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On the mechanism of methanol synthesis and the water-gas shift reaction on ZnO

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Zinc oxide catalyses both methanol synthesis and the forward and ’everse water-gas shift reaction (f- and r- WGSR). Copper also catalyses both reactions, but at lower temperatures than ZnO. Presently the combination of Cu and ZnO stabilized by Al_2O_3 is the preferred catalyst for methanol synthesis and for the f- and r- WGSR. On Cu, the mechanism of methanol synthesis is by hydrogenation of an adsorbed bidentate formate [1] (the most stable adsorbed species in methanol synthesis), while the f- and r-WGSR proceeds by a redox mechanism. The f-WGSR proceeds by H_2O oxidizing the Cu and CO, reducing the adsorbed oxide and the r-WGSR proceeds by CO_2 oxidising the Cu and H_2, reducing it [2–5]. Here we show that the mechanisms of both reactions are subtly different on ZnO. While methanol is shown to be formed on ZnO through a formate intermediate, it is a monodentate formate species which is the intermediate; the f- and r-WGS reactions also proceed through a formate – a bidentate formate - in sharp contrast to the mechanism on Cu.

1. Introduction

Following their success in discovering a commercially viable ammonia synthesis catalyst, researchers at Badische Anilin Soda and Fabrik (BASF) turned their attentions to discovering a catalyst which would convert CO/H_2 mixtures to hydrocarbons. In 1923 they discovered that ZnO would convert CO/H_2 mixtures not to hydrocarbons but to CH_3OH [6 and references therein]. Consequently much of the research that has been conducted on ZnO has focused on trying to elucidate the reaction pathway by which CO and H_2 are adsorbed on ZnO and transformed to CH_3OH [7–14].

A useful means of studying the mechanism of the synthesis of CH_3OH on ZnO is to look at its decomposition on that surface. Several authors have done this [7–14]. Having first characterized the vibrational spectrum of a formate species on ZnO by adsorbing HCO_2H on to the ZnO at 473 K and having shown that it was formed by CO_2/H_2 co-adsorption at 473 K and not by CO/H_2O co-adsorption at 473 K [7], Tamaru and co-workers showed that the same formate species was formed by adsorbing CH_3OH on the ZnO at 473 K [8]. The decomposition products of the adsorbed formate were shown to be H_2, CO_2 and CO. Using CD_3OD Tamaru and co-workers claimed that the CO_2 was produced by the reaction

$$CD_3OD + DCOO_{(a)} \rightarrow CD_3O_{(a)} + CO_2 + D_2.$$

Trapping out the CO_2 in the gas phase was found to have no effect on the rate of CO evolution and so Tamaru and co-workers concluded that the decomposition of CO_2 to CO on the ZnO surface did not occur [8]. Trapping out the CD_3OD allowed Tamaru and co-workers to monitor both the loss of the adsorbed formate species and the evolution of CO in the gas phase. They found a roughly linear correlation between the loss of the adsorbed formate and the evolution of gas phase CO, allowing them to conclude that the decomposition of the adsorbed formate species was exclusively to H_2 (or D_2) and CO [8].

Bowker and co-workers studied the adsorption of H_2, CO, CO_2, HCHO, CH_3OH and of H_2/CO and H_2/CO_2 mixtures on ZnO using temperature programmed desorption (TPD) [9]. They found 3 desorption states for H_2 adsorption and 4 for CO_2 adsorption, the adsorption into the highest energy states for both being activated. In addition, the highest energy adsorption state of CO_2 was found to be a carbonate. Co-adsorption of H_2 and CO_2 at6 450 K and above produced a formate species. The same formate was produced by the room temperature adsorption of HCHO and CH_3OH. Temperature programmed decomposition of the adsorbed formate *in vacuo* produced coincident desorption of H_2 and CO at 580 K with a small amount ($\sim$ 10%) of H_2 and CO_2 at 550 K. The H_2/CO_2 production occurred only at high coverages of the formate [9]. Among other things, this work showed that CO_2 production did not require the

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interaction of gas phase CH_3OH with adsorbed HCO_2 (reaction 1) as had been propounded by Tamaru and co-workers [8].

