background spectra corresponding to cell alone, cell plus flow streams of various compositions, and cell plus gas phase plus support (SiO_2) disk were recorded. These spectra with appropriate multiplication factors were subtracted from spectra of catalyst disks under reaction conditions as required to reveal features characteristic of adsorbed species on the copper. With appropriate scaling and smoothing, bands with absorbances of 0.01 or less could be investigated with considerable confidence.

The catalyst samples had maximum transmissions of 30–35% in the 2200- to 2100-cm^{-1} region. Transmission at low frequencies was limited by the strong absorption of the silica and the CaF_2 windows of the cell and no measurements were possible below 1300 cm^{-1}.

RESULTS AND DISCUSSION

A. Interaction of Methyl Formate with Cu/SiO_2 under Hydrogenolysis Conditions

The hydrogenolysis of methyl formate to methanol was studied at three temperatures (429, 447, 457 K) and four inlet partial pressures (3.5, 6.2, 9.4, 14.5 kPa) of methyl formate at each temperature using hydrogen to balance the total pressure to 101 kPa.

The following stoichiometric equations describe the reactions occurring in the system

$$CH_3OCHO + 2H_2 \rightarrow 2CH_3OH \quad (1)$$

$$CH_3OCHO \rightarrow CH_3OH + CO \quad (2)$$

Methyl formate conversion never exceeded 10% and the rates of reaction (r_A) were computed assuming

$$r_A = \frac{F_A^0 X}{W}$$

for a differential reactor (F_A^0, molar feed rate of MeF; W, mass of catalyst; X, conversion of MeF). At these low conversions, only traces of CO and CO_2 could be analysed in the product stream and the selectivity to methanol was always better than 95%.

Figure 1 shows the spectra of the catalyst after reduction in hydrogen (a) and under hydrogenolysis conditions (b). A summary of assignments is given in Table 1. Prominent differences include CH stretching and bending modes near 3000 and 1460 cm^{-1} and several carbonyl absorption bands near 1700 cm^{-1}. The former arise partly from physically adsorbed methyl formate and product methanol but are predominantly due to Si—O—CH_3 groups. Bands due to these groups increased steadily with time on stream but tended to a limiting value. They could not be removed by treatment in hydrogen at 230°C. They may be due to reaction of methanol with a limited number of strained siloxane linkages as described by Borello *et al.* (*15*).

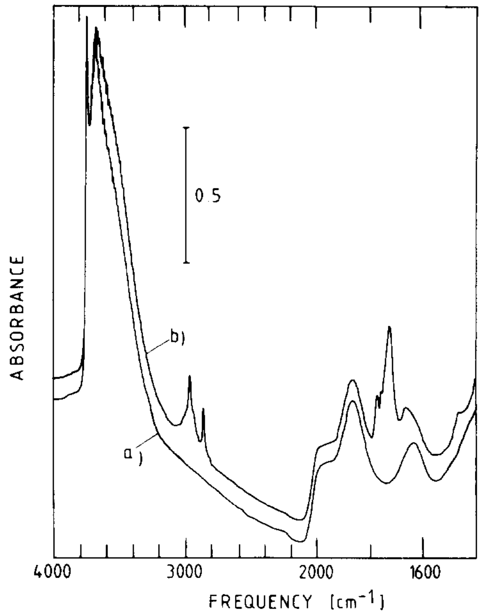

FIG. 1. Spectra of Cu/SiO_2 catalyst at 447 K. (a) After reduction (hydrogen, 101 kPa) and (b) under hydrogenolysis conditions (methyl formate, 13.0 kPa; methanol, 1.4 kPa; CO, 0.1 kPa; H_2, 85.5 kPa).

Features in the region 2000 to 1300 cm^{-1} were better revealed following subtraction of the background Si—O overtone at 1638 cm^{-1} and the combination modes at 1868 and 1975 cm^{-1} (shoulder). Figure 2 shows the resulting spectra for several methyl formate pressures. The contour comprising the peaks at 1766, 1754, and the shoulder at 1744 cm^{-1} is due to gas phase methyl formate in accordance with data of Wilmhurst

