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The partial oxidation of CH_3OH to CO_2 and H_2 over a $Cu/ZnO/Al_2O_3$ catalyst

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The partial oxidation of CH_3OH to CO_2 and H_2 over a $Cu/ZnO/Al_2O_3$ catalyst has been studied by temperature-programmed oxidation (TPO) using N_2O and O_2 as the oxidant. Post-reaction analysis of the adsorbate composition of the surface of the catalyst was determined by temperature-programmed desorption (TPD). The temperature dependence of the composition of the mixture of products formed by TPO was shown to depend critically on the partial pressure of the oxidant, with the highest partial pressure of oxygen used (10% O_2 in He, 101 kPa—the CH_3OH partial pressure was 17% throughout), producing marked non-Arrhenius fluctuations on temperature programming. Unsurprisingly, therefore, the adsorbate composition of the catalyst revealed by post-reaction TPD was also found to be determined by the partial pressure of the oxidant. Using high partial pressures of oxidant (5% and 10% O_2 in He, 101 kPa), the only adsorbate detected was the bidentate formate species adsorbed on Cu. Lowering the oxygen partial pressure to 2% in He (101 kPa) revealed a catalyst surface on which the bidentate formate on Cu was the dominant intermediate with the formate on Al_2O_3 also being present. A further lowering of the partial pressure of the oxidant, obtained by using N_2O as the oxidant (2% N_2O in He, 101 kPa), resulted in a surface on which the formate adsorbed on ZnO was the dominant adsorbate with only a small coverage of the Cu by the bidentate formate.

KEY WORDS: partial oxidation of methanol; $Cu/ZnO/Al_2O_3$; temperature programmed oxidation; temperature programmed desorption; bidentate formate on Cu; adsorbate.

1. Introduction

Methanol is a chemical whose applications are many and varied. It is therefore produced in large volume (~30 million tonnes per year). Its uses include the synthesis of acetic acid and methyltertiarybutylether (MBTE); it can be used as a solvent and it can be partially oxidized to formaldehyde. However, it can also be viewed as a source of easily transportable H_2. It contains more H atoms per C atom than any other hydrocarbon except CH_4 over which it has the advantage of being more generally transportable.

An expanding application in the use of H_2 is in fuel cells which produce electricity by the reaction of H_2 with O_2 to produce H_2O. In most fuel cells Pt is used for the electrodes. H_2 is dissociatively adsorbed at the anode and the protons produced migrate through the electrolyte to the Pt cathode where they react with the dissociatively adsorbed O_2. The electrons pass through the external circuit. Fuel cells are being considered as a replacement power unit to the internal combustion engine to drive automobiles. However, the major impediment to this application is in the need for the production, distribution and storage, both in filling stations and in the vehicle itself, of the liquid H_2 fuel which boils at 20 K. (Indeed NASA recently delayed the launch of its X-33 re-usable spacecraft by two years because of a rupture on heating and cooling of the seal of the composite liquid H_2 fuel tank [1].)

Methanol could be used as an alternative source of H_2. Its decomposition products are CO and H_2. However, it cannot be used in this mode since CO is strongly adsorbed on Pt and so poisons its catalytic activity. A means must therefore be found for the release of H_2 from CH_3OH without the concomitant production of CO. Partial oxidation of CH_3OH to CO_2 and H_2 using either O_2 or H_2O as the oxidant seems to provide a potential solution. Since the control and delivery of a flow of a reaction mixture containing CH_3OH and the required partial pressure of H_2O is problematical, the most practicable solution would be to use O_2 as the oxidant. Methanol is made over a $Cu/ZnO/Al_2O_3$ catalyst from the CO_2 component of a $CO/CO_2/H_2$ feed [2–4] and so its partial oxidation using either O_2 or N_2O as the oxidant over the same catalyst should produce the desired products, CO_2 and H_2.

2. Experimental

2.1. The catalyst

The catalyst employed was a $Cu/ZnO/Al_2O_3$ (60 : 30 : 10) industrial methanol synthesis catalyst. It was

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prepared by Na_2CO_3 precipitation of the nitrate solution of the metals. The carbonate precipitate was filtered, washed to remove the Na and calcined in air at 573 K for 6 h. The catalyst was supplied by ICI. Prior to use in the adsorption and partial oxidation experiments, the catalyst was crushed and sieved to retain the 300–355 μm fraction. Adventitiously adsorbed H_2O and CO_2 were removed by temperature programming from ambient to 523 K in an He stream (25 $cm^3\,min^{-1}$, 101 kPa) at 5 K min^{-1}. The catalyst was then reduced in an H_2/He stream (5% H_2, 25 $cm^3\,min^{-1}$, 101 kPa) by raising the temperature from ambient to 513 K (5 K min^{-1}) and holding it at that value for 16 h under that flow. The hydrogen adsorbed on the surface of the Cu by this process was desorbed by switching flows from H_2/He to He (25 $cm^3\,min^{-1}$, 101 kPa) and holding under that flow at 513 K for 1 h. The total surface area of the catalyst measured *in situ* by nitrogen adsorption at 77 K was 58 $m^2\,g^{-1}$ and the Cu metal area measured *in situ* by N_2O reactive frontal chromatography was 29.8 m^2 (g catalyst)$^{-1}$.

2.2. The gases

He was supplied by Linde and was 99.999% pure; before use it was passed through a Chromapack Gas Clean moisture filter. The H_2/He (5% H_2) mixture was supplied by Electrochem Ltd (ECM) and was 99.999% pure. It was used directly from the cylinder.

The N_2/He (10%N_2) mixture was supplied by ECM and was 99.999% pure. It was used directly from the cylinder. H_2 was supplied by BOC. It was 99.995% pure and was used directly from the cylinder.

The CH_3OH/N_2O mixture was obtained by passing an N_2O/He (2% N_2O, 101 kPa, 25 $cm^3\,min^{-1}$) stream through liquid CH_3OH contained in a saturator held at 300 K. The saturation vapor pressure of CH_3OH at 300 K is 17 kPa. CH_3OH/O_2 mixtures containing different amounts of O_2 were obtained by saturating O_2/He streams containing 2, 5 and 10% O_2 in He with CH_3OH held at 300 K.