Steady state rate measurements using H_2/CO did not produce CH_3OH, but produced CO_2 only and a ZnO containing a higher anion vacancy population than is produced by H_2 pretreatment [10]. Reaction of H_2/CO_2 with this highly defected ZnO produced a transiently higher rate of CH_3OH synthesis, this rate decaying back to that produced by H_2 pretreatment aa the anion vacancies were healed [10].

Single crystal stides by Bowker and co-workers showed that all of the adsorptions and reaction on the ZnO were confined to the polar faces of the ZnO [11].

Chadwick and Zheng [12], using TPD virtually duplicated Bowker and co-workers' data [9]. Having dosed CH_3OH on to the ZnO, on temperature programming they found two peaks of H_2 and CO at 580 and 610 K. They also found a smaller CO_2 peak (~1/17th of the CO peak) at 595 K. Chadwick and Zheng found that pre-adsorption of H_2O to a coverage of 1.7×10^{14} molecule cm^{-2} prior to dosing CH_3OH, or co-adsorption of H_2O with CH_3OH followed by temperature programming, increased the amount of CO_2 desorbed so that the CO_2:CO ratio was increased from 1:17 to 2:1. No explanation was offered for this other than that the "CH_3OH or some dehydrogenated intermediate reacted with the co-adsorbed H_2O to form CO_2 and H_2". Chadwick and Zheng [12] detected no H_2 evolution during H_2O adsorption, eliminating the possibility that H_2O reacted with O vacancies on the ZnO and liberated H_2.

Shido and Iwasawa studied the forward and reverse water gas shift reactions (f-WGSR and r-WGSR) using infrared spectroscopy and TPD [13, 14]. In the f-WGSR ($CO + H_2O \rightarrow CO_2 + H_2$), they found that a formate species was formed by the reaction of CO with surface OH species, the OH species being produced by pre-dosing the ZnO with H_2O. This formate species decomposed principally (70%) back to CO and OH species *in vacuo*. In the presence of 4×10^{-2} Pa of H_2O, however, this formate species decomposed entirely to CO_2 and H_2O. Furthermore, the activation energy for the decomposition of the formate decreased from 155 kJ mol^{-1} *in vacuo* to 109 kJ mol^{-1} in H_2O.

In respect of the r-WGSR ($CO_2 + H_2 \rightarrow CO + H_2O$), Shido and Iwasawa found that a formate species which was produced by the interaction of CO_2 and H_2 was the same as that produced by CO + OH [14]. The activation energy for the decomposition of this formate decreased from 171 kJ mol^{-1} *in vacuo* to 138 kJ mol^{-1} in H_2. The presence of H_2 had no effect on the selectivity of the decomposition of the formate, which was only 30%, to CO and H_2O. Noting that the decomposition selectivity of the formate produced from $CO_2 + H_2$ was significantly different from that produced from CO + OH, the authors suggested that these formates existed on different sites on the ZnO [14]. However, since this suggestion violates the principle of microscopic reversibility it is therefore rejected.

Campbell and co-workers studied the adsorption of CO and HCO_2H on O-terminated ZnO$(000\bar{1})$ and Zn-terminated ZnO (0001) on both of which surfaces Cu had been deposited [15–17]. The materials were considered to be models for the Cu/ZnO methanol synthesis catalyst. In the course of these studies, CO and HCO_2H were adsorbed on the polar single crystal ZnO surfaces which had no Cu on them as a basis for determining the effect of Cu. The Zn-terminated ZnO (0001) face was considered to be the more appropriate model, it having been shown that this surface was much ore reactive in the chemisorption of small molecules than the O-face [18–22]. It was thought that the more reactive Zn-face would interact more strongly with the Cu. However, this was found not to be the case; the Cu interacted identically with both faces. The adsorbed Cu was also found to have no effect on the adsorption of CO and HCO_2H on the Zn-terminated ZnO (0001) surface. The adsorbed formate species decomposed on desorption at 580 K to CO, CO_2 and H_2 on the clean Zu-terminated ZnO (0001) surface and on that surface with the Cu deposited on it.