TABLE 1

Assignment of the Infrared Bands of Cu/SiO$_2$ under Hydrogenolysis Conditions

Frequency (cm^{-1})	Assignment	Species
3738	OH stretch	SiO—H
3650	OH stretch	SiO—H...OSi
2960	CH$_3$ asymmetric stretch	SiOCH$_3$
2859	CH$_3$ symmetric stretch	SiOCH$_3$
1769 1755	C=O stretch	CH$_3$OCHO(gas)
1726	C=O stretch	SiOH...O=C(H)(OCH$_3$)
1666	C=O stretch	Cu...O=C(H)(OCH$_3$)
1463	C—H bend	SiOCH$_3$

(*16*). Features due to adsorbed species comprise a strong band at 1726 cm^{-1} and a weaker one at 1666 cm^{-1}. The former was also observed when the gas stream was passed over a disk of silica alone and can be attributed to methyl formate molecules hydrogen-bonded to surface SiOH groups in a manner similar to that found for adsorbed acetone by Young and Sheppard (*17*).

Figure 3 compares spectra of SiO$_2$ and Cu/SiO$_2$ disks in the presence of similar methyl formate pressures after subtraction of Si—O and gas phase methyl formate bands. The band due to physically adsorbed methyl formate is identical in the two cases except for a slightly lower frequency for Cu/SiO$_2$ (1726 cm^{-1} versus 1730 cm^{-1} for SiO$_2$ alone). The band at 1666 cm^{-1} with Cu/SiO$_2$ alone clearly arises from a species present on the surface of the copper component of the catalyst under reaction conditions. The most likely assignment is to the C=O vibration of intact methyl formate molecules bound to a surface copper atom via the carbonyl group. This is in accord with recent EELS observations by Sexton *et al.* (*18*) of a peak at an identical frequency for a methyl formate monolayer on Cu(110). They believe that coordination takes place via the oxygen lone pair of the carbonyl resulting in bond weakening and producing a vibrational frequency much below the gas phase value. While we believe the assignment to intact methyl formate is the most reasonable there are other possibilities. Measurements of skeletal frequencies beyond the spectral range of our cell/support combination would be highly desirable.

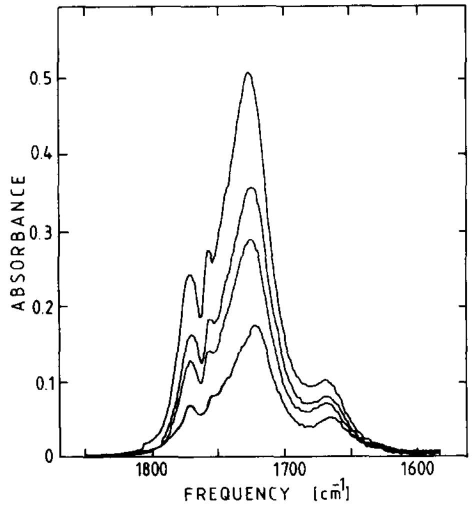

FIG. 2. Spectra of methyl formate adsorbed on Cu/SiO$_2$ at 447 K for methyl formate pressures of 3.5, 6.2, 9.4, and 14.5 kPa; balance to 101 kPa: hydrogen. (Spectra of reduced catalyst subtracted.)

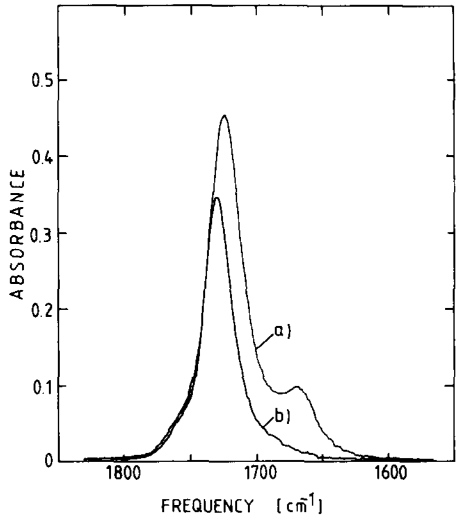

FIG. 3. Spectra of methyl formate adsorbed on (a) Cu/SiO$_2$ and (b) SiO$_2$ at 447 K. (Methyl formate, 14.5 kPa; hydrogen, 86.5 kPa; background due to sample disk and gas phase methyl formate subtracted.)

