A DRIFTS study of the morphology and surface adsorbate composition of an operating methanol synthesis catalyst

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The nature of the species adsorbed on a $Cu/ZnO/Al_2O_3$ catalyst while it was producing methanol has been elucidated in this study using DRIFTS. The species are carbonates, formate, CO, oxygen atoms (~ 2% of a monolayer) and methoxy on the Cu and methoxy on the ZnO. The frequencies observed for the C–O stretch on Cu, 2076, 2092, 2105 and 2132 cm^{-1}, have revealed the morphology of the copper component of the operating catalyst. The surface of the copper is predominantly the (111) face (~ 65%) (the 2076 cm^{-1} peak) with the (755) (the 2092 cm^{-1} peak) and the (311) (the 2105 cm^{-1} peak) faces occupying roughly 20% and 15%, respectively, of the copper area. The 2132 cm^{-1} peak derives from CO adsorbed on Cu^+ site on the copper which is ~ 2% of a monolayer.

Keywords: morphology; methanol; operating catalyst; adsorbate composition

1. Introduction

The systematic development of new catalysts depends, to a large extent, on our obtaining a practically useful understanding of the mode of action of those catalysts presently in use. The core of this understanding is a postulate of the mechan-

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ism of the reaction occurring on the surface of the catalyst. Postulates of reaction mechanisms derive from a variety of techniques, principal among which are steady state and transient rate measurements. When both the catalyst and reactant mixture are multicomponent, mechanisms derived from this type of experimentation are often controversial.

Such is the case in methanol synthesis. The catalyst ($Cu/ZnO/Al_2O_3$, 60 : 30 : 10 typically) and the gas phase ($CO/CO_2/H_2$, 10 : 10 : 80) are three component. Consequently, many views exist as to the nature of the active centre on the catalyst and, therefore, as to the nature of the reaction occurring on these differing active centres. Klier and co-workers, using quantified X-ray diffraction, have published that the active centre is a Cu^+ ion substituted in the ZnO lattice for the isoelectronic Zn^{2+} ion. This Cu^+ site is thought to adsorb CO strongly where it is sequentially hydrogenated by H atoms migrating from the ZnO. The role of the CO_2 is considered to be that of an oxidant, maintaining a high steady state population of Cu^+ sites [1].

Rozovsky and co-workers, using labelled CO, concluded that it was the CO_2 component of the gas mixture which was the precursor to methanol [2]. This was confirmed by Chinchen and co-workers using labelled CO_2 [3], it being subsequently rationalised that this occurred because the CO_2/H reaction to form a formate, the most stable intermediate in the reaction sequence, was facile [4]. This reaction was considered to be confined to the copper component of the catalysts – the active phase [5].

Frost, while not disputing the role of either the CO_2 or of the formate, suggested that the active centre is an anion vacancy in the zinc oxide lattice. An increased population of these anion vacancies is thought to be stabilised at the Cu/ZnO boundary by the copper metal [6]. The active phase according to Frost, therefore, is the zinc oxide component of the catalyst.

Burch and co-workers have considered that the role of the zinc oxide is that of a reservoir of hydrogen atoms [7]. The hydrogen is thought to adsorb dissociatively on the copper and spillover to the zinc oxide component of the catalyst where it is held as a source of hydrogen atoms for the synthesis reaction occurring on the surface of the copper.

A clearer view as to the nature of the reactions taking place on prescribed components of the catalyst would be provided by a knowledge of the adsorbate composition of the components of the catalyst while it was operating at, or near, industrial conditions. Infrared spectroscopy allows measurement of the vibrational spectra of adsorbates and intermediates under high pressure conditions and so is the ideal method of obtaining this type of information. This paper, therefore, reports the results of a DRIFTS study of adsorbate composition of a $Cu/ZnO/Al_2O_3$ (60 : 30 : 10) methanol synthesis catalyst. The study will investigate the steady state coverage and type of the species adsorbed on the components of the catalyst in different H_2/CO_2 mixtures at 413 K and 30 bar. The temperature dependence of the surface species at a fixed H_2/CO_2 ratio will also be determined.