In this paper we will show that the co-adsorption of CO_2/H_2 on to the ZnO results in the formation of two different formate species on the surface of ZnO. The surface population of each formate is strongly dependent on the temperature of the adsorption. Low temperature of dosing CO_2/H_2 on to the ZnO ($<$ 500 K) produces a formate species which decomposes to CO_2 and H_2 (a bidentate formate) on temperature programming. The formate species, which is produced by high temperature dosing of CO_2/H_2 on to the ZnO ($>$ 500 K), decomposes principally to CO and H_2– a monodentate formate. Post reaction analysis of the surface by TPD after the f-WGSR shows only one type of formate species on the surface, the bidentate formate which decomposes to $CO_2 + H_2$. Carrying out TPD on a surface which had been catalysing the r-WGSR and CH_3OH synthesis (both reactions occur concurrently) showed the existence of both formates. Therefore the formate which decomposes to $CO + H_2$ (the monodentate formate) is that which is responsible for CH_3OH synthesis, while the bidentate formate which decomposes to $CO_2 + H_2$ is responsible for the f- and r-WGSR.

2. Experimental

2.1. Microreactor

The multipurpose microreactor has been described in detail elsewhere [23]. It is a single tube reactor (20 cm long, 0.4 cm id) connected via a capillary to a mass spectrometer (Hiden Analytical, Warrington, England) capable of following 16 masses continuously with time/temperature.

2.2. The catalyst

The ZnO studied here was provided by Johonson Matthey. It was prepared by Na_2CO_3 precipitation of a $Zn(NO_3)_2$ solution. The $ZnCO_3$ was dried, and calcined at 620 K for 16 h in air to produce the ZnO. The total surface area was measured by N_2 frontal chromatography at 77 K and was 48 m^2/g. Electron micrographs of this material showed that the polar faces of ZnO predominated [11]. The catalyst was crushed and sieved to retain the 300–350μm finings. Typically 0.50 g of sample of the catalyst was loaded into the reactor.

2.3. Gases

Helium was supplied by Linde and was 99.999% pure. Before use, it was passed through a Chrompack Gas Clean moisture filter. The H_2/He (5% H_2), CO_2/He (10% CO_2), CO/He (10% CO) and CO_2/H_2 (10%CO_2) were obtained by Electrochem Ltd. Their quoted purities were 99.999%. They were used from the cylinder after passage through a liquid nitrogen cooled zeolite to remove water. Methanol was from B.D.H. and AnalaR grade.

3. Results and discussion

3.1. Characterisation of the types of surface formate on ZnO

3.1.1. Formate produced by methanol decomposition

Before the adsorption of methanol on to the ZnO, the catalyst was pre-treated by heating in a He stream (101 kPa, 25 cm^3/min) from ambient to 650 K at 5 K min^{-1}, holding the temperature at 650 K for 1 h before lowering it to 333 K. The flow was then switched to a He stream saturated with CH_3OH at 300 K. The saturation vapour pressure of CH_3OH at 300 K is 17 k Pa; the flow rate was 25 cm^3,min^{-1} and the duration of the flow was 20 min. The total number of CH_3OH molecules dosed on to the ZnO was 2.1×10^{21} molecules which would correspond to a coverage of 8.7×10^{15} molecules cm^{-2} ($\sim$ 9 monolayers (ML)) if they all stuck. Having dosed the CH_3OH for 20 min, the flow was switched to He and, after flushing the system for 20 min to remove gas phase and physisorbed CH_3OH, the temperature was raised at 5 K min^{-1}. This produced the desorption spectrum shown in figure 1.

The spectrum shows a broad H_2 peak whose maximum is at 580 K. The total number of H_2 molecules in the peak is 2.8×10^{19} corresponding to a H atom coverage of the ZnO of 2.4×10^{14} H atom cm^{-2}. There is a CO peak coincident with the H_2 peak maximum at 580 K. The total number of CO molecules in this peak is 4.3×10^{19} molecules, corresponding to a coverage of 1.8×10^{14} CO molecules cm^{-2}. In addition, there is a smaller CO_2 peak at 530 K comprising 1.1×10^{19} molecules or a coverage of 4.3×10^{13} CO_2 molecules cm^{-2}. The total C desorbed in the CO and CO_2 is 2.25×10^{14} atom cm^{-2} and the H:C ratio therefore is 1:1. The stoichiometry of the adsorbates corresponds to that of formates. The selectivity to CO_2 desorption is 25%. This is consistent with all that has been published previously [7–14]. (It should be noted that the low coverage by the formate species (2.25×10^{14} species cm^{-2} ($\sim$20% ML)) after a dosage of $\sim$ 9 ML suggests either specific adsorption sites on the surface or activated adsorption of the CH_3OH.)