Having established the presence of a species adsorbed on the copper, measurements were made to see if its spectral intensity could be related to the reaction rate. The procedure here was to measure spectra simultaneously with reaction rates for a series of methyl formate pressures at a fixed temperature. The contribution of Si—O vibrations, gas phase methyl formate and methyl formate adsorbed on SiO_2 (allowing for the 4-cm^{-1} difference in peak frequency) to the spectra were then subtracted to leave the 1606-cm^{-1} component alone. Figure 4 shows a plot of its intensity versus reaction rate at 457 K for four methyl formate pressures. The relationship is linear within experimental error. This is consistent with a simple reaction scheme of the type

$$CH_3OCHO(g) \rightleftarrows CH_3OCHO(ads) \rightarrow \text{products} \quad (3)$$

in which the rate is proportional to the quantity of adsorbed methyl formate. The power law kinetic order in methyl formate gas was assessed from log–log plots of rate versus pressure. The value was 0.45 in good agreement with our previous value of 0.39 obtained at much higher conversion levels in a recirculating reactor (*11*).

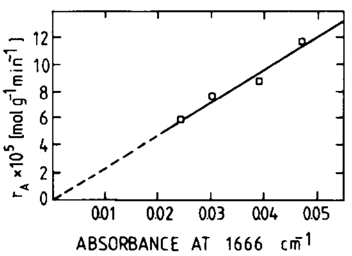

FIG. 4. Correlation between absorbance at 1666 cm^{-1} due to methyl formate absorbed on copper and the rate of hydrogenolysis at 457 K. The points correspond in succession to pressures of 3.5, 6.0, 9.3, and 14.4 kPa (balance to 101 kPa, hydrogen).

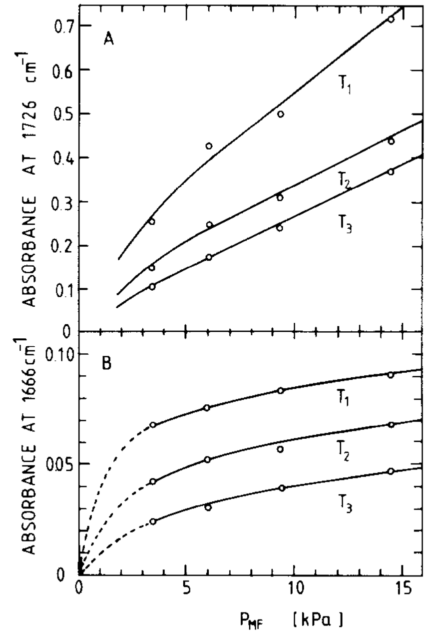

FIG. 5. Adsorption isotherms of methyl formate on Cu/SiO_2. (a) On silica; (b) on copper (total pressure 101 kPa, balance hydrogen; temperatures T_1 = 429 K, T_2 = 447 K, T_3 = 457 K).

It proved impractical to obtain data similar to Fig. 4 at significantly different temperatures due to the constraints imposed by the small catalyst mass in the infrared reactor. At higher temperatures spectral intensities became too weak while below 457 K the accuracy with which conversion and hence rate could be determined fell off. However, it was possible to measure infrared band intensity as a function of reactant pressure at lower temperatures and hence plot the analogue of an isotherm. Figure 5 shows such plots for methyl formate both physically adsorbed on the support (the 1726-cm^{-1} band) and bound to copper (the 1666-cm^{-1} band). Application of the Clausius–Clapeyron equation to this data gave the following apparent heats of adsorption:

methyl formate on silica ≅ 65 ± 10 kJ mol^{-1}

methyl formate on copper ≅ 140 ± 20 kJ mol^{-1}

The correlations of Hertl and Hair (*19*) indicate that the former is realistic for attachment of methyl formate to SiOH groups by hydrogen bonding. One might expect adsorption on copper to show a higher value on the grounds that the carbonyl frequency has been shifted still further from that for the free molecule. Also, as we show later, methyl formate is able to partially displace carbon monoxide which has a heat of adsorption of 60 kJ mol^{-1} on copper. The above value for the heat of adsorption of methyl formate on copper does seem rather high but is not without precedent. In a careful study of the dehydrogenation of 2-butanol to 2-butanone Echevin and Teichner (*20*) directly measured a heat of adsorption for the ketone of 127 kJ mol^{-1} by gravimetric means and inferred an identical value under reaction conditions by a Langmuir–Hinshelwood analysis of the rate data. Our estimate for methyl formate is consistent with this given the experimental error.

