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The Mechanism of Methanol Synthesis on Copper/Zinc Oxide/Alumina Catalysts

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This paper deals with the adsorption and temperature-programmed reaction spectroscopy of (i) formaldehyde on polycrystalline copper, polycrystalline zinc oxide and (ii) methanol on a copper/zinc oxide/alumina (60 : 30 : 10) catalyst. It shows that the energetics of formate hydrogenation/hydrogenolysis on the copper component of the catalyst, which is the rate-determining step in methanol synthesis on the copper/zinc oxide/alumina catalyst, is unaffected by the intimate mixing of copper and zinc oxide in the catalyst. The coverages of the individual components of the copper/zinc oxide/alumina catalyst which had been producing methanol at a rate of 1.9×10^{-9} mol^{-1} s^{-1} g^{-1} from a carbon dioxide/hydrogen feed (10% CO_2, 1 bar, 500 K, 36 liters h^{-1}) by oxygen, hydrogen, and formate species was determined by carbon monoxide titration and by temperature-programmed desorption. The copper component of the catalyst was covered with oxygen to between 3.5×10^{14} and 3.9×10^{14} atoms cm^{-2} (i.e., between 70 and 78% of saturation). Coexisting with this on the copper component of the catalyst was a formate species, the upper limit of its coverage being 2.6×10^{14} molecules cm^{-2}. The zinc oxide component of the catalyst appeared to be hydrided or to contain interstitial hydrogen to a value greater than monolayer coverage during steady-state reaction.

INTRODUCTION

Methanol is made industrially from a carbon monoxide/carbon dioxide/hydrogen feed (normally 10 : 10 : 80) at between 50 and 100 bar, in the temperature range 250–300°C over a copper/zinc oxide/alumina catalyst.

In a series of papers, Klier and coworkers (*1*, and references therein) have advanced the view that methanol is synthesised from the carbon monoxide component of the reactant mixture, carbon dioxide being there to maintain the catalyst in a partially oxidised state. The active centre for the reaction was proposed to be a Cu^+ ion substituted in the zinc oxide lattice. Carbon monoxide was supposed to be adsorbed strongly at this centre and to be sequentially hydrogenated to methanol. Indirect experimental evidence for an increased heat of adsorption of carbon monoxide on this Cu^+ ion has been obtained by Giamello and Fubini (*2*) who, using a Tian–Calvet microcalorimeter, measured a heat of adsorption at low coverage of 80 kJ mol^{-1}. This view of the reaction coincided with a certain intuitive logic about the nature of the synergy which appeared to exist between copper and zinc oxide in relation to methanol synthesis and it was therefore accorded a fairly general acceptance.

The above view of the mechanism of methanol synthesis on copper/zinc oxide/alumina catalysts was constructed in spite of the evidence provided by Kagan *et al.* (*3*) that it was the carbon dioxide component of the feed which was hydrogenated to methanol. Using labelled carbon monoxide (^{14}CO) at 50 bar and at 180 and 218°C, the product methanol and carbon dioxide molecules of a carbon monoxide/carbon dioxide/hydrogen/nitrogen (~1 : 20 : 75 : 4) feed were found to have identical specific radio-

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activities. Additionally, we had shown that on zinc oxide alone, methanol was synthesised from carbon dioxide and not from carbon monoxide (*4, 5*).

Chinchen *et al.* (*6, 7*) therefore carried out further radiolabelling experiments to identify the source of methanol when mixed carbon monoxide/carbon dioxide feeds are reacted with copper/zinc oxide/alumina catalysts. Using a 10 : 10 : 80 carbon monoxide/carbon dioxide/hydrogen feed in which the carbon dioxide was labelled, they arrived at the conclusion identical to that of Kagan *et al.* (*3*), namely, that all of the methanol was made from the carbon dioxide. At high space velocities (low conversions) the methanol had a specific radioactivity identical to that of the carbon dioxide feed, while at lower space velocities the specific radioactivity of the methanol was roughly the average of the inlet and exit carbon dioxide activities. The experiments were carried out at 50 bar and at 240°C. These experiments provided direct and irrefutable evidence that it is the carbon dioxide molecule of the feed which is the immediate precursor to methanol when synthesised on copper/zinc oxide/alumina catalysts.

In addition, it has recently been shown that the role of the carbon monoxide component of the gas feed is that of a reducing agent (*8*), scavenging the oxygen produced in the synthesis of methanol from carbon dioxide from the surface of the copper component (the active centre) of the catalyst. In that paper (*8*) a linear relationship was obtained between methanol synthesis activity and the initial copper areas of differently supported copper/metal oxide catalysts. The amount of oxygen existing on the surface of the copper was found to be a function of the carbon dioxide : carbon monoxide ratio. This work has been repeated by Denise *et al.* (*9*), who concurred with the findings that part of the surface of the copper component of the catalyst is oxidised during methanol synthesis by the carbon dioxide component of the feed, while Bridgewater *et al.* (*10*) found that the methanol synthesis activity per copper atom was the same on a Raney copper catalyst as on a commercial copper/zinc oxide/alumina catalyst.