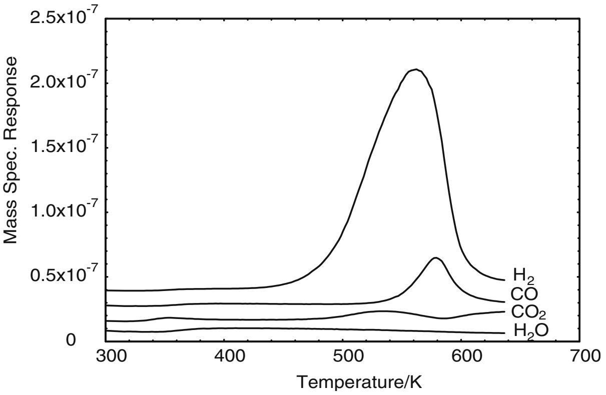


Figure 1. The temperature programmed desorption spectrum resulting from dosing a CH_3OH/He (17% CH_3OH, 101 k Pa, 25 cm^3 min^{-1}) mixture over ZnO at 333 K for 20 min.

3.1.2. Formate produced by the co-adsorption of CO_2/H_2

Co-adsorption of CO_2/H_2 mixture onto the ZnO catalyst was investigated at two different dosing temperatures (453 and 600 K). Figure 2 is the desorption spectrum resulting from the co-adsorption of CO_2/H_2 (10% CO_2, 101 kPa, 25 cm^3 min^{-1}, 15 min) at 453 K, cooling in the presence of reactant gases to ambient temperature and subsequently flushing in He for 20 min before temperature programming in He. Figure 3 shows

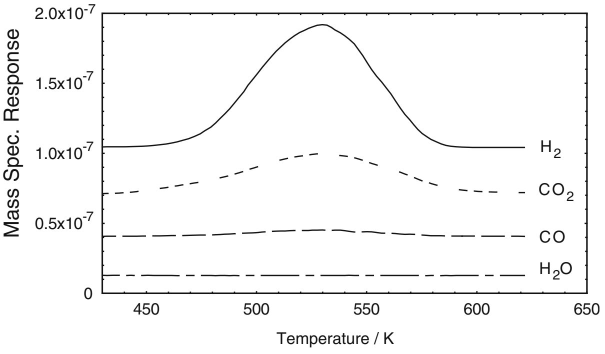


Figure 2. The temperature programmed desorption spectrum resulting from the co-adsorption of CO_2 and H_2 (10% CO_2, 90% H_2, 101 k Pa, 25 cm^3 min^{-1}) for 15 min at 453 K.

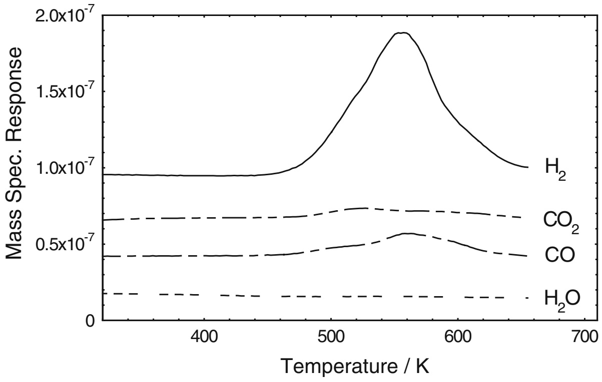


Figure 3. The temperature programmed desorption spectrum resulting from the co-adsorption of CO_2 and H_2 (10% CO_2, 90% H_2, 101 k Pa, 25 cm^3 min^{-1}) for 15 min at 600 K.

the desorption spectrum obtained after the co-adsorption of CO_2/H_2 at 600 K. Co-dosing CO_2 and H_2 at 453 K produces a formate species which desorbs exclusively to CO_2 and H_2 at 530 K. Co-dosing CO_2 and H_2 at 600 K produces formate species which desorb mainly to CO and H_2 at 560 K with a small amount of CO_2 and H_2 at 530 K.