B. Influence of Carbon Monoxide

The effect of CO on the reaction is of particular interest since it inhibits hydrogenolysis and leads to a continuous loss of activity. First, the spectrum of CO adsorbed from CO/H_2 mixtures was characterized for three temperatures (447, 457, and 472 K) and five CO pressures, in the range 1.2 to 20 kPa, with H_2 to balance to a total of 101 kPa in each case. The 447 K spectra, after subtraction of the gas phase and silica contributions, are presented in Fig. 6. They show a single intense peak due to CO linearly bonded to copper at 2116–2118 cm^{-1}. This is somewhat higher than observed by Pritchard *et al.* (*21*) for adsorption at room temperature in the absence of hydrogen. Using the same procedure described for methyl formate the measured band intensities of adsorbed CO were used to construct "isotherms" at the three temperatures and hence estimate the heat of adsorption. The calculated value was 60 ± 5 kJ mol^{-1}. The isotherms were approximately Langmuir in shape with a saturation coverage corresponding to an absorbance of approximately 0.25.

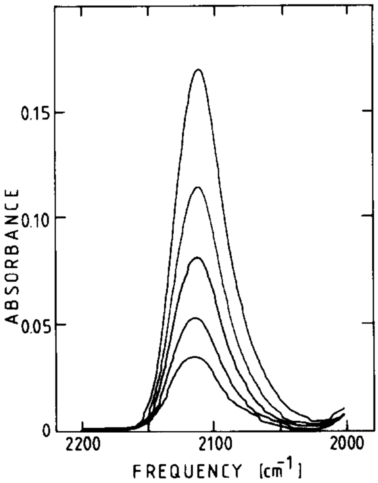

FIG. 6. Spectra of carbon monoxide adsorbed on silica-supported copper at 441 K for five CO pressures (1.25, 2.5, 5.,0, 10.0, and 20.0 kPa; balance to 101 kPa, hydrogen; spectra of reduced catalyst and of gas phase CO subtracted).

The influence of CO on methyl formate hydrogenolysis was then studied in the following way. The reduced catalyst was exposed to a CO/H_2 stream and an initial spectrum recorded. Methyl formate was then introduced into the CO/H_2 stream. A second spectrum and the hydrogenolysis rate were then determined. Finally, the CO gas was shut off and a third spectrum together with its corresponding rate was measured.

The spectra obtained in experiments using a CO pressure of 12.5 kPa are compared in Fig. 7. It can be seen from the change in intensity of the band at 2116 cm^{-1} that the amount of CO adsorbed decreased in the presence of methyl formate. On the other hand, when the CO was deleted from the feed stream, the band at 1666 cm^{-1} attributed to methyl formate adsorbed on copper was little changed. Even so, the hydrogenolysis rate increased from 3.9×10^{-5} mol min^{-1} g^{-1} with CO present to 6.1×10^{-5} mol min^{-1} g^{-1} in its absence. The effects were reversible and experiments using the opposite order gave the same result—namely addition of carbon monoxide to a methyl formate/hydrogen stream lowered the rate without affecting the quantity of methyl formate adsorbed.

These effects can be explained in terms

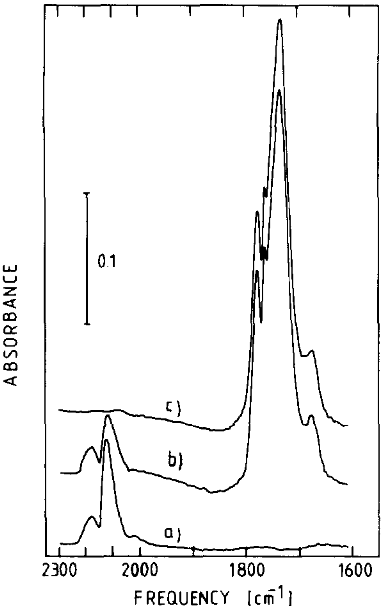

FIG. 7. Spectra of CO and methyl formate coadsorbed on Cu/SiO_2 at 447 K. (a) CO, 12.5 kPa; H_2, 88.5 kPa. (b) CO, 12.5 kPa; methyl formate 9.5 kPa; H_2, 79 kPa. (c) methyl formate, 9.5 kPa; H_2, 91.5 kPa. (Spectra of reduced catalyst subtracted.)