Broad agreement therefore now exists that it is the carbon dioxide component of the mixed carbon oxides/hydrogen feed which is responsible for the synthesis of methanol and that it is the total surface area of the copper which is the active component of the catalyst. However, the mechanism of the interaction of carbon dioxide and hydrogen on the surface of the copper/zinc oxide/alumina catalyst has not yet been elucidated and it is the purpose of this paper to address this problem.

EXPERIMENTAL

Apparatus

The techniques employed were temperature-programmed reaction spectroscopy (tprs), temperature-programmed desorption (tpd), and microreactor rate measurements.

Two types of apparatus were used in the tprs experiments: (i) a high vacuum machine which has been described in detail previously (*4, 11, 12*) and (ii) a microreactor which has also been described previously (*13*). The microreactor used to obtain steady-state rate measurements, temperature-programmed desorption spectra, *in situ* copper metal areas of the copper/zinc oxide/alumina catalysts, total surface areas, and oxygen coverages of the copper component of these catalysts has also been described before (*8*). In many respects it is a conventional microreactor but it does include several improvisations to allow *in situ* measurement of the total surface areas and copper metal surface areas of the catalyst. Among others, these involve configuring the finned reactor tubes and gas feed lines in a U-shape to permit immersion in a liquid nitrogen flask for the adsorption of nitrogen at 77 K (total surface area measurements), mass spectrometric and gas chromatographic analysis being used for the analysis of the products of the methanol synthesis reaction, while a mass spectrometer and thermal conductivity detectors were used for the determination of the extent of nitrous oxide decomposition by reactive frontal chromotography for copper metal area measurement (*13*).

Gases

The hydrogen (Air Products) was 99.99% pure; carbon monoxide (Matheson) was 99.997% pure. Carbon dioxide (Distillers Co.) was 99.965% pure, containing 0.025% air and 0.01% moisture. The nitrous oxide (Air Products) was 99.9% pure, the 0.1% impurity being oxygen. All these gases were used directly from the cylinder without further purification (the 0.1% oxygen impurity in the nitrous oxide was of negligible importance to the determination of copper metal areas). The helium (British Oxygen Co.) was purified by being passed through a rare-gas purifier (British Oxygen Co., mk 3), which removed (i) nitrogen and oxygen by reaction with titanium at 1000 K, (ii) hydrogen, hydrocarbons, and carbon monoxide by reaction with copper oxide at 1000 K, and (iii) water and carbon dioxide by adsorption on a molecular sieve at room temperature. The oxygen content in the helium at the exit from the rare-gas purifier was <1 ppm as measured on a Hersch oxygen meter (Engelhard Industries Ltd.).

Adsorbents/Catalysts

The copper/zinc oxide/alumina catalyst. The industrial methanol synthesis catalyst is made by coprecipitation (*14*) and has a composition of 60% copper/30% zinc oxide/10% alumina by weight. Approximately 0.2 g of the material was used in the tprs experiments in the high-vacuum apparatus, having been pretreated in one of three ways: (i) heating from ambient to 700 K under vacuum at a heating rate of 25 K min^{-1}, (ii) reducing in 10^{-3} Torr hydrogen (1 Torr = 133 Pa) for 15 min at 520 K followed by raising the temperature to 700 K under vacuum to desorb any retained hydrogen, or (iii) reducing the catalyst more thoroughly by repeating the hydrogen dosing and desorption between 5 and 10 times.

In the microreactor experiments approximately 2 g of the copper/zinc oxide/alumina catalyst was used and was prereduced in a 5% hydrogen/nitrogen mixture (1 bar, 24 liters h^{-1}), raising the temperature from ambient to 390 K rapidly and thereafter to 500 K at a heating rate of 0.5 K min^{-1}. The rate measurements were carried out on the prereduced catalyst in a hydrogen/carbon dioxide/helium stream (80 : 10 : 10, 1 bar, 36 liters h^{-1}, 500 K), oxygen titrations and desorption spectra being obtained after approximately 4 h, i.e., after steady state had been achieved.

The polycrystalline copper adsorbent. The polycrystalline copper was prepared by reduction of AnalaR cupric oxide (BDH) by successive doses of both hydrogn and carbon monoxide, separately and in combination, at about 1 Torr total pressure for 15 min at 252 K, followed by evacuation at 700 K. This reduction process continued for ~8 h.

The purity of the cupric oxide was quoted as >98%, the major quoted impurities being alkali sulphates (<0.3%). X-ray photoelectron spectroscopy (XPS) failed to detect any alkali in this cupric oxide. The detection limit of the instrument as used (single scan) was about 1% of the topmost 50-Å layer, a value which is consistent with the quoted impurity.

Secondary ion mass spectrometry (SIMS) did detect both sodium and potassium in the surface layer of the cupric oxide but at a much lower level (<1 ppm of the surface) than the quoted bulk impurity. The SIMS machine was calibrated by the addition of known amounts of alkali to the samples.