A study of this type benefits from the voluminous literature of infrared spectra which exists of reactants and likely intermediates (e.g. formates, carbonates etc.) on both single crystal and polycrystalline copper and on polycrystalline zinc oxide (table 1) [8–35].

2. Experimental

The experimental equipment and method are the same as described previously [29]. The Fourier transform infrared spectrometer is a Bruker IFS 48 interferometer controlled by a Bruker Aspect 1000 computer. The DRIFT environmental chamber has ZnSe windows and is capable of operating up to 820 K and 70 bar. It is housed in a Spectra Tech collector accessory.

The catalyst, supplied by ICI, is the one used previously [29]. It is a Cu/ZnO/Al_2O_3 (60 : 30 : 10) catalyst and is used as before diluted with 90% of KBr in the environmental chamber. Experiments with KBr alone showed that none of the bands observed derived from it.

The gases and the purification train were the same as those used previously [29]. Different H_2/CO_2 mixtures were prepared simply by flow measurement. The IR data were taken at pressure (30 bar) under the flowing gas mixture 60 $cm^3\ min^{-1}$ (measured at 295 K, 1 bar).

3. Results and discussion

3.1. THE INTERACTION OF CO_2/H_2 (AT VARIOUS $CO_2 : H_2$ RATIOS) WITH A Cu/ZnO/Al_2O_3 CATALYST AT 30 bar AND 413 K

The infrared spectra which are indicative of the species adsorbed at steady state on an industrial Cu/Zn/Al_2O_3 (60 : 30 : 10) catalyst at 413 K under flows of various composition of CO_2 and H_2 at 30 bar (total flow rate 60 $cm^3\ min^{-1}$ measured at 1 bar and 298 K) are shown in fig. 1. These spectra divide themselves naturally into four main regions: (i) between 900 and 1100 cm^{-1}, (ii) between 1300 and 1550 cm^{-1}, (iii) between 1550 and 1650 cm^{-1} and (iv) between 1950 and 2200 cm^{-1}. The assignments which follow are made not only with reference to infrared data alone (table 1) but also, where close overlap of the infrared peaks occurs, with regard to thermochemical and mass spectrometric data [4,29,36].

3.1.1. The region 900–1100 cm^{-1}

The peaks at 1005, 1029 and 1060 cm^{-1} derive from gas phase methanol [37]. These are most clearly seen at the highest $H_2 : CO_2$ ratio (12.6 : 1) in curve (a). Curiously, as the $H_2 : CO_2$ ratio decreases, so the gas phase methanol peaks become less distinct, with the progressive onset of peaks at 1078 and 978 cm^{-1} which over-

Table 1

Adsorbate	Adsorbent	Frequency (cm^{-1})	Ref.	ΔH (kcal)
CO	Cu(111)	2071 (1) 2075 (2,3) 2076 (7)	[8,11,12, 13,9,10,14]	10–12
CO	Cu(110)	2088 and 2104 low coverage 2093 high coverage	[15]	13.2
CO	Cu(100)	2085 (2) 9 2076 → 2071 (5)	[9,12,16]	14
CO	low index plane Cu	2085–2667	[17]	
CO	high index plane Cu	2104–2099	[17]	
CO	Cu(311)(11), Cu(755)(11) Cu(211)	2103, 2098 and 2100 respectively 2115 (12)	[14,18] [19]	
CO	Cu/O or Cu_2O or oxidised Cu	2125	[19,20,21]	
CH_3O methoxy	Cu(100)	990	[22,23]	
CO_3^{2-} carbonate/ symmetrical	Cu	1415, 1410 (17)	[24,25]	
HCO_2 bidentate formate	Cu Cu(110) (27) (28)	ν_s 1360, ν_a 1560, 1350 ν_a 1604–1600	[26,27,28] [29]	
HCO_2^- unidentate formate	Cu/O	1583	[26,30]	
CO_3^{2-} bidentate	Cu	1530, 1332	[29]	
CO_3^{2-} unidentate	Cu	1466, 1383	[29]	
CO	ZnO	2184	[31]	
CO_3^{2-} bidentate carbonate	ZnO	1. 1595 1339 low coverage 2. 1615 1346 higher coverage 3. 1580 1348 long stand 4. 1665 1303 highest coverage	[13]	
CO_3^{2-} polydentate carbonate	ZnO	5. 1522 1327 (heat 4)	[13]	
CO_2 linear	ZnO	6. 2358 1370 high coverage	[13]	