of the relative strengths of adsorption of the three components: methyl formate, carbon monoxide, and hydrogen. Both the heat of adsorption measurements and the displacement experiments above indicate that CO is adsorbed less strongly than methyl formate. Hydrogen is certainly adsorbed still less strongly, the amount of hydrogen adsorbed being probably less than 5% of the amount of CO if measurements (*22*) with Raney copper are relevant. On the basis of the *in situ* measurements of Figs. 3, 4, and 5 one expects that in the presence of methyl formate/hydrogen mixtures copper will be only partially covered by intact methyl formate molecules. These will be bound at one position (and perhaps sterically interfere with others). Unoccupied sites will be available to adsorb and dissociate the hydrogen required for the four hydrogen additions per methyl formate molecule reacted. If CO is now introduced, it is unable to displace the methyl formate but some adsorbs on the remaining sites or displaces hydrogen from them. It is the latter process which reduces the hydrogenolysis rate. As noted later, reduced hydrogen availability has the second consequence of raising the concentration of partially hydrogenated intermediates such as formaldehyde.

The exact coverage by methyl formate under reaction conditions cannot be assessed. However, the CO coverage can be estimated using the saturation value given earlier. For the conditions of Fig. 7 the CO coverage is roughly 10% when methyl formate is present and 30% in its absence. In the experiments in the IR cell the amount of carbon monoxide produced as a by-product to hydrogenolysis was too small, by itself, to result in significant CO coverage.

In our previous work (*11*) using a recycle reactor at relatively high conversions we noticed a second effect when carbon monoxide in excess of a limiting value was included in the feed stream. In addition to the reversible inhibition found above, the catalyst also showed a gradual loss in activity when monitored over a period of hours. (Raney copper and copper chromite show this effect in the absence of added CO (*8*)). If this effect could be duplicated in the infrared cell/reactor then one might expect to see a continual build-up in the height of bands corresponding to the surface blocking residue paralleling the decline in reaction rate. Figure 8 shows spectra recorded after different times on stream with a methyl formate, CO, and hydrogen gas mixture at 447 K. A new band appeared at 1483 cm^{-1} and its intensity increased with time on stream. However, measurements of the reaction rate showed no significant decline over a period of 8 h. Correspondingly there were no changes in the intensities of the bands assigned to methyl formate and CO adsorbed on the copper. Similar measurements using support alone indicated that the 1483-cm^{-1} peak was associated in part or in whole with adsorption on the silica and hence substantial quantities would be required to interfere with the reaction itself. The absence of significant

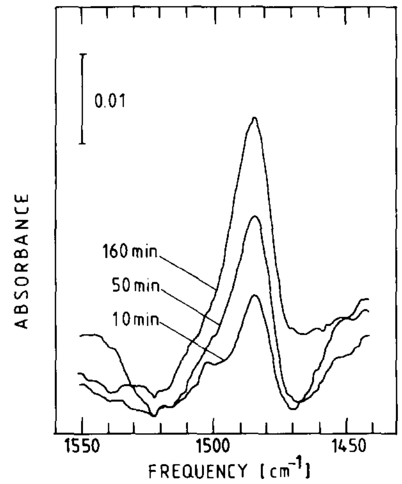

FIG. 8. Time dependence of adsorption band at 1483 cm^{-1} in the presence of 12.5 kPa CO, 9.5 kPa methyl formate, and 79 kPa H_2. (Spectra of reduced catalyst subtracted.)

deactivation in the infrared cell/reactor compared to our earlier work under recirculation conditions probably reflects the much higher conversions in the latter case and the consequent much higher levels of methanol and trace by-products. This tentative conclusion led us to look at the reverse methanol dehydrogenation which is well known to be prone to deactivation (*9*, *10*).