RESULTS AND DISCUSSION

Temperature-Programmed Reaction Spectra Having Dosed (i) Formaldehyde on to Partially Oxided Polycrystalline Copper, (ii) Formaldehyde on to Polycrystalline Zinc Oxide, and (iii) Methanol on to the Copper/Zinc Oxide/Alumina (60:30:10) Catalyst

Temperature-programmed reaction spectroscopy (tprs) is a variant of the much-used temperature-programmed desorption (tpd). In tpd an adsorbate, A_{ad}, is removed from the catalyst or single crystal surface, S, normally by heating in a linear temperature/time mode. The information gained is the desorption activation energy E_d, i.e., the activation energy of the forward reaction (1) and the surface coverage of the adsorbate,

$$A_{ad}S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_g + S, \qquad (1)$$

where the subscript g relates to a gas phase component. [Additional information about the adsorption process (reaction (−1)) can be obtained by varying (i) the dosage of A_g from which the initial sticking probability can be obtained and (ii) the adsorption temperature from which the adsorption activation energy can be derived].

The essence of tprs, however, is that it provides information about the mechanism of surface reactions by defining the stoichiometry of the surface intermediates. Having dosed adsorbate A_g onto a prepared surface, A_{ad} transforms into a new species BC_{ad} during the dosing:

$$A_{ad}S \rightarrow BC_{ad}S', \qquad (2)$$

where the prime denotes a changed catalyst surface after reaction (2). On temperature programming, not only does the unchanged A_{ad} desorb at its characteristic peak maximum temperature according to Eq. (1), but BC_{ad} decomposes and B and C necessarily desorb in coincidence (Eq. 3) at a temperature higher than they would have done had they been separately dosed

$$BC_{ad}S' \rightarrow B_g + C_g + S'. \qquad (3)$$

The stoichiometry of the surface intermediate can be gleaned from the stoichiometry of B and C in the gas phase. A knowledge of the stoichiometry of the reactant A, the intermediate BC, and of the ultimate product allows definition of the reaction mechanism.

The tprs spectrum shown in Fig. 1 is obtained on temperature programming (heating rate 0.7 K s^{-1}) after dosing formaldehyde (1 Torr, 15 min, 295 K) onto as fully reduced a sample of cupric oxide as could be achieved by the reduction process outlined under Experimental. Several points are worthy of note. By the principles defined above, the coincident desorption of carbon dioxide (B) and hydrogen (C) at 440 K, having dosed formaldehyde (A_g) at room temperature onto the partially oxidised copper, is indicative of a surface formate having been formed. Since nothing desorbs at higher temperatures, this formate species is the most stable intermediate extant on

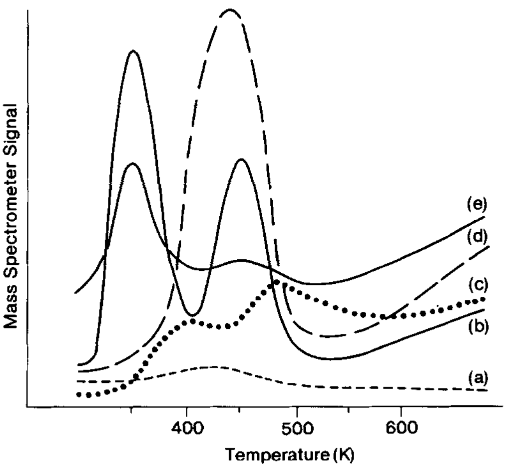

FIG. 1. Temperature-programmed reaction spectrum resulting from the room-temperature adsorption of formaldehyde onto a partially oxidised polycrystalline copper surface. (a) Dimethyl ether ×33; (b) hydrogen ×10; (c) water ×10; (d) carbon dioxide ×10; (e) methanol ×300, formaldehyde ×33.

the surface. Ying and Madix (*15*) first identified this coincident desorption of hydrogen and carbon dioxide at 440 K as formate following the adsorption of formic acid on a copper (110) surface. (The smaller water peak in Fig. 1 seen at about 480 K is confirmation of the oxidised nature of the copper surface and probably derives from readsorption and further reaction of the gaseous hydrogen obtained from formate decomposition.)

The second point to note is the coincident desorption of hydrogen, formaldehyde, and methanol at 340 K. This is characteristic of the temperature-programmed reaction spectrum of a methoxy species adsorbed on copper and has been characterised as such by Wachs and Madix (*16*) following methanol adsorption on a copper (110) surface. (The reassuring aspect of the near identity of our methoxy and formate decomposition spectra from this polycrystalline copper with those of Madix *et al.* from pure single crystal copper is that the quoted alkali impurity in the cupric oxide appears not to have segregated to the surface on reduction and the desorption is characteristic therefore of the interaction of formate and methoxy species with an unpoisoned (or promoted) copper surface.)