continued on next page

Table 1 (continued).

Adsorbate	Adsorbent	Frequency (cm^{-1})	Ref.	ΔH (kcal)
HCO_3^- hydrogeno carbonate	ZnO	1635 1424	[13]	
HCO_2^- bidentate formate	ZnO	ν_a 1577 ν_s 1364	[32,33]	
HCO_2^- bidentate formate	ZnO	ν_a 1597 ν_s 1381 1610 1371	[34]	
HCO_2^- formate	$ZnAl_2O_4$	1590 1392 sharp 1370	[35]	
CH_3O methoxy	ZnO	1080	[29]	
HCO_2^- formate	ZnO	ν 1589 ν_s 1363	[29]	

lap with the gas phase methanol peaks at 1060 and 1005 cm^{-1} respectively. The peak at 1078 cm^{-1} is assigned to a methoxy species adsorbed on the ZnO component of the catalyst [29] (table 1). The peak at 978 cm^{-1} is assigned to methoxy adsorbed on the Cu component of the catalyst [22,23].

These spectra show, that as the H_2 : CO_2 ratio decreases so the final hydrogenation step of the adsorbed methoxy species becomes increasingly rate determining. This would indicate that the surface hydrogen atom population is critically dependent on the H_2 : CO_2 ratio. This might appear to be a curious result in view of the fact that, even at the lowest H_2 : CO_2 ratio (1 : 1.6), the hydrogen partial pressure

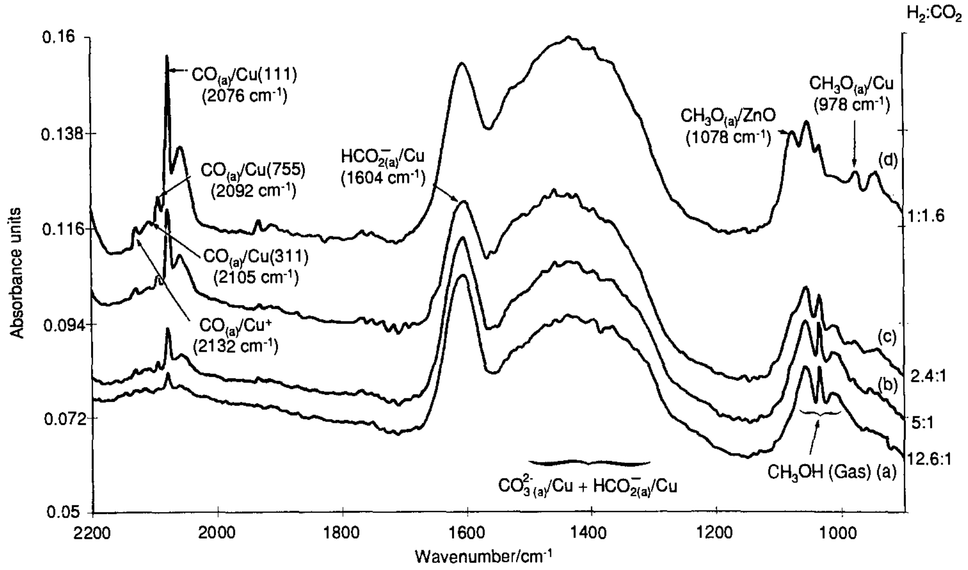

Fig. 1. The infrared spectra of the species adsorbed on a $Cu/ZnO/Al_2O_3$ catalyst at steady state in various H_2/CO_2 gas mixtures (30 bar, 413 K).