These spectra suggest that there are two distinctly different types of formate species produced by CO_2/H_2 co-dosing: (i) which decomposes to CO_2 and H_2at 530 K and (ii) which decomposes to CO and H_2 at between 560 and 580 K. The coverage of the formate species which decomposes to CO_2 and H_2 at 530 K is 1.8×10^{14} species cm^{-2} while that of the same species produced by CO_2/H_2 co-dosing at 600 K is only 6.6×10^{13} species cm^{-2}. The coverage of the CO/H_2 desorbing species resulting from CO_2/H_2 co-dosing at 600 K is 1.7×10^{14} species cm^{-2}. These coverages are roughly the same as those produced by dosing saturation levels of CH_3OH at 333 K, leading us to conclude that their value is determined by a number of specific adsorption sites on the surface of the ZnO.

Figure 4 shows the effect on the H_2 desorption peak maximum temperature of the formate formed by co-dosing CO_2 and H_2 (10% CO_2, 90% H_2, 101 kPa, 25 cm^3 min^{-1}, 15 min) at 453, 493, 533 and 573 K. Increasing the dosing temperature results in the temperature of the H_2 peak maximum moving from 530 K (CO_2/H_2 desorbing formate) to 580 K (CO/H_2 desorbing formate). Since no H_2O is observed to desorb with the CO/H_2, the O atom from the dosed CO_2/H_2 must heal an O vacancy in the ZnO lattice.

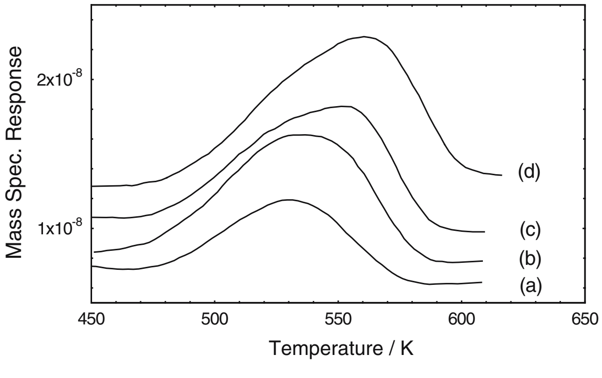
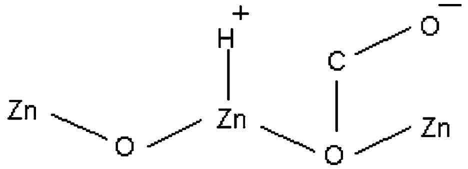


Figure 4. The dependence of the H_2 desorption peak maximum temperature from the decomposition of surface formate on the temperature of co-dosing the CO_2/H_2 mixture.

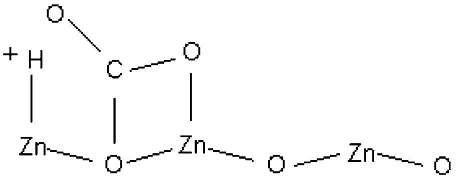
It is probable that the formation of anion vacancies in the ZnO lattice produced by reaction with H_2 is activated, and so increasing the dosing temperature of the CO_2/H_2 mixture will result in the formation of an increased number of anion vacancies. These vacancies will house a trapped electron (the other electron from the lost O^{2-} will probably reduce the Zn^{2+} species to Zn^{+}). The CO_2 will probably adsorb by inserting an O atom into the vacancy and picking up the trapped electron to become CO_2^{-}, which is bent. Adsorbed H atoms will react with the adsorbed CO_2^{-} species to produce an adsorbed formate HCO_2^{-}. We shall designate this type of formate bonded monodentate at an anion vacancy as a Vo-formate. On temperature programming, this Vo-formate species will leave an O atom in the vacancy and desorb as CO and $1/2H_2$.

We have shown that adsorption and reaction on ZnO is confined to the polar faces of ZnO [11]. Other authors [18–22] have shown the Zn-terminated ZnO (0001) surface to be the more active surface. Structure 1 is a representation of H bonded to a Zn^{+} species and CO_2 bonded to the electron trapped at the anion vacancy on the Zn-terminated surface. Structure 1 shows that the formation of a Vo-type formate can be accomplished relatively easily.



Structure 1.