Third, and most importantly, a small peak of formaldehyde and methanol is observed at about 440 K, coincident with the decomposition of the adsorbed formate species. The importance of this observation is that it indicates that when the hydrogen from the adsorbed formate becomes mobile on the surface it can (i) combine with another hydrogen atom to give a hydrogen molecule in the gas phase or (ii) hydrogenate an adsorbed formate species, producing an intermediate which either desorbs as formaldehyde or which, after further hydrogenation, desorbs as methanol. The adsorption of methanol on the same partially oxidised copper gave a formate decomposition spectrum identical to that shown in Fig. 1 after formaldehyde adsorption, and so, since the formate species is involved in both the synthesis and decomposition of methanol, it is a true reaction intermediate.

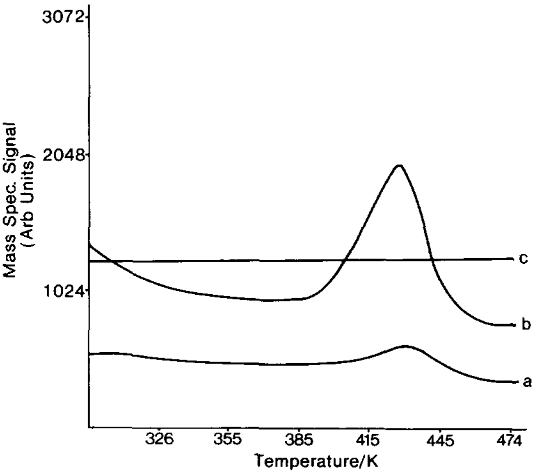

FIG. 2. The temperature-programmed reaction spectrum resulting from the codosing of carbon dioxide and hydrogen onto polycrystalline copper at 32°C. (a) Hydrogen; (b) carbon dioxide; (c) water.

The tprs spectrum shown in Fig. 2 results from the codosing of carbon dioxide and hydrogen (61 Torr CO_2, 61 Torr H_2, 638 Torr He, 25 cm^3 min^{-1} flow rate, 10 min) on to polycrystalline copper (2.06 g, 1.5 m^2 g^{-1}) at 32°C. (The polycrystalline copper was prepared by reduction of AnalaR cupric oxide as described under Experimental.) The coincident evolution of hydrogen and carbon dioxide at about 440 K indicates that the surface reaction of the adsorbed carbon dioxide and hydrogen on the polycrystalline copper produces the same formate intermediate as that obtained after the adsorption of formaldehyde or methanol. The coverage of the copper by hydrogen was 6.2×10^{18} atoms and by carbon dioxide was 7×10^{18} molecules or a total formate coverage of about 2.5×10^{14} ions cm^{-2}. Since we have shown that the adsorbed format species is the pivotal intermediate in methanol synthesis on polycrystalline copper and since we have found that it is not formed by carbon monoxide/hydrogen codosing, we conclude from these experiments (i) that methanol is formed from the carbon dioxide component of a mixed carbon oxides/hydrogen feed, (ii) that the mechanism of methanol synthesis is by the interaction of the adsorbed carbon dioxide and hydrogen to form a formate species which is subsequently hydrogenated to methanol, and (iii) since the formate species can be formed from carbon dioxide and hydrogen at 32°C, its hydrogenation/hydrogenolysis is the rate-determining step in methanol synthesis.

The significantly lower temperature for the decomposition/hydrogenation of the formate on the copper (440 K) compared with the value of 580 K for its decomposition on zinc oxide (where it has also been shown to be the pivotal intermediate in methanol synthesis (*4*)) suggests that the copper component of the catalyst is the more active in methanol synthesis in a mixed copper/zinc oxide/alumina catalyst. This conclusion explains our observation of the linear relationship between methanol synthesis activity and copper metal area (*8*). The total coverage of the polycrystalline copper with methoxy and formate species by dosing formaldehyde on to the copper, calculated from the integral of the desorption peaks of Fig. 1, was 9 × 10^{14} ions cm^{-2} which is about a factor of 10 higher than achieved on zinc oxide with the same dosing of formaldehyde (*4*).

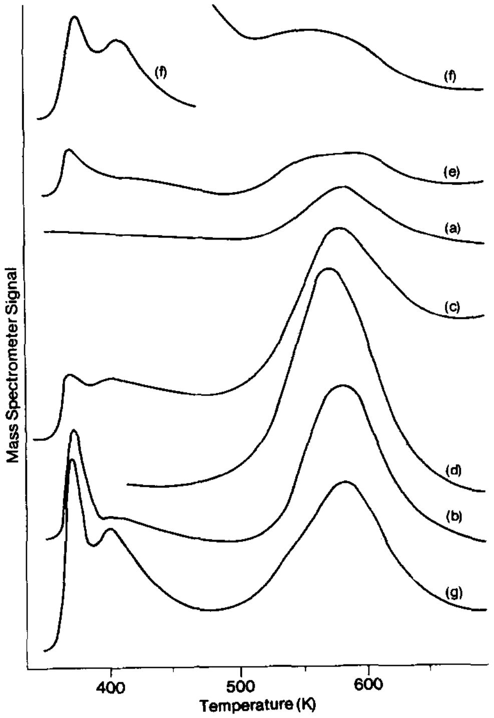

FIG. 3. Temperature-programmed reaction spectrum resulting from the room-temperature adsorption of formaldehyde onto zinc oxide. (a) Dimethyl ether ×30; (b) hydrogen ÷3; (c) water ×10; (d) carbon dioxide ×3; (e) methanol ×10; (f) formaldehyde ×10; (g) carbon monoxide.