is ~ 12 bar, corresponding to a collision rate of 9×10^9 collisions $site^{-1}$ s^{-1}. Hayden and Lamont have shown that the hydrogen sticking probability, as atoms, is unity for hydrogen molecules in the $v = 1$ vibrational state [38]. This state is ~ 0.5 eV above the $v = 0$ ground state so that, on this basis at 413 K, the hydrogen sticking probability, as atoms, is 7.2×10^3 atom $site^{-1}$ s^{-1} at the lowest $H_2 : CO_2$ ratio. This is ~ 10^5 times greater than the methanol synthesis turnover number (1.6×10^{-2} molecule CH_3OH $site^{-1}$ s^{-1}) [39] and so, after allowing for desorption, some other fate must befall the adsorbed hydrogen atoms, so that the steady state surface hydrogen atom coverage decreases as the $H_2 : CO_2$ ratio decreases.

Two routes other than desorption exist for the loss of hydrogen atoms from the surface of the copper. They are: (i) the migration from the surface of the copper into the bulk of that material and (ii) spillover from the copper to the zinc oxide where they can also be absorbed into the bulk of the material. Both routes are likely to occur. Rieder and Stocker have shown that the migration of hydrogen atoms from the surface of copper to the bulk, though activated, is reasonably facile, the transition occurring at ~ 240 K [40]. Additionally, Bowker and co-workers showed by temperature programmed desorption of the adsorbates extant on the surface/bulk of a $Cu/ZnO/Al_2O_3$ after the methanol synthesis reaction, that, in addition to formate adsorbed on the copper component of the catalyst, the zinc oxide component contained ~ 10 monolayers of hydrogen [4]. The hydrogen, subsurface in the copper component of the catalyst, was only released in these experiments after reduction of the surface oxygen by carbon monoxide [4].

3.1.2. The region 1300–1550 cm^{-1}

This region is complex and indistinct. Consultation of table 1 shows that it potentially contains the C–O stretches of the carbonate and bidentate formate species on Cu [24–29] together with those of the carbonate, hydrogenocarbonate and formate species adsorbed on ZnO [13,32–35]. Further specification of the species adsorbed giving rise to the peaks observed in this region requires recourse to thermal desorption data [4,29]. The only peaks seen to desorb from a $Cu/ZnO/Al_2O_3$ catalyst which had been synthesising methanol from a $CO_2/H_2/He$ mixture (8% CO_2, 80% H_2, 12% He, 1 bar, 523 K) was the formate species adsorbed on the copper component of the catalyst together with copious amounts of hydrogen (~ 10 monolayers) from the zinc oxide component [4]. Combined infrared and temperature programmed desorption experiments using a CO_2/H_2 feed (45 bar, 473 K) and a $Cu/ZnO/Al_2O_3$ catalyst showed the major infrared peaks to be at 1360 and 1600 cm^{-1} (formate on copper), with smaller peaks at 1530 and 1332 cm^{-1} (bidentate carbonate on copper) and at 1466 and 1383 cm^{-1} (unidentate carbonate on copper) [29]. These data taken in combination with the temperature dependence of the 1600 cm^{-1} peak (see below) confirm that the species giving rise to peaks in this region 1300–1550 cm^{-1} derive from carbonate and formates adsorbed on the copper component of the catalyst.