2.3. The liquids

Formic acid (99.5% pure) was supplied by Fisons Ltd. It was used without further purification. Methanol (99% pure) was supplied by Fisons Ltd. The Pyrex glass sample tube containing it was connected to the microreactor system. Dissolved gases were removed by several freeze–pump–thaw cycles.

2.4. The microreactor system

The microreactor system used to carry out the *in situ* measurements of total area, metal area and temperature programmed desorption and reaction experiments has been described in detail previously [5]. It is a single stainless steel tube reactor (20 cm long, 0.4 cm i.d.) connected *via* a heated capillary to an on-line mass spectrometer (Hiden Analytical, Warrington, UK). The mass spectrometer was capable of following 16 masses continuously with temperature/time.

3. Results and discussion

3.1. Characterization of the formate species adsorbed on the Cu/ZnO/Al_2O_3 catalyst

3.1.1. Formic acid adsorption on the Cu/ZnO/Al_2O_3 catalyst

Since the products of the partial oxidation of methanol were expected to be CO_2 and H_2 and since the decomposition products of formate species adsorbed on Cu are known to be CO_2 and H_2 [6], the nature of the formate species adsorbed on the surface of the Cu/ZnO/Al_2O_3 catalyst as a whole was determined by TPD, having dosed formic acid on from the gas phase.

Formic acid (4.88×10^{20} molecules) was introduced into the He stream using a microsyringe (volume 10^{-3} cm^3) and dosed onto the catalyst (pre-treated and reduced as described in the experimental section) at 303 K. H_2 evolution was observed (figure 1) following the injection of the formic acid, resulting from its dissociative adsorption.

$$HCO_2H + 2S \Leftrightarrow HCO_{2(a)} + HS \tag{1}$$

$$HS + HS \Leftrightarrow H_2 + 2S. \tag{2}$$

(In equations (1) and (2), S can be any of the three components Cu, ZnO or Al_2O_3.)

Therefore every molecule of H_2 evolved in the gas phase corresponds to two formate species adsorbed on the surface. The integral of the hydrogen evolved in figure 1 is 3.88×10^{19} molecules, corresponding to 7.76×10^{19} formate species (1 g catalyst) or a coverage 1.29×10^{14} of formate species (cm catalyst)$^{-2}$. It is interesting to note that while the injection of the formic acid could be regarded as instantaneous (1 s), the evolution of H_2 takes place over 40 min, rising slowly to a maximum rate 10 min after the injection of the formic acid. The delay in the evolution of the H_2 is probably due to the desorption of the H_2 being rate limiting, since the formic acid has been dosed on, at, or slightly below, the H_2 desorption peak maximum [6], of the Cu component of the catalyst which is the weakest bond that H makes to any of the catalytic components. (The septum for the injection of the formic acid onto the catalyst is located at a T-junction 1 cm above the catalyst. The formic acid therefore will encounter the catalyst mainly; the observed H_2 evolution will therefore derive from decomposition on the catalyst and not on the walls of the reactor.)

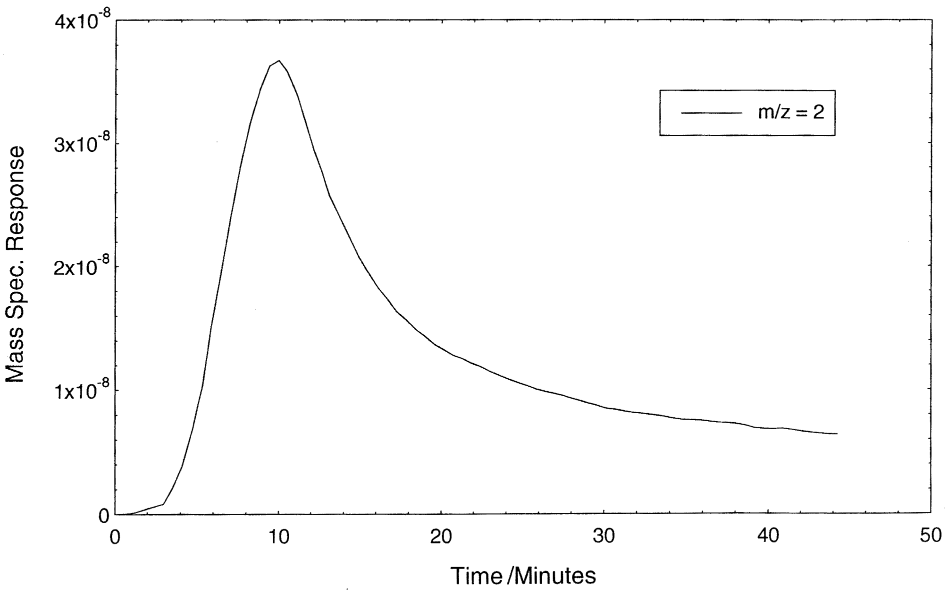

Figure 1. The time dependence of the evolution of H_2 following the dosing of HCO_2H (4.88×10^{20} molecules) onto a $Cu/ZnO/Al_2O_3$ catalyst at 303 K, by near instantaneous injection by a microsyringe.

3.1.2. Formic acid desorption from $Cu/ZnO/Al_2O_3$, Cu/ZnO, Cu/Al_2O_3 and Al_2O_3

Figure 2 is the TPD spectrum obtained by heating the adsorbed formate species which had been dosed onto the $Cu/ZnO/Al_2O_3$ as described above from ambient to 700 K at 5 K min^{-1}. H_2 alone is observed at a peak maximum temperature, T_m, of 340 K. This derives from the recombination and desorption of H atoms adsorbed on Cu. The T_m obtained here is higher than that (300 K) obtained by dosing H_2 alone [6], which may be due to the influence of the other adsorbates. Its high value, however, is the reason for suggesting that the slow evolution of H_2 during the dosing of HCO_2H at 303 K is desorption-rate limited.