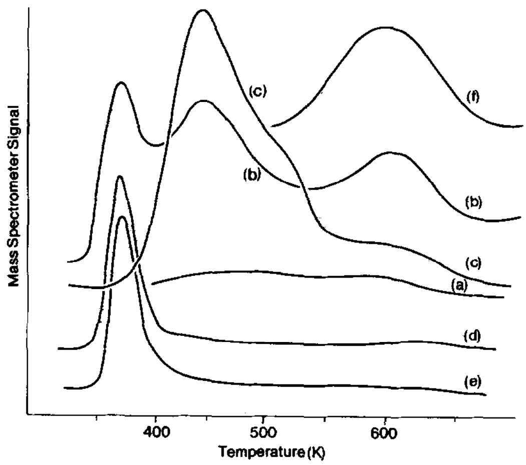

FIG. 4. Temperature-programmed reaction spectrum resulting from the room-temperature adsorption of methanol onto the prereduced (slightly oxidised, see Experimental) copper/zinc oxide/alumina (60 : 30 : 10) catalyst. (a) Dimethyl ether ×33; (b) hydrogen ×1; (c) carbon dioxide ×3.3; (d) methanol ×1; (e) formaldehyde ×10; (f) carbon monoxide ×1.

The desorption spectrum deriving from the room-temperature adsorption of formaldehyde on AnalaR zinc oxide (BDH), published previously (*4*), is shown in Fig. 3. It is reproduced here to show that if its salient features (the coincident desorption of *carbon monoxide* and hydrogen at ~580 K from the surface formate species) are superimposed on the tprs spectrum of formaldehyde on partially oxidised copper (Fig. 1), the resulting trace would closely resemble the one shown in Fig. 4, which is the temperature-programmed reaction spectrum of methanol on the reduced but necessarily partially oxidised copper/zinc oxide/alumina catalyst. (The tprs spectra of formaldehyde and methanol from the polycrystalline copper, zinc oxide (*4*) and from the copper/zinc oxide/alumina catalyst are essentially identical. The spectrum of methanol rather than that of formaldehyde is shown here since the main features are better exemplified in it.) The individual components, the copper and the zinc oxide, therefore appear to act independently and no effect of one component on the other in terms of a change in the peak maximum temperatures of the formate decomposition/hydrogenolysis is seen. These spectra therefore demonstrate that no particular synergy exists between the copper and the zinc oxide with respect to changing the energetics of the rate of the formate decomposition/hydrogenolysis reaction. (The lack of a methanol/formaldehyde peak at 440 K in the spectrum shown in Fig. 4 is probably simply a function of the lowered sensitivity used in recording the spectrum.)

The only postulate evidently remaining to account for what has been described as the unique synergy of copper and zinc oxide in methanol synthesis (*1*) is that the zinc oxide acts as an adsorber and source of carbon dioxide to the copper, where it is hydrogenated at the copper/zinc oxide interface to formate and thereafter to methanol, as described diagramatically in Ref. (*8*). (This was propounded since carbon dioxide had been shown to be held only weakly (~4 kcal mol^{-1}) when coadsorbed with hydrogen on copper (*8*).) However, the constancy of the methanol turnover number on copper for catalysts with different copper areas, including catalysts in which the copper was supported on silica, magnesia, and alumina (*8*), leads us to conclude that all of the copper is involved in the synthesis of methanol and no special synergy attaches to the copper/zinc oxide combination.

Hydrogen and Oxygen Coverages of the Separate Components of a Copper/Zinc Oxide/Alumina (60 : 30 : 10) Catalyst Having Produced Methanol at a Specified Rate from a Carbon Dioxide/Hydrogen/Helium (10 : 80 : 10) Feed

The steady-state methanol concentration obtained from a hydrogen/carbon dioxide/helium stream (80 : 10 : 10, 1 bar, 36 liters h^{-1}, 500 K) over the copper/zinc oxide/alumina catalyst (60 : 30 : 10) prereduced as described under Experimental was 0.011 vol%, corresponding to a rate of 1.9×10^{-9} mol $\mathrm{s}^{-1}\ \mathrm{g}^{-1}$, a value that remained constant for the final 2 h of the experiment.

The oxygen coverage of the copper component of the catalyst was obtained by titration with carbon monoxide by means of the following technique:

(i) Switching the flow to helium and lowering the temperature to 470 K over ~30 min.