The amount of carbonate adsorbed on the copper component of the catalyst increases on increasing the $CO_2 : H_2$ ratio (i.e. increases in curves (a)–(d)) consistent with the lower gas phase hydrogen concentrations leading to low hydrogen atom coverages of the copper and concomitantly reduced levels of hydrogenation of intermediates and products (cf. increased levels of adsorbed methoxy species relative to gas phase methanol on increasing the $CO_2 : H_2$ ratio (section 3.1.1)).

3.1.3. *The region 1550–1650 cm^{-1}*

As had been observed previously [29], this is the dominant region of the spectrum. Of itself, however, the information provided by it is completely ambiguous since the peak could derive either from formate adsorbed on the ZnO component, which has peaks attributed variously at 1597 or 1610 cm^{-1} [27], or from formate adsorbed on the Cu component whose peak is at 1600–1604 cm^{-1} [29]. Resolution of the ambiguity can only be achieved by recourse to complementary thermokinetic data [4,29]. Previous infrared studies of the interaction of CO_2 and H_2 45 bar, 473 K on a $Cu/ZnO/Al_2O_3$ catalyst showed, on temperature programming in He after having cooled the system in the CO_2/H_2 mixture, that a significant loss in the initial intensity of the 1604 cm^{-1} peak was observed at 390 K, leading to its complete loss by 540 K. The point of inflection in the temperature dependence of the intensity of this peak was observed at 460 K, the temperature which coincided with the maximum in the rate of the co-evolution of CO_2 and H_2 in the gas phase [29]. Coincident desorption of CO_2 and H_2 at between 440 and 460 K (depending on heating rate) has been established as emanating from the decomposition of a formate species adsorbed on copper. The principal confirmation of this was provided by a temperature programmed reaction spectroscopy study of formic acid adsorption on Cu(110) where CO_2/H_2 co-desorption was observed at 440 K on temperature programming following formic acid adsorption [36]. The same coincident desorption of CO_2 and H_2 at 440 K was observed on polycrystalline copper after CO_2/H_2 co-adsorption at 305 K [4]. The infrared peak at $\sim$ 1600 cm^{-1} derives therefore from a formate species adsorbed on the copper component of the catalyst.

The amount of formate adsorbed on the copper component of the catalyst decreases on increasing the $CO_2 : H_2$ ratio (curves (a)–(c)) consistent with a reduction of the hydrogen atom population on the surface and with an increase in the carbonate species which has previously been shown to be the precursor to the formate on the surface [41] (section 3.1.2).

3.1.4. *The region 1950–2200 cm^{-1}*

This region is phenomenally informative. It is the region of the C–O stretch of CO adsorbed on Cu and since this stretch is structure sensitive, it contains a wealth of information on the morphology of the copper component of the catalyst. Indeed, it was an explicitly stated rationale for Pritchard's body of work on the evaluation of the C–O stretching frequencies on different single crystal copper faces that it should be used in the determination of the morphology of polycrystalline copper in real catalysts [14].

The peak at 2076 cm^{-1} derives from CO adsorbed on Cu(111) [8–14]; the peak at 2092 cm^{-1} derives from CO adsorbed on Cu(775) [14,18,19]; the peak at 2105 cm^{-1} originates from CO adsorbed on Cu(311) [18] and that a 2132 cm^{-1} from CO adsorbed on Cu^+ [19–21]. The height of these peaks increases on going through curves (a) to (d) (i.e. as the $CO_2 : H_2$ ratio increases), a trend which is consistent with the increase in the adsorbed carbonate signal on going through the same curves. Therefore, as the $CO_2 : H_2$ ratio increases the trend is for the CO_2 to adsorb dissociatively forming adsorbed CO and a surface oxygen ($O_{(s)}$) and for subsequent CO_2 adsorption to form a carbonate on the oxided surface. Additionally lesser amounts of the adsorbed carbonate are hydrogenated to the formate. Therefore, in moving from a $H_2 : CO_2$ ratio 12.6 : 1 (curve (a)) to a $H_2 : CO_2$ ratio of 1 : 1.6 (curve (d)) the copper surface moves from hydrogen rich to hydrogen depleted.