Shido and Iwasawa [14] showed that a bidentate formate was formed by reaction of an adsorbed bidentate carbonate with an adsorbed H atom. This adsorbed bidentate formate decomposed principally (70%) to CO_2 and H_2. The adsorbed formate which we observe desorbing as CO_2 and H_2 at 530 K is probably a bidentate formate. Structure 2 shows how this bidentate formate could be formed on the Zn-terminated ZnO (0001) face.



Structure 2.

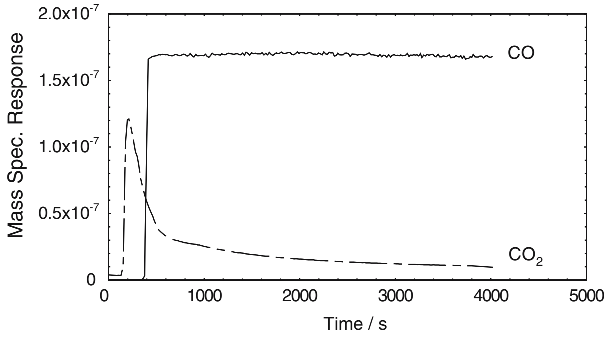


Figure 5. The time dependence of the rate of CO_2 production from the reaction of a CO/H_2 stream (10% CO, 101 k Pa, 25 cm^3 min^{-1}) with ZnO at 600 K.

3.2. *The Formation of anion vacancies on ZnO by reaction with CO/H_2 at 600 K*

Figure 5 shows the time dependence of the reaction of a CO/H_2 mixture (10% CO, 90% H_2, 101 k Pa, 25 cm^3 min^{-1}) with ZnO at 600 K. The only product of the reaction is CO_2 whose rate of production maximizes about 25 s after the onset of reaction after which it falls exponentially and asymptotically to zero after about 4000 s. This is similar to what we have reported previously [10]. Integrating the amount of CO_2 produced up to 4000 s gives a total of 6.0×10^{18} molecules on 0.5 g, giving a surface vacancy population which is increased by 2.5×10^{13} vacancies cm^{-2}.

The reaction involved is

$$CO + ZnO \leftrightarrow CO_2 + Zn - \square, \qquad (2)$$

where $\square$ is an anion vacancy. The reaction is obviously reversible. However, like Tamaru and co-workers previously [8], we saw no decomposition of the CO_2 on ZnO up to 700 K. This is extremely important when we come to discuss the r-WGSR which we will show occurs through the bidentate formate and not through decomposition of CO_2 on the ZnO.

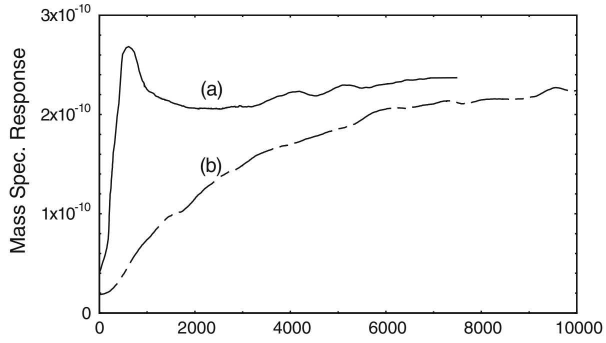


Figure 6. The time dependence of the rate of CH_3OH synthesis from a CO_2/H_2 feed (10% CO_2, 101 k Pa, 25 cm^3 min^{-1}) over ZnO which had been pre-reduced in a CO/H_2 (10% CO) stream at 600 K as described above (curve (a)), and over ZnO which had been pre-treated in He at 650 K for 1 h.

3.3. *The time dependence of the rate of CH_3OH synthesis over highly defected and less defected ZnO*