(ii) At 470 K, switching the flow from helium to a carbon monoxide/helium stream (10% carbon monoxide, 1 bar, ~40 liters h^{-1}), monitoring water $m/e = 18$, hydrogen $m/e = 2$, and carbon dioxide $m/e = 44$ continuously on the mass spectrometer (see Fig. 5).

Titration of the oxygen on the surface of the copper by reduction with carbon monoxide at 470 K has been shown to be a quantitative measurement (*13*). It has also been shown (*5*) that the carbon monoxide will not reduce the zinc oxide component of the catalyst at this temperature. Additionally, all of the adsorbed formate species existing on the surface of the copper during methanol synthesis will have decomposed into the helium stream during the time of cooling (30 min) from 500 to 470 K. (The desorption half-life of the formate species adsorbed on copper, which is the most stable and longest lived adsorbed species in methanol synthesis, calculated from the

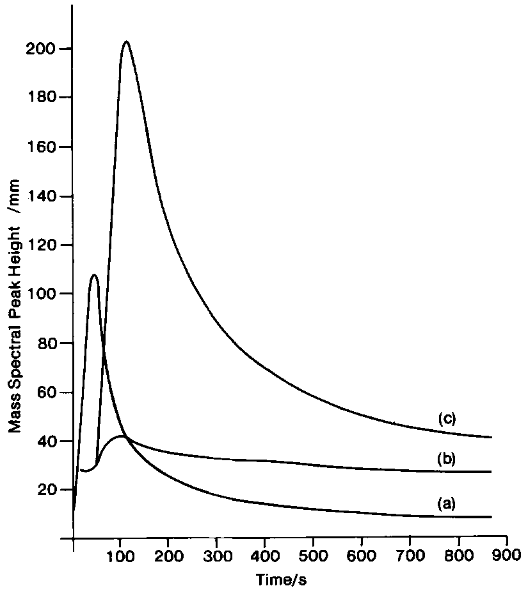

FIG. 5. Reduction of the copper component of copper/zinc oxide/alumina (60 : 30 : 10) catalyst by carbon monoxide at 470 K. (a) Carbon dioxide; (b) water; (c) hydrogen. Immediately prior to the reduction the catalyst had been producing methanol at a rate of 1.9×10^{-9} mol s^{-1} g^{-1} from a carbon dioxide/hydrogen/helium (10 : 80 : 10) feed at 500 K and 1 bar total pressure.

published desorption rate constant, $k = 8 \pm 2 \times 10^{13} \exp(-32 \times 10^3/RT)$, ($R = 1.987$ cal mol^{-1} K^{-1}, 1 cal = 4.182 J) (*16*) is 5 s at 470 K.) Therefore the carbon dioxide produced by reduction of the catalyst at 470 K (Fig. 5) will be specific to the oxygen coverage of the copper component of the catalyst under the specified reaction conditions of 500 K, 1 bar, methanol synthesis rate = 1.9×10^{-9} mol s^{-1} g^{-1}, feed = hydrogen/carbon dioxide/helium 80 : 10 : 10, flow rate = 36 liters h^{-1}.

The total amount of carbon dioxide produced was 2.9×10^{20} molecules, corresponding to an oxygen coverage of the copper of 3.2×10^{14} atoms cm^{-2} or 64% of saturation. (The copper metal area of the catalyst had previously been evaluated *in situ* by reactive frontal chromatography using nitrous oxide decomposition (*13*) at 38 m^2 g^{-1}.)

However, a small amount (6.2×10^{19} molecules) of water was also produced during this reduction by carbon monoxide (see Fig. 5). This is probably due to some reduction of the copper surface by the copious quantities of hydrogen which are also evolved. If this is the origin of the water, then it corresponds to an oxygen coverage of the copper of 6.9×10^{13} atoms cm^{-2} and a total oxygen coverage of 3.9×10^{14} atoms cm^{-2}, roughly 78% of saturation. Although this value is the same as was found previously at 50 bar with a carbon monoxide/carbon dioxide/hydrogen/helium (10 : 13 : 52 : 28) feed (*8*), the correspondence appears to be fortuitous since the rate of methanol synthesis measured here is 10^3 times lower than that measured previously, which would be expected to result in a net lower standing population of adsorbed oxygen species. However, the rate of impact of hydrogen molecules with the surface at 1 bar is 25 times lower than that at 50 bar total pressure, which would produce a compensating effect of not scavenging the population of the adsorbed oxygen species to the same extent.

The evolution of the large amounts of hydrogen (6.57×10^{20} molecules, corresponding to about one monolayer of the copper area) during the reduction with carbon monoxide is surprising. Indeed, during the time of cooling from 500 to 470 K (30 min) the major species seen on the on-line mass spectrometer to be desorbing from the catalyst was hydrogen, so the above figure is a lower estimate of the amount adsorbed on the surface during methanol synthesis.

Additional information as to the origin of this hydrogen is to be found in the temperature-programmed desorption spectrum shown in Fig. 6. This has been obtained from the catalyst which had been producing methanol at 500 K at a rate of 1.9×10^{-9} mol s^{-1} g^{-1} from the carbon dioxide/hydrogen/helium (10 : 80 : 10) feed (again constantly for 2 h duration), the temperature being lowered in the reactant mixture to ambient before temperature programming to 700 K was begun.