The ratio of the peak intensities of the CO adsorbed on the (311), (755) and (111) surfaces remains constant on moving through curves (a) to (d) with relative heights of 15 : 18 : 100. Taking this to be representative of the morphology of the surface of copper component of the catalyst it is possible to conclude that the surface is dominated by the (111) plane having roughly equal but lesser amounts of the stepped (311) and (755) planes. (The assumptions involved in making this conclusion are considerable. They are: (i) that the other intermediates (the carbonates and formates) are proportionally distributed on these faces – this assumption could be justified on the basis that the methanol synthesis reaction is a linear function of copper metal area [5] – (ii) that the CO bond strength on these surfaces is roughly the same and (iii) that no intensity transfer occurs between the peaks [42].)

The peak at 2132 cm^{-1} (CO on Cu^+) increases relative to that at 2076 cm^{-1} (CO on Cu(111)) on moving through curves (d) to (a) i.e. as the CO_2 and therefore the CO partial pressure decreases, indicating that CO adsorbed on this site has a higher heat of adsorption than on the uncharged surfaces. For curves (d), the curve for which the most accurate measurements can be made, this peak is $\sim$ 13% of the (111) peak. This cannot be considered to be surface coverage of oxidised copper, the peaks in this region (1950–2200 cm^{-1}) constituting $<20\%$ of the total spectrum. (This crude estimate is made simply by integrating the intensities of the peaks of species known to be present.) The steady state coverage of copper in an oxidised state in a $CO_2 : H_2$ stream (1.6 : 1, 30 bar 413 K, 60 cm^3 min^{-1}) is therefore $\sim$ 2% of the total copper area. This is much lower than the value $\sim$ 40% previously reported for methanol synthesis from a $CO_2/H_2/He$ (10 : 80 : 10) feed (523 K, 1 bar) [4] and closer to the value $\sim$ 1% reported by the Topsøe group for a CO_2/H_2 stream (5% CO_2, 95% H_2, 473 K, 1 bar) [43]. The difference between these sets of results is that in the former [4] the oxygen coverage was measured after thermal decomposition of all the adsorbed carbonate species, a process which would have left surface oxygen, whereas these results and those of the Topsøe group [43] relate to the oxide coverage of the copper in steady state with the surface carbonate species deriving from a given CO_2/H_2 stream – the value obtained here.

3.2. THE TEMPERATURE DEPENDENCE OF THE INTERACTION OF A CO_2/H_2 MIXTURE (2·4 : 1) WITH A $Cu/ZnO/Al_2O_3$ CATALYST AT 30 bar

Fig. 2 shows the infrared spectra indicative of the adsorbates species which coexist, at a steady state, with a CO_2/H_2 (2.4 : 1, 30 bar) mixture on a $Cu/ZnO/Al_2O_3$ catalyst at 373, 413, 443 and 473 K. All of the species observed in fig. 1, with the notable exception of the methoxy species adsorbed on Cu and ZnO, are observed here.

3.2.1. The region 900–1100 cm^{-1}

Gas phase methanol is denoted by peaks at 1005, 1029 and 1060 cm^{-1}. It is undetectable at 373 K but shows an exponential increase as the temperature is raised to 473 K. A plot of the logarithm of the absorbance versus $1/T$ gives an activation energy for the synthesis of methanol of 13 kcal mol^{-1}. This is remarkably close to the value of 16.5 kcal mol^{-1} obtained by Rasmussen and co-workers for the synthesis of methanol from a H_2/CO_2 (1 : 1) mixture at 2 bar in the temperature range 483 to 563 K [44]. The lower activation energy obtained in this study may result from the higher pressure (30 bar) or from the high H_2 : CO_2 ratio (2.4 : 1) used here.