The coincident desorption of CO_2 and H_2 in a CO_2 : H ratio of 1 : 1 at 390 and 450 K derive from monodentate and bidentate formate species adsorbed on the Cu component of the catalyst [7]. The coincident desorption of CO, CO_2 and H_2 in a CO_x : H ratio of 1 : 1 at 490 K has previously been assigned to a formate species straddling the Cu/ZnO interface [8]. However, calculation of an average number of Cu sites at the Cu/ZnO interface, from the Cu metal area (29.8 m^2/g catalyst), gives an average particle size of 70 Å leading to an average number of Cu interfacial sites of 10^{19} sites/g catalyst. This is a factor of 30 smaller than the number of formate species desorbing at 490 K so that, even allowing for the approximations involved in the calculation, it appears

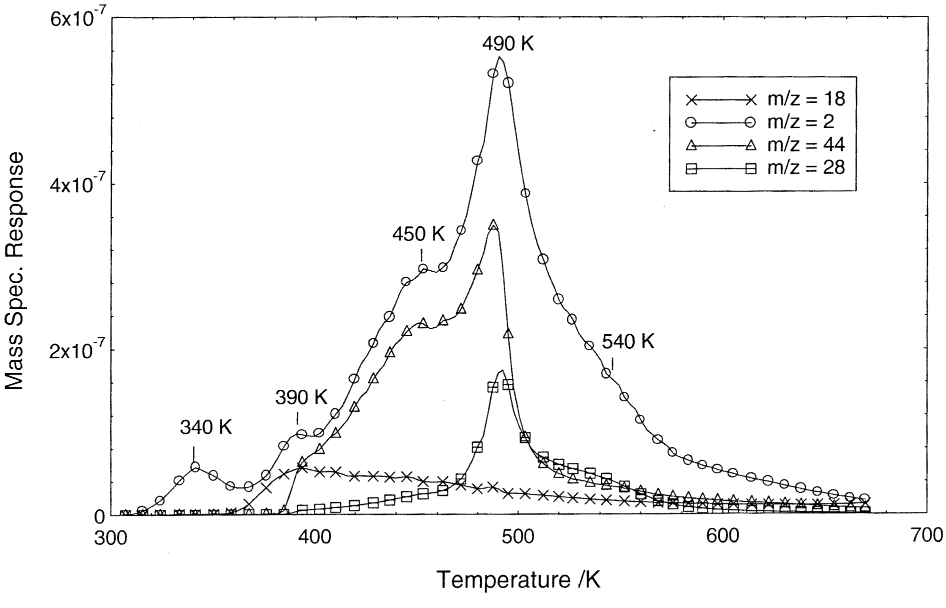

Figure 2. TPD spectrum obtained after dosing HCO_2H (4.88×10^{20} molecules) onto a $Cu/ZnO/Al_2O_3$ catalyst held at 303 K.

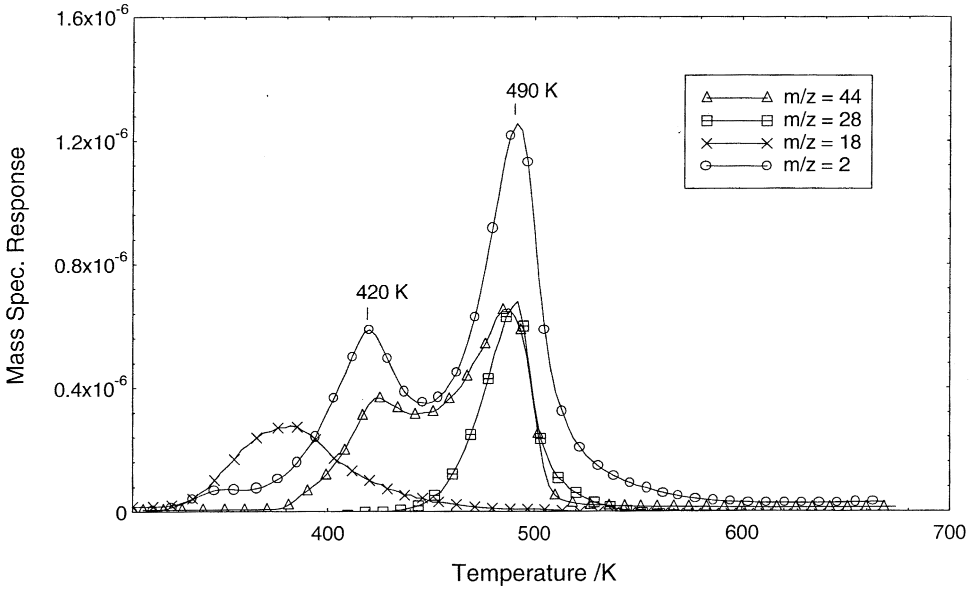

Figure 3. TPD spectrum obtained after dosing HCO_2H (8×10^{20} molecules) onto a Cu/ZnO catalyst held at 303 K.

unlikely that an interfacially bonded formate is the origin of the 490 K desorbing CO, CO_2, H_2 peak.

Figures 3, 4 and 5 are desorption spectra obtained after dosing HCO_2H (8×10^{20} molecules) onto Cu/ZnO, Cu/Al_2O_3 and Al_2O_3 catalyst respectively. It is clear from these (i) that the CO, CO_2, H_2 peak at 490 K derives from the ZnO component of the catalyst in a zone which is somehow influenced by the Cu since, on ZnO alone, the formate decomposes to CO, CO_2 and H_2 as it desorbs at 580 K [8] and (ii) that the CO, H_2 peak at 540 K derives from a formate species adsorbed on Al_2O_3. (The interactive effect of the supports on the morphology of the Cu metal and correspondingly of the Cu metal on the defect state of the oxide at the interface will be discussed in detail in a later paper.)

For the adsorbates produced by dosing HCO_2H (4.88×10^{20} molecules) onto the Cu/ZnO/Al_2O_3 catalyst, table 1 lists (i) the temperatures of each of the peak maxima, (ii) the molecular composition of each of the peaks, (iii) the amounts of each molecule desorbing in these peaks and (iv) the assignment of the adsorbates responsible for these peaks derived from the combination of the molecular species desorbing in the given quantity at the given temperature. These can now be used to assign the species existing on the catalyst, after reaction, by post-reaction TPD.