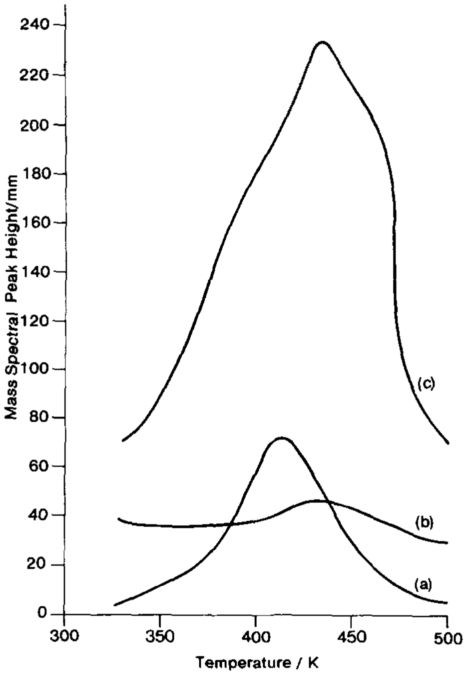

FIG. 6. Temperature programmed-desorption spectrum from the copper/zinc oxide/alumina catalyst (60 : 30 : 10) which had been producing methanol for 2 h at a rate of 1.9×10^{-9} mol s^{-1} g^{-1} from a carbon dioxide/hydrogen/helium (10 : 80 : 10) feed at 500 K, the temperature being lowered to ambient under the reactant mixture before the switch to helium and temperature programming (heating rate 20 K min^{-1}). (a) Carbon dioxide; (b) water; (c) hydrogen.

The major species desorbing are hydrogen and carbon dioxide, the latter maximising at 420 K. This peak maximum temperature and the shoulder observed on the hydrogen desorption peak at the same temperature are consistent with the view that these derive from the decomposition of a formate species adsorbed on the copper component of the catalyst. The integral of the carbon dioxide desorption peak deriving from the decomposition of the formate on the copper component of the catalyst was 2.35×10^{20} molecules, or a coverage of the copper by the formate species of 2.6×10^{4} ions cm^{-2}. This is probably greater than the standing formate surface population during methanol synthesis from the carbon dioxide/hydrogen/helium stream at 500 K since this temperature is well above the decomposition peak maximum. However, the result does indicate that the formate species can be adsorbed on a copper surface on which an oxygen atom is adsorbed to ~40% saturation.

No other carbon dioxide desorption peaks at higher temperatures are obtained, eliminating the possibility that, under these reaction conditions, carbon dioxide, either itself or as the formate, is adsorbed on the zinc oxide component of the catalyst. (We had shown previously (*4*) that dosing carbon dioxide onto zinc oxide at 500 K and lowering the temperature under the gas gave rise to carbon dioxide desorption peaks at 390, 420, 510, and 560 K. The formate species, which had shown to be the pivotal intermediate in methanol synthesis on zinc oxide, was formed by carbon dioxide/hydrogen codosing at temperatures greater than 400 K and was characterized in a tprs spectrum by the coincident desorption of carbon monoxide and hydrogen at 580 K.) The absence of a carbon monoxide peak at 580 K in Fig. 6 shows that under these reaction conditions the formate does not exist on the surface of the zinc oxide, eliminating the possibility of that component of the catalyst synthesising methanol by a route parallel to, but at higher energy than, that on the copper component. Additionally, the absence of carbon dioxide tpd peaks at 510 and 560 K in Fig. 6 shows, rather surprisingly, that carbon dioxide also is not absorbed on the zinc oxide component of the catalyst and is therefore not the source of carbon dioxide to the copper/zinc oxide interface as we had proposed earlier (*8*).

The broad hydrogen desorption spectrum shown in Fig. 6 with a peak at 430 K and shoulders at 420 and 480 K resembles the desorption spectra obtained when hydrogen is dosed onto zinc oxide at between 450 and 520 K and cooled to ambient temperature in the absorbing gas before temperature programming (*4*). Apart from that bound in the formate, the hydrogen is only weakly held on the copper surface, desorbing at a peak maximum temperature of 323 K from the (110) surface (*15*) and at 230 and 300 K from the (111) surface (*17*). Therefore the hydrogen desorbing from the catalyst in Fig. 6 most probably derives from the zinc oxide component of the catalyst. The total amount evolved is 1.22×10^{21} molecules. If a value of 100 $m^2\ g^{-1}$ is taken for the zinc oxide component of the catalyst (which is probably an overestimate of this area), the hydrogen atom coverage of this component is 3×10^{15} atoms cm^{-2} or greater than monolayer coverage. Surprisingly, then, in the competitive adsorption of hydrogen and carbon dioxide (8 : 1, $H_2 : CO_2$, 1 bar total pressure) on the zinc oxide component of the catalyst at 500 K, the hydrogen wins totally and the zinc oxide is hydrided or contains interstitial hydrogen to a value equivalent to at least three monolayers depth.