3.2.2. The region 1300–1550 cm^{-1}

This region is again unresolved, deriving from a combination of bidentate and unidentate carbonate and formate species adsorbed on the copper component of

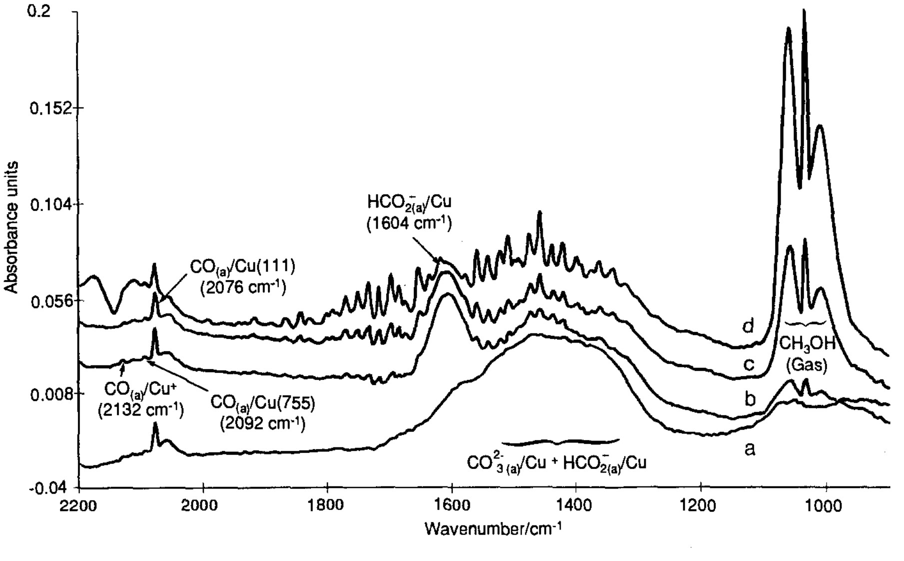

Fig. 2. The temperature dependence of the infrared spectra of the species adsorbed on a $Cu/ZnO/Al_2O_3$ catalyst at a fixed H_2/CO_2 gas mixture (2.4 : 1, 30 bar); curve (a) 373, (b) 413, (c) 443 and (d) 473 K.

the catalyst. The maximum height of the composite peak at ~ 1460 cm^{-1} decreases with increasing temperature, showing their formation to be a thermodynamic function and not a kinetic one. The corollary of this argument is that the adsorption and decomposition of CO_2 to form the carbonate on copper is only weakly activated.

The increasing amounts of fine structure superimposed on the carbonate peaks in this region derive from the rotational states of gas phase water produced by the reverse shift reaction. A crude estimate of the activation energy of this reaction can be obtained by plotting the logarithm of the height of one of the most prominent of these peaks (e.g., the 1460 cm^{-1} peak) as a function of reciprocal temperature. The value so obtained is 11 kcal mol^{-1}, which is roughly the same as that for the synthesis of methanol so that the rates of the reverse shift and methanol synthesis will be roughly the same. This result demonstrates the need, industrially, for including CO in the reaction mixture. Being a better reducing agent than hydrogen, it removes the surface oxygen resulting from the methanol having been synthesised from the CO_2 component of the $CO_2/CO/H_2$ mixture, producing a drier methanol and thereby reducing the need for distillation of the product.

3.2.3. The region 1550–1650 cm^{-1}

The formate species at ~ 1600 cm^{-1} is seen only as a shoulder at 373 K. It increases to a maximum value at 413 K and then decreases on further increasing the temperature. Its formation is therefore activated. It is not certain that the maximum value observed here at 413 K is the absolute maximum in the temperature range 373 to 473 K. However, a crude heat of formation of this species, which is in effect the heat of the reaction

$$H(a) + CO_3^{2-}(a) \rightleftharpoons HCO_2(a) + O(a)^{2-} \qquad (1)$$

can be obtained from the decline in the height of this species at 443 and 473 K. Its value is 7 kcal mol^{-1}.