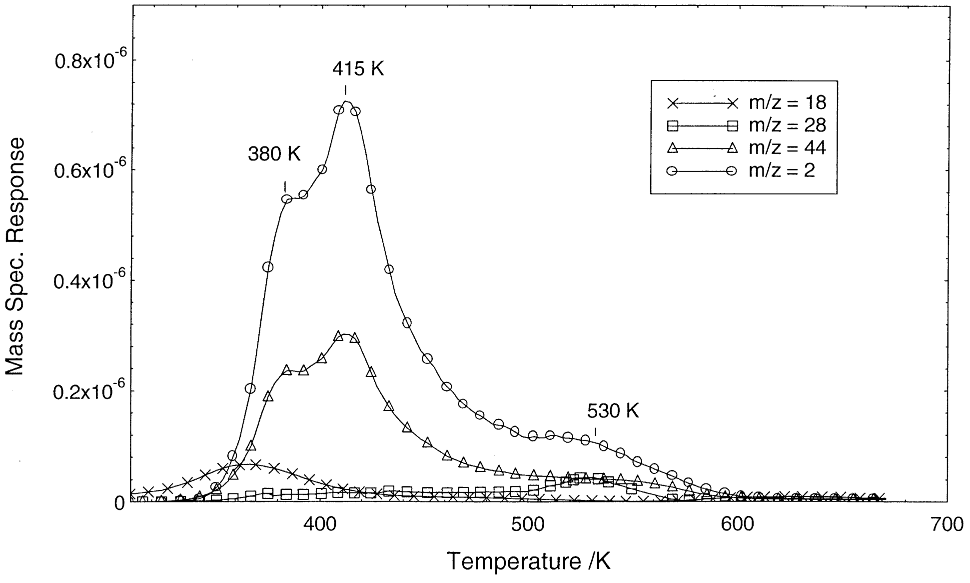

Figure 4. TPD spectrum obtained after dosing HCO_2H (8×10^{20} molecules) onto a Cu/Al_2O_3 catalyst held at 303 K.

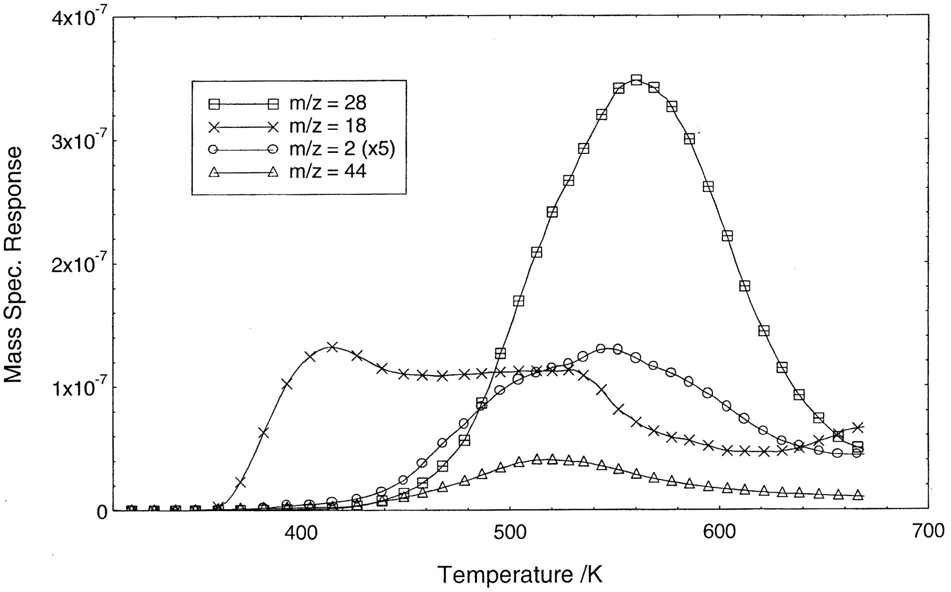

Figure 5. TPD spectrum obtained after dosing HCO_2H (8×10^{20} molecules) onto an Al_2O_3 catalyst held at 303 K.

3.2. TPO of CH_3OH over the $Cu/ZnO/Al_2O_3$ catalyst using CH_3OH/O_2 and CH_3OH/N_2O mixtures

The reduced $Cu/ZnO/Al_2O_3$ catalyst (0.5g) was prepared by the method described in the experimental section. Figures 6 and 7 are the TPO profiles obtained by passing CH_3OH/O_2 and CH_3OH/N_2O mixtures of 8.5 : 1 ratio over the $Cu/ZnO/Al_2O_3$ catalyst while raising the temperature at 5 K min^{-1}. The different CH_3OH/O_2 and CH_3OH/N_2O mixtures were prepared by bubbling O_2/He or N_2O/He mixtures (2% O_2 or N_2O) through CH_3OH held at 300 K—the saturation vapor pressure of CH_3OH at this temperature is 17 kPa. The profiles obtained using these low partial pressures of oxidant (2% O_2 and 2% N_2O, figures 6 and 7) are remarkably similar and are distinctly different from the oscillatory type of behavior seen for the lower CH_3OH/O_2 ratios (higher O_2 partial pressures)—see later.

Closer inspection of figures 6 and 7, however, reveals telling differences which might be expected remembering that figure 6 is obtained with twice the level of oxidant of figure 7. Significantly for the CH_3OH/O_2 (8.5 : 1) profile (figure 6), the rate of production of H_2 shows a shoulder at 420 K and a maximum at 450 K, both of which are coincident with a shoulder and a maximum in the rate of production of CO_2. One can conclude therefore that these features result from the decomposition of monodentate and bidentate formate species adsorbed on Cu. A second maximum is observed in the rate of production of H_2 at 540 K which is coincident with a maximum in the rate of production of CO but a minimum in the rate of production of CO_2. This feature results from the decomposition of the formate adsorbed on Al_2O_3. At temperatures above 540 K the rate of production of CO drops to a weak minimum at ~650 K, which is coincident with a weak maximum in the rate of production of CO_2 and H_2. So far no assignment can be made of this feature.