After the formate and hydrogen were desorbed by temperature programming in the helium stream to 700 K, the temperature was lowered to 470 K under the helium and the oxygen adsorbed on the copper component of the catalyst was titrated by switching to a carbon monoxide/helium stream (10% CO in He), giving the result shown in Fig. 7. The experiment is in effect a repeat of that shown in Fig. 5, the good reproducibility of the result being found in the similarity of the figures and the fact that the oxygen coverage of the copper measured here by the sum of the integrated water and carbon dioxide peaks was 3.5×10^{14} oxygen atoms cm^{-2} (cf. 3.93×10^{14} oxygen atoms cm^{-2} of Fig. 5). This good correspondence in the oxygen coverage of the copper obtained by two different methods of treatment of the catalyst after cessation of the steady-state rate of methanol synthesis gives added confidence to the view that the value obtained does correspond to the oxygen coverage of the copper component of the catalyst at the prescribed steady-state rate conditions.

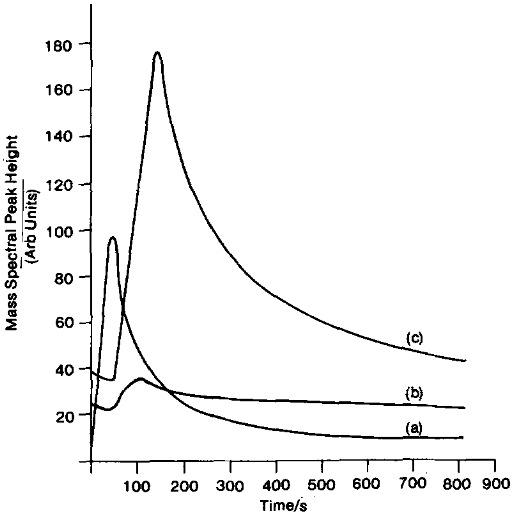

FIG. 7. Reduction of the copper component of the copper/zinc oxide/alumina (60 : 30 : 10) catalyst by carbon monoxide at 470°C. Prior to the reduction the catalyst had been producing methanol at a rate of 1.9×10^{-9} mol $s^{-1}\ g^{-1}$ from a carbon dioxide/hydrogen/helium (10 : 80 : 10) mixture at 500 K before the temperature under the reactant mixture was lowered to ambient and the switch to helium and temperature programming at 20 K min^{-1}. (a) Carbon dioxide; (b) water; (c) hydrogen.

It can also be seen from Fig. 7 that after about 40% of the oxygen has been removed from the surface of the copper, hydrogen begins to evolve. (It should be remembered that this hydrogen is evolving from a catalyst from which the hydrogen had been supposedly removed by temperature programming to 700 K.) The total amount of hydrogen evolved at 473 K is 5.9×10^{20} molecules, a value which is 90% of that obtained in Fig. 5 in a nearly identical experiment. (Both the total amounts of oxygen removed as carbon dioxide and of hydrogen evolved in Fig. 7 are 90% of those in Figure 5, suggesting that the copper component of the catalyst has sintered slightly and that these constitute the same fraction of the copper area.) This abrupt evolution of hydrogen after the removal of roughly 40% of the surface oxygen of the copper suggests that the hydrogen is somehow being locked in by this oxygen and that therefore the hydrogen emanates from the subsurface layers of the copper, a notion which finds corroboration in a recent paper by Rieder and Stocker (*18*). Using a combination of techniques (He and Ne diffraction and low-energy electron diffraction), they concluded that upon the room-temperature adsorption of atomic hydrogen on Cu(110), the hydrogen moves below the surface and causes a recontruction in deeper layers. This process they find to be activated which after large exposures (800 L, 1 L = 10^{-6} Torr s) results in the uptake of between 1.5 and 2 monolayers.

CONCLUSIONS

1. The mechanism by which methanol is made on a copper/zinc oxide/alumina catalyst from a carbon dioxide/hydrogen/helium feed and probably from a carbon dioxide/carbon monoxide/hydrogen feed is by the coadsorption of hydrogen and carbon dioxide on the copper component of the catalyst, forming a formate species, whose hydrogenation/hydrogenolysis is the rate-determining step in the synthesis.

2. The zinc oxide component acts neither as adsorber and provider of carbon dioxide to the copper component of the catalyst nor as a catalyst for the synthesis of methanol by a route parallel to, but at higher energy route than, that on the copper. Under synthesis conditions it is hydrided or contains interstitial hydrogen to a value equivalent to at least three monolayers depth.

3. No synergy exists between the copper and the zinc oxide components of the catalyst, at least in terms of the energetics of the rate-determining step. The activation energy of the hydrogenation/hydrogenolysis of the formate species adsorbed on the copper component of the catalyst, which is the rate-determining step, is unaffected by being intimately mixed with zinc oxide.

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