Figure 6 (curve (a)) shows the time dependence of the rate of CH_3OH synthesis from a CO_2/H_2 stream (10% CO_2, 90% H_2, 101 kPa, 25 cm^3 min^{-1}) at 600 K over the ZnO which had an increased number anion vacancies of 2.5×10^{13} vacancies cm^{-2} produced by reaction with the CO/H_2 stream. The rate of CH_3OH synthesis rises to a peak value of 2.7×10^{-10} mbar after $\sim$ 800 s and then falls to a plateau value of $\sim 2 \times 10^{-10}$ mbar after 2000 s. Figure 6 (curve (b)) shows the rate of CH_3OH synthesis from the same CO_2/H_2 mixture at 600 K over a ZnO which had been pretreated simply by heating to 650 K in He at 5 K min^{-1} and holding it at 650 K under the He flow for 1 h. Curve (b) shows that the rate of CH_3OH synthesis rises exponentially to the same steady state value as that seen in curve (a) after about 10000 s ($\sim$ 3 h). The integral of the total amount of CH_3OH produced over the CO/H_2 defected ZnO from the CO_2/H_2 mixture up to 7000 s, minus that made by CO_2/H_2 over the less defected ZnO produced by He pretreatment, is 3.6×10^{18} molecules. This is roughly the same as the number of anion vacancies produced by reduction in the CO/H_2 stream.

Several points can be made from these results. These are: (i) the reaction of CO/H_2 over ZnO at 600 K does not produce CH_3OH; it produces CO_2 and a limiting number of anion vacancies ($\sim 2.5 \times 10^{13}$ vacancies cm^{-2}) in excess of those produced thermally in a He flow at 650 K, (ii) the near equivalence of the additional CH_3OH produced over a more defected ZnO surface suggests that the anion vacancies are responsible for CO_2 adsorption as CO_2^- and its hydrogenation to CH_3OH through a V_o-formate species, (iii) the gradual increase in the rate of CH_3OH synthesis from a CO_2/H_2stream at 600 K over ZnO which had been pretreated in a flow of He at 650 K to a rate asymptotically approaching that produced on a ZnO pretreated in CO/H_2 at 600 K for 4000 s suggest that the reaction of H_2 with ZnO can produce anion vacancies on the ZnO, albeit at a lower surface coverage than produced by CO/H_2 pre-treatment and (iv) the steady state rate of CH_3OH synthesis from a $CO/CO_2/H_2$ mixture over ZnO would be faster than that from CO_2/H_2.

It should be emphasized here that although the formation of anion vacancies by reduction by H_2 (reaction 3), like that of CO reduction, is inherently reversible,

$$H_2 + ZnO \leftrightarrow Zn - \square + H_2O \qquad (3)$$

we observed no H_2 production on dosing H_2O up to 700 K, in agreement with Chadwick and Zheng [7]. H_2 production by H_2O decomposition, therefore, is not a component of the f-WGSR.

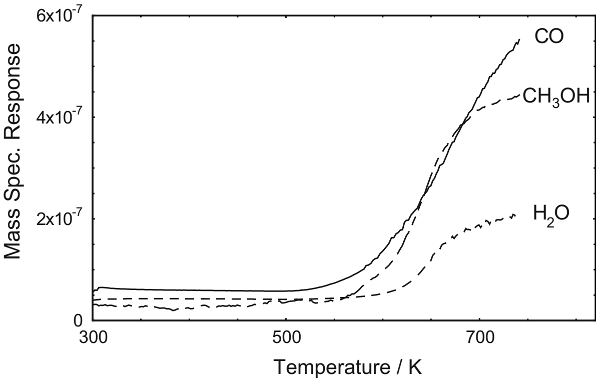


Figure 7. The temperature programmed reaction profile obtained by passing a CO_2/H_2 mixture (10% CO_2, 101 k Pa, 25 cm^3 min^{-1}) over the ZnO while raising the temperature from ambient to 700 K at 5 K min^{-1}.

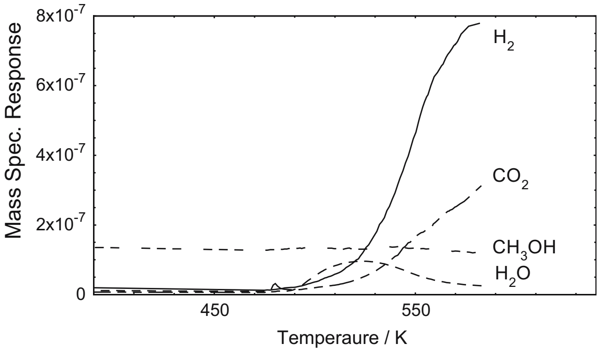


Figure 9. The temperature programmed reaction profile obtained by passing a CO/H_2O misture (10% CO, 20% H_2O, 88% He, 101 k Pa, 25 cm^3 min^{-1}) over the ZnO while raising the temperature from ambient to 600 K at 5 K min^{-1}.