The main difference between the (8.5 : 1) CH_3OH/O_2 temperature-programmed reaction (TPR) profile (figure 6) and the (8.5 : 1) CH_3OH/N_2O profile (figure 7) is the absence of the shoulder at 420 K. Curiously, therefore, the monodentate formate appears not to be formed when N_2O is used as the oxidant. There is a distinct shoulder in the rate of H_2 evolution at 450 K which is coincident with the maximum in CO_2, evolution both

Table 1
Assignment of the nature of the adsorbates formed by dosing formic acid (4.88 × 20 molecules) onto the $Cu/ZnO/Al_2O_3$ catalyst

Peak maximum temperature, T_m (K)	Molecules desorbed	Amount desorbed/molecule	Assignment	Coverage
340	H_2	1×10^{19}	H adsorbed on Cu	7×10^{13} atom (cm Cu)$^{-2}$
390	H_2, CO_2	1.5×10^{19}, 3×10^{19}	Monodentate HCO_2 adsorbed on Cu	10^{14} species (cm Cu)$^{-2}$
450	H_2, CO_2	4.5×10^{19}, 9×10^{19}	Bidentate HCO_2 adsorbed on Cu	3×10^{14} species (cm Cu)$^{-2}$
490	H_2, CO_2, CO	1.6×10^{20}, 2.5×10^{20}, 9×10^{19}	HCO_2 adsorbed on defect ZnO at Cu/ZnO interfacial zone	8×10^{14} species (cm ZnO)$^{-2}$
540	H_2, CO	3.5×10^{19}, 7×10^{19}	HCO_2 adsorbed on Al_2O_3 at Cu/Al_2O_3 interfacial zone	

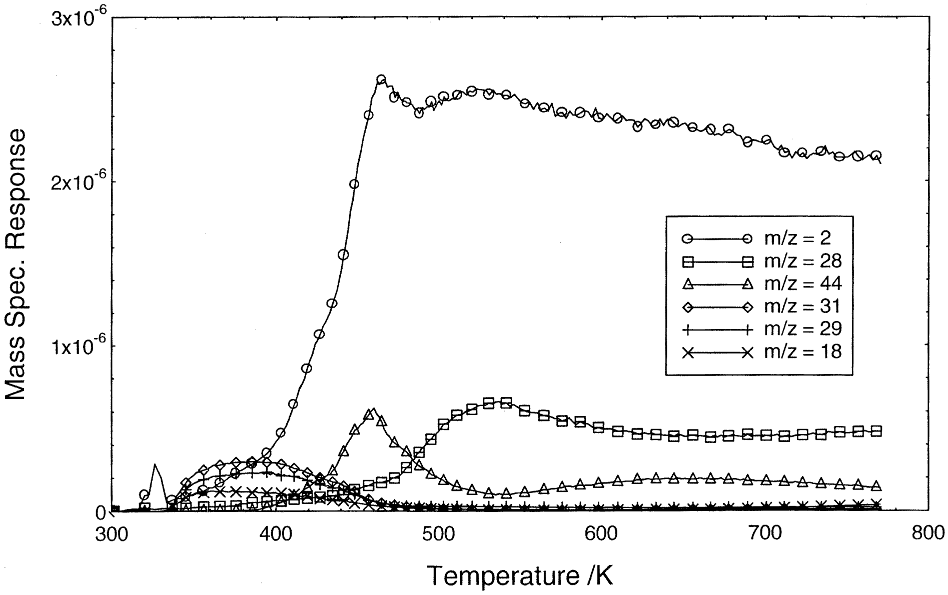

Figure 6. TPO profile obtained by passing a CH_3OH/O_2 mixture (17% CH_3OH, 2% O_2, 81% He (8.5 : 1), 101 kPa, 25 $cm^3\,min^{-1}$) over a $Cu/ZnO/Al_2O_3$ catalyst while raising the temperature at 5 K min^{-1}.

of which are the result of the decomposition of the bidentate formate species on the Cu component of the catalyst.

3.3. Post-reaction surface analysis by TPD after CH_3OH/O_2 and CH_3OH/N_2O (8.5 : 1) TPO

The most significant difference between the nature of the reaction produced using 2% O_2 and 2% N_2O as the oxidant is to be found in post-reaction analysis of the surface by TPD (figures 8 and 9). Figure 8 is the TPD spectrum obtained, after the CH_3OH/O_2 (8.5 : 1) TPO, by cooling the catalyst to ambient under the reactant mixture and then temperature programming in He (25 $cm^3\,min^{-1}$, 101 kPa) from ambient to 700 K at 5 K min^{-1}. The main peak at 440 K is of the coincident desorption of CO_2 and H_2 deriving from the decomposition of a bidentate formate adsorbed on Cu. A broad CO and H_2 peak is seen at ~520 K which derives from the decomposition of a formate adsorbed on Al_2O_3. Therefore, using O_2 (2%) as the oxidant the majority of the reaction occurs on the Cu component of the catalyst through the bidentate formate adsorbed on Cu, with a smaller fraction of the reaction occurring on the Al_2O_3 component also through a formate.

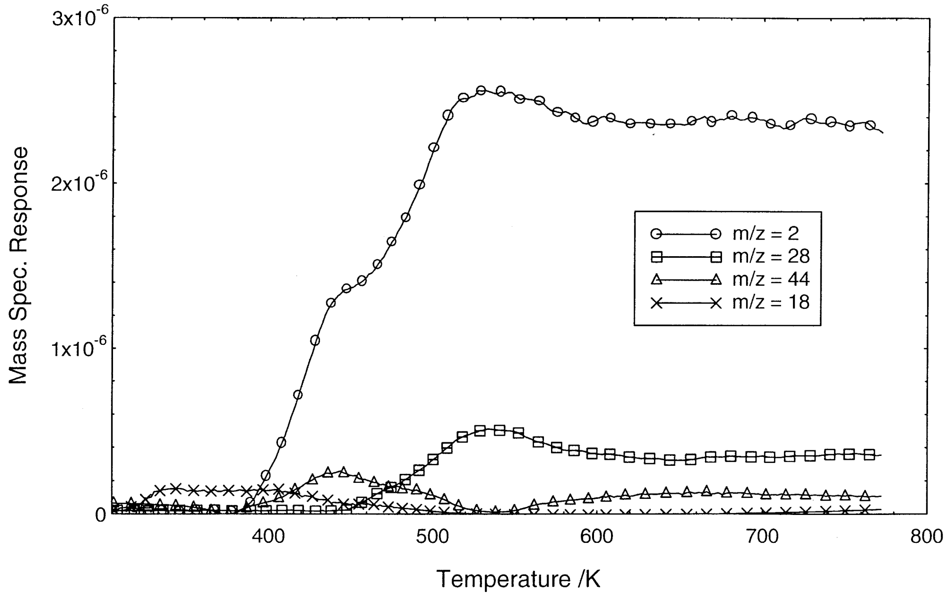

Figure 7. TPO profile obtained by passing a CH_3OH/N_2O mixture (17% CH_3OH, 2% N_2O, 81% He (8.5 : 1), 101 kPa, 25 $cm^3\,min^{-1}$) over a $Cu/ZnO/Al_2O_3$ catalyst while raising the temperature at 5 K min^{-1}.