C. Interaction of Methanol with Cu/SiO$_2$ under Dehydrogenation Conditions

With a hydrogen-free feed, containing only methanol with helium as a diluent, the dehydrogenation of methanol to methyl formate [Reaction (1)] was studied in the IR cell at 503 K. The experiments were performed with a freshly reduced catalyst pellet and an inlet methanol pressure of 3.8 kPa (balance 97.2 kPa helium). Product methyl formate decarbonylated easily at this high temperature to produce CO concentrations which were about half the methyl formate concentrations measured. Spectra were recorded at regular intervals and the corresponding methanol conversion was obtained from the measurements of the concentration difference between inlet and outlet stream. The initial spectrum recorded at a methanol conversion of 55.3% showed the bands for exchanged methoxy groups on the silica (2960, 2859, 1463 cm^{-1}) and of product methyl formate in the gas phase (1769 cm^{-1}), on the silica (1726 cm^{-1}) and on the copper (1666 cm^{-1}). For longer times on stream, an increase in intensity of bands located at 1483, 1463, and 1375 cm^{-1} took place as illustrated in Fig. 9. The band at 1463 cm^{-1} increased at a lower rate than the other two and is due to methoxy groups on the support since the change in its height paralleled the increases in intensity of the corresponding 2960- and 2859 cm^{-1} CH stretching bands. It is important to note that the band at 1483 cm^{-1} appeared at the same frequency as for the hydrogenolysis reaction studied earlier but the intensity reached is much greater and, in contrast to those long-term experiments, the activity of the catalyst did decrease for longer times on stream as shown in Fig. 10. After an induction period of 2 h, a continuous loss of activity commenced. The height of the band located at 1375 cm^{-1} (which was too small to be detectable above background fluctuations during methyl formate

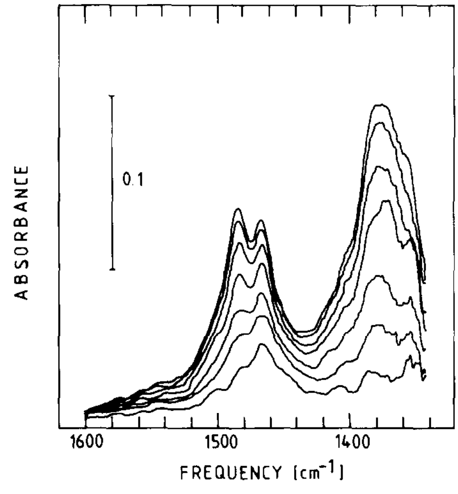

FIG. 9. Spectra of Cu/SiO$_2$ after different times on stream (0.4, 1, 2, 3, 4.5, 6, and 7 h) for the dehydrogenation of methanol at 503 K. (Spectra of reduced catalyst subtracted.)

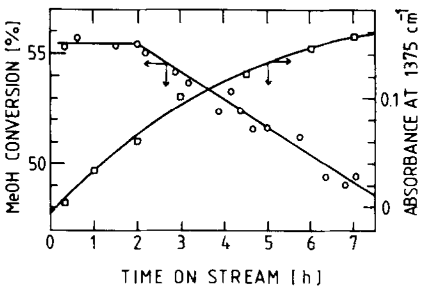

FIG. 10. Absorbance at 1375 cm^{-1} and conversion of methanol as a function of time at 503 K.

hydrogenolysis) exhibited a linear increase during the first 3 h and the rate at which it formed decreased later on as shown in Fig. 10. Evidently, fouling of the copper catalyst is paralleled by a build-up of the compound giving rise to infrared bands at 1483 and 1375 cm^{-1}.

Infrared bands in this region can either be attributed to C–O bonds with partial double-bond character (e.g., carbonates), to aromatic ring modes or to C—H bending and wagging modes (*23*). To discriminate between these possibilities, the dehydrogenation of methanol was performed with methanol-d_4 (CD_3OD) as a reactant. If the bands at 1483 and 1375 cm^{-1} were due to carbon–hydrogen vibrations they should shift to frequencies below the 1300-cm^{-1} silica cutoff and hence go undetected. The full spectrum recorded under the same conditions as for the undeuterated methanol is shown in Fig. 11. The OH groups of the silica exchanged rapidly and produced the sharp SiOD bands at 2753 and 2727 cm^{-1} for free and deuterium-bonded species, respectively. Replacement of OD groups by OCD_3 on the silica was comparatively slow and gave rise to CD_3 stretching vibrations at 2244, 2142, and 2082 cm^{-1}. However, no bands appeared near 1483 or 1375 cm^{-1} even after long periods on stream (7 h), although the catalyst deactivated and conversion decreased from an initial 23 to 16% after 7 h. The much lower reaction rate of CD_3OD compared to CH_3OH is due to an isotope effect as described in detail previously (*24*).