3.2.4. The region 1950–2200 cm^{-1}

The height of the 2076 cm^{-1} peak (the C–O stretch on Cu(111)) decreases only slightly on increasing the temperature from 373 to 473 K. This lowering of the coverage of CO on increasing the temperature is simply the consequence of the lowering of the $\exp(\Delta H_{CO}/RT)$ term in the adsorption isotherm (ΔH_{CO} is the heat of adsorption of CO). It confirms, however, that the decomposition of CO_2 on polycrystalline copper is negligibly activated. This is in accord with the findings of Bonicke and co-workers [45], of Fu and Somorjai [46] and of Schneider and Hirschwald [47]. Bonicke and co-workers found CO_2 to dissociate at 95 K on Cu(332) [45]. Fu and Somorjai reported that CO_2 decomposed on Cu(311) at 150 K but did not decompose on Cu(110) [46]. Schneider and Hirschwald, however, reported that CO_2 decomposed on Cu(110) at 85 K [47], conceding later that this decomposition might be confined to stepped defects on their (110) surface [48]. The consensus is then that CO_2 decomposition on stepped copper surfaces is facile. The surface of the copper component of this catalyst has an estimated step density of ~ 15% of a monolayer of the (311) surface and ~ 20% of a monolayer of the (755) surface. The lack of a temperature dependence of CO_2 decomposition therefore is not surprising.

Another point of interest to be noted from this region of the spectrum is that, within the limits of accuracy allowed by fig. 2, the ratio of the 2092 cm^{-1} (the (755) face) to the 2076 cm^{-1} peak (the (111) face) remains constant over the temperature range 373 to 473 K. Therefore, the morphology of the copper component of the catalyst remains unchanged in spite of the changes in adsorbate composition resulting from different degrees of reaction at different temperatures. Adsorbate induced reconstruction appears not to occur here.

4. Conclusions

(i) Infrared spectroscopy alone could not have provided unambiguous identification of the species present on the surface of a $Cu/ZnO/Al_2O_3$ catalyst during methanol synthesis from a CO_2/H_2 stream. The combination of temperature programming methods using mass spectrometric detection and DRIFTS was required.

(ii) The majority surface of the polycrystalline copper component of the catalyst operating at 30 bar in a CO_2/H_2 stream is the (111) face which occupies approximately 65% of the area. The remaining ~ 35% is made up of the (755) face (~ 20%) and the (311) face (~ 15%).

(iii) Temperature dependent studies ($H_2 : CO_2$, 2.4 : 1, 30 bar) have shown (a) CO_2 decomposition to form adsorbed CO_3^{2-} and CO to be negligibly activated, (b) formate formation to be activated and (c) the overall synthesis reaction to have an activation energy of 13 kcal mol^{-1}.

(iv) Varying the $H_2 : CO_2$ ratio at a fixed temperature (413 K, 30 bar) has revealed a remarkable dependence on the partial pressure of hydrogen on moving from a $H_2 : CO_2$ ratio of 12.6 : 1 to 1 : 1.6. This is thought to result from the migration of hydrogen atoms from the surface of the copper to the bulk of that material and to the surface and bulk of the zinc oxide.

(v) The species observed on the surface of the $Cu/ZnO/Al_2O_3$ catalyst are carbonates, formate, CO, oxygen atoms (~ 2% of a monolayer) and methoxy on the copper component of the catalyst and methoxy only on the zinc oxide component. The methoxy on both components of the catalyst was observed only at the lowest $H_2 : CO_2$ ratio (1 : 1.6). The adsorbed species observed here confirm previous postulates of the mechanism of methanol synthesis, namely that the reaction proceeds by prior formation of the carbonate on the copper, followed by hydrogenation of the carbonate to the formate and thereafter to methoxy and methanol [4,41].

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