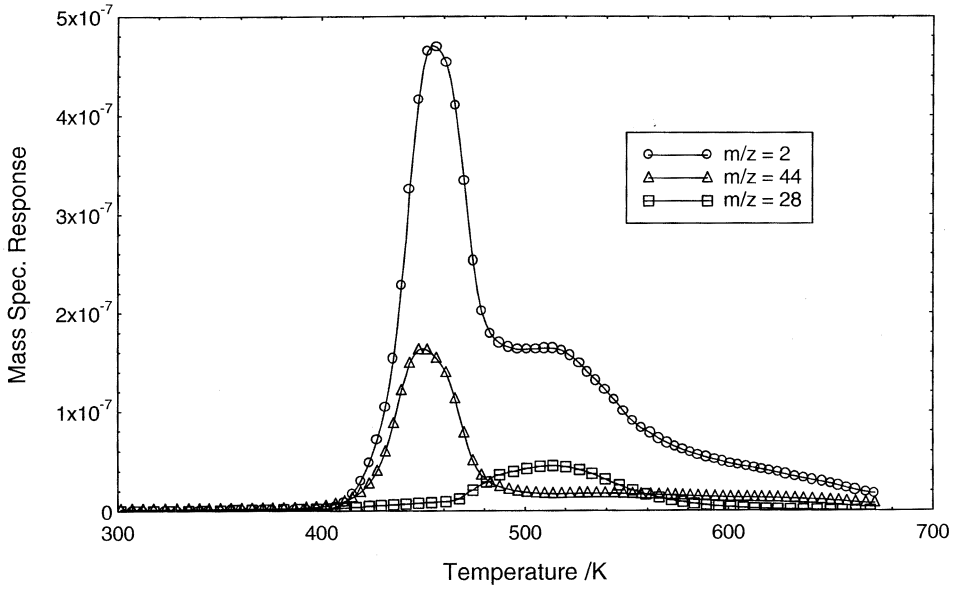

Figure 8. TPD spectrum obtained after the TPO in a CH_3OH/O_2 (8.5 : 1) mixture shown in figure 6.

Figure 9 is the TPD spectrum obtained after the CH_3OH/N_2O TPR, by cooling the catalyst under the reactants to ambient and temperature programming under He (25 $cm^3 min^{-1}$, 101 kPa) from ambient to 700 K at 5 K min^{-1}. Here, in complete contrast to the desorption spectrum obtained after the CH_3OH/O_2 (8.5 : 1) reaction, the main peak is of the coincident desorption of CO and H_2 at 560 K. We have shown previously that the desorption of a formate adsorbed on ZnO produces the coincident desorption of CO, CO_2 and H_2 at this temperature [9]. The amount of CO desorbing depended on the number of anion defects on the ZnO. Our observation here of only CO and H_2 desorbing coincidently suggests that the ZnO involved in the reaction has a high defect concentration. A second minor peak of CO_2/H_2 is observed at 440 K, deriving from the decomposition of the bidentate formate adsorbed on Cu. Surprisingly, therefore, using 2% N_2O as the oxidant, the majority of the reaction occurs on the ZnO component of the reaction.

3.4. *TPO of CH_3OH over the $Cu/ZnO/Al_2O_3$ catalyst using CH_3OH/O_2 ratios of 3.4 : 1 and 1.7 : 1*

Figures 10 and 11 are the TPO profiles obtained using CH_3OH/O_2 mixtures of 3.4 : 1 and 1.7 : 1 ratios produced

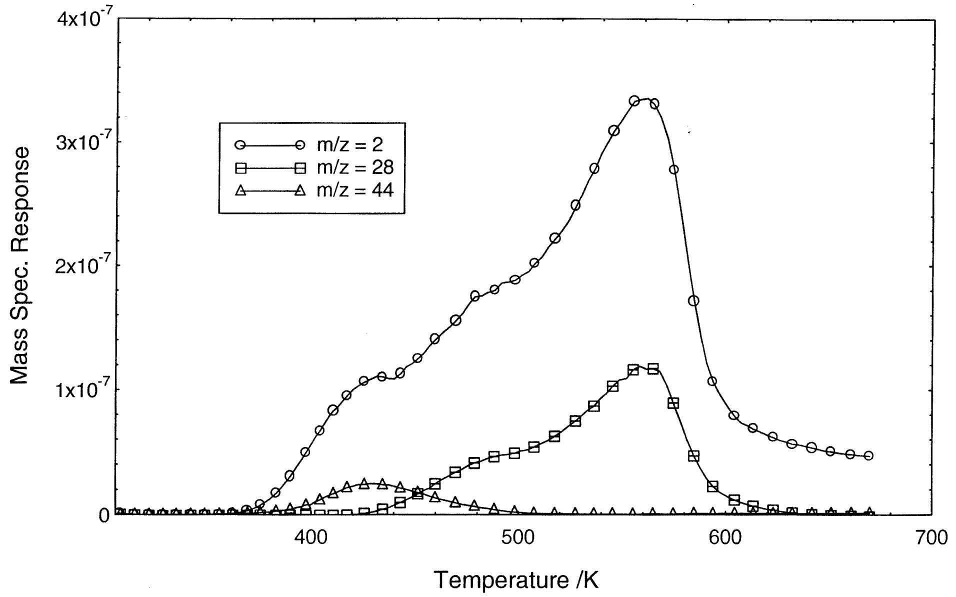

Figure 9. TPD spectrum obtained after the TPO in a CH_3OH/N_2O (8.5 : 1) mixture shown in figure 7.