From the experiments with methanol-d_4, it is obvious that the bands at 1483 and 1375 cm^{-1} observed with CH_3OH but not CD_3OD arise from carbon–hydrogen rather than carbon–oxygen modes. Further insight into the cause for the deactivation can be gained by considering the mechanism of the dehydrogenation reaction. Although a certain degree of uncertainty still exists, it is generally assumed that formaldehyde is a reaction intermediate (*25–27*) and this has been detected as a product with a Raney copper catalyst where there is no support to adsorb it (*9*). It has been suggested that methyl formate is either produced by formaldehyde dimerization (*25*, *26*) or by reaction with adsorbed methoxy groups (*27*). The deactivation of Raney copper during the dehydrogenation of methanol has been attributed to a polymerized form of formaldehyde (*9*). Polyoxymethylene was therefore considered as a possible surface blocking polymer residue. The infrared spectrum of polyoxymethylene (POM) in the crystalline state (*28*) exhibits bands at 1471 and

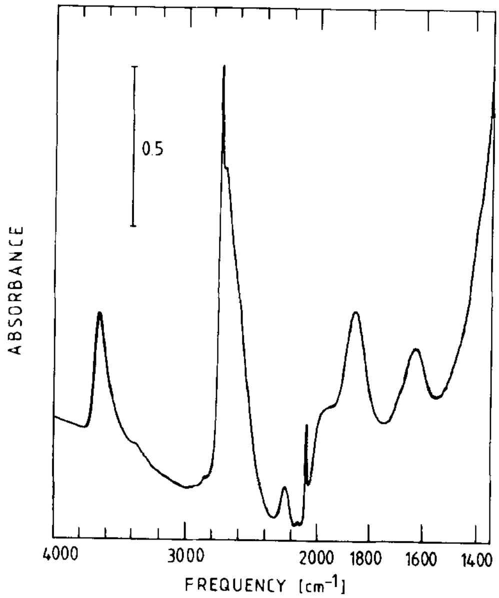

FIG. 11. Spectrum of Cu/SiO_2 under dehydrogenation conditions with methanol-d_4 as reactant at 503 K. (Inlet methanol-d_4, 3.8 kPa; He, 97.2 kPa; time on stream, 7 h.)

1381^{-1} cm^{-1} assigned to CH_2 bending and wagging vibrations, respectively. For trioxane, a cyclic trimer of formaldehyde, the corresponding bands are located at 1483 and 1383 cm^{-1} (*29*). These frequencies are almost identical to the location of the bands building up when deactivation occurs (1483 and 1375 cm^{-1}). Probably due to the presence of large bands originating from exchanged methoxy groups, a search of the 2800- to 3000-cm^{-1} region for stretching CH bands characteristic for POM was not successful.

The reason for the much higher rate of polymer accumulation during methanol dehydrogenation is almost certainly the much lower hydrogen to CO ratio in these experiments. Such conditions lower the concentration of adsorbed hydrogen and thus favor the less hydrogenated species such as formaldehyde and the polymers derived from it. Under methyl formate hydrogenolysis conditions very high pressures of added carbon monoxide or very high conversions would be required to achieve the same thing.

A comparison of the time dependence of deactivation and polymer accumulation (Fig. 10) reveals a time lag before the activity declines. The presence of strong adsorption bands due to POM before deactivation occurs, indicates that the polymer is probably not bound to the copper.

The deactivation process should therefore be regarded as an overall blocking of the surface which eventually renders part of the copper surface inaccessible to the reactants. The formaldehyde is produced on the copper and is incorporated in a polymer chain mostly attached and growing on the support.

It is well known (*10, 11*) that highly dispersed copper is less affected by deactivation compared to pure coppers such as Raney copper. Assuming a similar rate of polymer accumulation and unspecific deposition as detailed above, it is evident that copper dispersed on a high-surface-area support will be less affected compared to catalysts containing copper alone. For the latter every increment of surface area blocked by polymer results in a proportional decrease in active area.

CONCLUSIONS

1. *In situ* infrared spectral measurements show that the hydrogenolysis of methyl formate over copper on silica involves an adsorbed species with a carbonyl absorption band at 1660 cm^{-1}.
2. Reversible inhibition of hydrogenolysis by CO is not due to displacement of methyl formate.
3. Sufficiently high CO levels also lead to deposition of residue material probably originating from polymerization of a formaldehyde intermediate.
4. Deposition of this polymer is more rapid during the reverse methanol to methyl formate reaction and is then sufficient to cause continuous deactivation of the catalyst.

In the following paper (*30*) it is shown how this information can be combined with deuterium-labeling studies to build a fairly complete picture of this interesting example of catalytic C_1 chemistry.

ACKNOWLEDGMENT

Funding of this project under the Australian Research Grants Scheme (ARGS) is gratefully acknowledged.

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