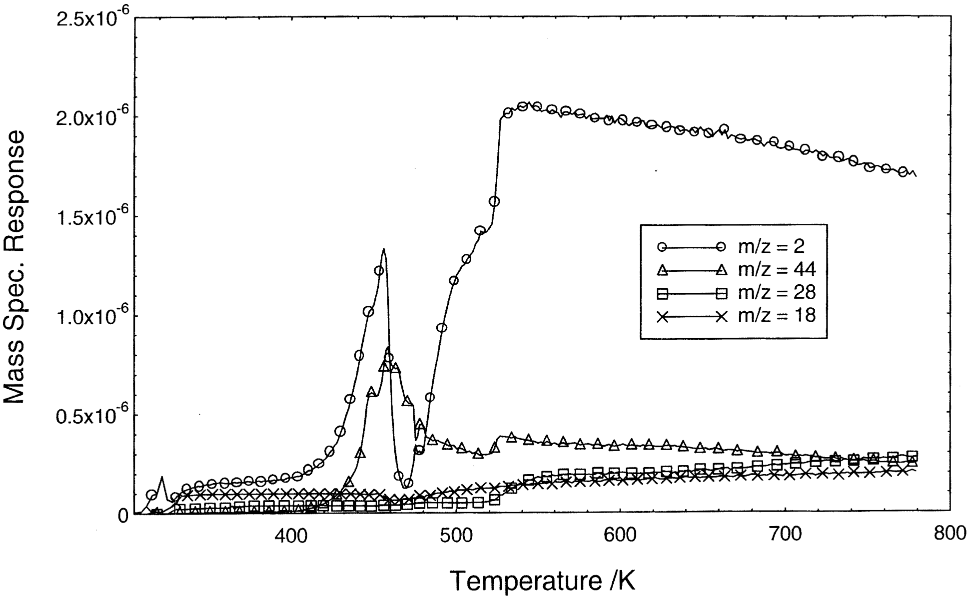

Figure 10. TPO profile obtained by passing a CH_3OH/O_2 mixture (17% CH_3OH, 5% O_2, (3.4 : 1), 78% He, 101 kPa, 25 cm^3 min^{-1}) over a $Cu/ZnO/Al_2O_3$ catalyst while raising the temperature at 5 K min^{-1}.

by bubbling O_2/He (5% O_2 and 10%, 101 kPa) through CH_3OH held at 300 K. Both exhibit a quite remarkable oscillatory type of behavior. Figure 10 (CH_3OH/O_2 (3.7:1)) shows a peak at 450 K with a shoulder at 430 K of coincident CO_2/H_2, probably deriving from the decomposition of monodentate and bidentate formates adsorbed on Cu. After the maximum at 450 K the rate of H_2 production falls to near zero at 470 K and then increases again in a complex manner to a plateau at 540 K. Also after the maximum at 450 K the rate of production of CO_2 falls in a complex manner to a minimum at 520 K followed by a low maximum (coincident with the onset of CO production) at 530 K indicating the decomposition of a formate adsorbed on Al_2O_3.

The higher oxygen partial pressure (10% O_2, CH_3OH/O_2, 1.7 : 1) produces a TPO profile (figure 11) remarkably different from that produced using 5% O_2 (figure 10). Figure 11 shows that the rate of H_2 production increases abruptly at 340 K to a plateau value (about one-third of the overall maximum rate) and then rises to a peak at 450 K which is roughly coincident with the peak in CO_2 production (bidentate formate decomposition on Cu). There is no CO_2/H_2 peak (or shoulder) at ~430 K and so the decomposition of

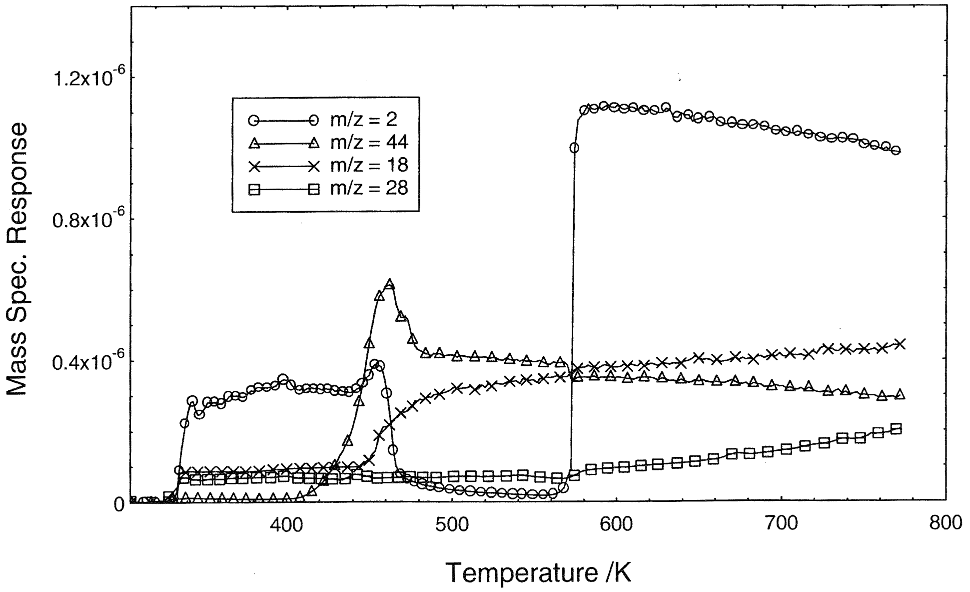

Figure 11. TPO profile obtained by passing a CH_3OH/O_2 mixture (17% CH_3OH, 10% O_2, (1.7 : 1), 73% He, 101 kPa, 25 cm^3 min^{-1}) over a $Cu/ZnO/Al_2O_3$ catalyst while raising the temperature at 5 K min^{-1}.

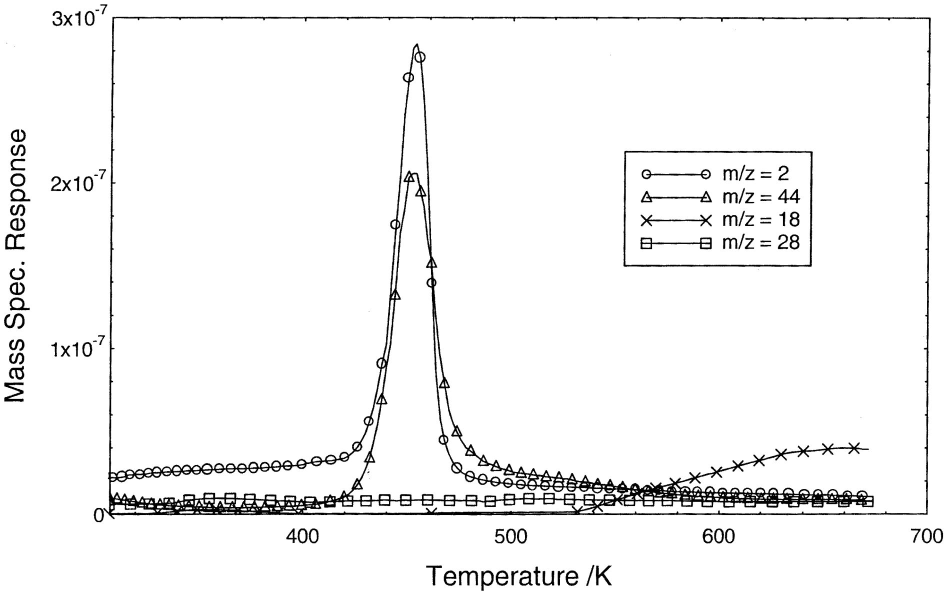

Figure 12. TPD after the TPOs in CH_3OH/O_2 mixtures (3.4 : 1 and 1.7 : 1) shown in figures 10 and 11.

monodentate formate adsorbed on Cu plays no role under these conditions.

After the maximum in the rate of H_2 production at 450 K, the rate falls to near zero at 470 K, after which it falls further to 560 K, at which point it rises near vertically to a plateau value. Again, after the maximum at ~450 K, the rate of CO_2 production falls to a plateau value at 490 K where it remains until 580 K, at which temperature it steps down to a lower value coincident with the stepped increase in H_2 production.

Considerable quantities of H_2O are observed at an onset temperature of 450 K—the temperature of the maximum in the rate of formate decomposition. The rate of production of CO shows a step change increase at 570 K—the temperature of the step change increase in the rate of production of H_2. This could have been thought to be due to the decomposition of a formate species adsorbed on ZnO but no evidence of a formate species on ZnO is seen in the post-reaction TPD (figure 12). It is also not observed with the lower oxygen (5% O_2/He) partial pressure. The increase in the H_2O and CO signals coupled with the decrease in the H_2 and CO_2 signals above 580 K could derive from the reverse water–gas shift reaction.

A possible cause for the decrease in the rate of oxidation of CH_3OH after 450 K in all concentrations of oxidant (a reaction which has been shown to proceed *via* a bidentate formate adsorbed on Cu) must relate to a poisoning of the Cu surface since, after initiation of reaction on this surface at 400 K, one would have expected an exponential increase in rate. This poisoning could derive from the oxygen-driven reconstruction of the Cu surface (which has been shown to be activated [10]), producing regions of a stable oxide overlayer on the Cu. The higher the oxygen partial pressure, the more extensive will be the regions of stable oxide overlayer, resulting in the prolonged duration of cut-off in reaction seen at the highest oxygen partial pressure (figure 11).

3.5. Post-reaction surface analysis after TPO using CH_3OH/O_2 mixtures of 3.4 : 1 and 1.7 : 1

Figure 12 is the TPD spectrum obtained, having cooled both CH_3OH/O_2 3.4 : 1 and 1.7 : 1 mixtures from 700 K to ambient under the reaction mixture and temperature programming from ambient to 700 K in an He stream (25 cm^3 min^{-1}, 101 kPa) at 5 K min^{-1}. One sharp peak of CO_2 and H_2 is observed with a maximum at 450 K which is a fingerprint for the decomposition of a bidentate formate species adsorbed on Cu. There is no evidence of a formate species adsorbed on the ZnO component of the catalyst. The higher oxygen partial pressures used in these experiments appears to produce a defect-free ZnO, the defects (anion vacancies) appearing to be a prerequisite for reaction on ZnO.

4. Conclusions

1. The temperature-dependent behavior of CH_3OH oxidation over a $Cu/ZnO/Al_2O_3$ catalyst revealed in TPO experiments can be divided into two temperature regimes: (i) below 500 K, where the oxidation takes place predominantly on the Cu component of the catalyst proceeding through a bidentate formate intermediate and (ii) about 500 K, where surprisingly reaction on the Cu component of the catalyst ceases and the product distribution is dominated by reaction on the ZnO and Al_2O_3 supports.
2. The nature of the intermediates adsorbed on the catalyst revealed by post-reaction analysis by TPD

depends critically on the CH_3OH:oxidant ratio used in the TPO. For the lowest CH_3OH:oxidant ratio (CH_3OH/N_2O, 8.5:1) the dominant intermediate on the surface was a formate species adsorbed on the ZnO component of the catalyst with only a small amount (~10% of that) of the bidentate formate adsorbed on Cu. The reaction therefore takes place predominantly on the defect surface of the ZnO component of the catalyst.

Lowering the CH_3OH:oxidant ratio (CH_3OH/O_2, 8.5:1) resulted in the bidentate formate adsorbed on Cu being the dominant intermediate and the formate adsorbed on Al_2O_3 and ZnO being only ~10% of that. Decreasing the CH_3OH:oxidant ratio further, *i.e.*, the CH_3OH/O_2 ratio to 3.4:1 and 1.7:1, results in the observation of the bidentate formate adsorbed on Cu to be the only intermediate extant on the surface of the catalyst. The higher oxygen partial pressure produces an inactive ZnO due to its being defect free.

3. From the TPO experiments performed here, the prediction of the optimum conditions for the production of CO-free H_2 is the use of a CH_3OH/N_2O ratio of 8.5:1 at 430 K (a CH_3OH/O_2 ratio of 17:1 would probably function equally well). Paradoxically, higher oxygen partial pressures result in the formation of higher CO concentrations at lower temperature, *i.e.*, <400 K. (We have shown that H_2O does decompose on Cu [11] and so it could be used as an oxidant in place of N_2O, giving the advantage that its decomposition produces one molecule of H_2.)
4. Since the Al_2O_3 and ZnO supports in the Cu/ZnO/Al_2O_3 catalyst produce CO and H_2 by the decomposition of formate species adsorbed on them, a Cu alone or SiO_2-supported Cu would be likely to produce CO-free H_2 by the partial oxidation of CH_3OH.

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