3.4. *The reverse water gas shift and methanol synthesis reactions*

Figure 7 is the temperature programmed reaction profile obtained by passing a CO_2/H_2 stream (10% CO, 90% H_2, 101 k Pa, 25 cm^3 min^{-1}) over ZnO which had been pretreated in He at 650 K for 1 h under a flow of He while raising the temperature at 5 K min^{-1}. The onset of the r-WGSR is observed at ~520 K with the appearance of CO in the gas phase. The onset of CH_3OH synthesis is observed at ~ 550 K.

A plot of the logarithm of the initial rates of production of CO and CH_3OH give activation energies of 73 and 104 kJ mol^{-1} for the r-WGSR and CH_3OH respectively. These different activation energies suggest that the reactions must proceed through different intermediates.

Figure 8 is the post reaction analysis of the ZnO surface by TPD following the r-WGSR and CH_3OH synthesis reactions. It shows that the V_o-type formate (CO/H_2 co-desorption at 580 K) and bidentate formate (CO_2/H_2 co-desorption at 530 K) co-exist on the surface. Since we have concluded that the V_o-formate is responsible for CH_3OH synthesis, the bidentate formate must be the intermediate for the r-WGSR and, by the principle of microscopic reversibility, must be the intermediate for the f-WGSR.

3.5. *The forward water gas shfit reaction*

Figure 9 is the temperature programmed reaction profile obtained by passing a CO/H_2O mixture (10% CO, 2% H_2O, 88% he, 101 k Pa, 25 cm^3 min^{-1}) over ZnO which had been pre-treated in He at 650 K for 1 h. The only reaction observed was the f-WGSR. No CH_3OH is formed. The onset of H_2 production is observed at 480 K. The activation energy for the f-WGSR is obtained by line shape analysis of the initial rates of H_2 production; its value is 68 kJ mol^{-1}.

Post f-WGSR analysis of the ZnO surface by TPD (figure 10) reveals that only the bidentate formate (CO_2/H_2 co-desorption at 530 K) exists on the surface of the ZnO. The H:CO_2 ratio is 1:1 consistent with its being a formate and the coverage is 1.6×10^{13} species cm^{-2}.

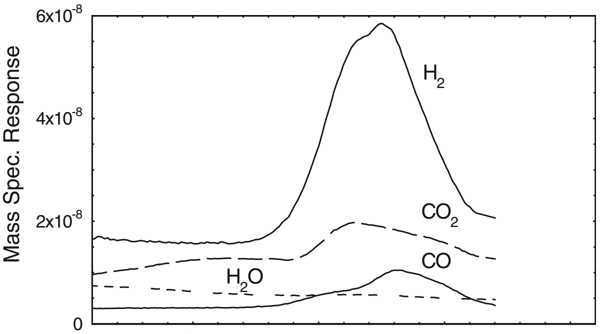


Figure 8. The temperature programmed desorption spectrum obtained after the temperature programmed reaction of CO_2/H_2 with the ZnO described in figure 7.

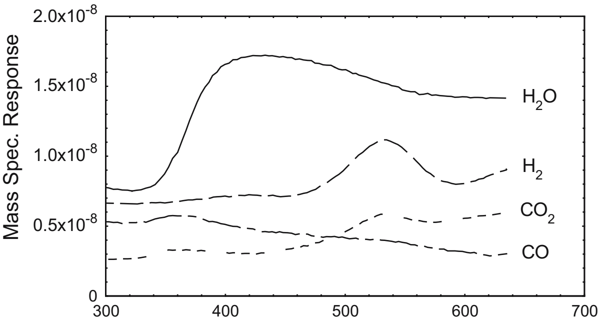


Figure 10. The temperature programmed desorption spectrum obtained after temperature programmed reaction of the CO/H_2O mixture with the ZnO described in figure 9.

3.6. *Ionic representation of the Zn-terminated ZnO (0001) face and of the intermediates adsorbed on it*

A better appreciation of the structure of the Zn-terminated ZnO (0001) face is obtained from the ionic model of ZnO shown in figure 11. (The larger red balls are O^{2-} species and the smaller blue balls are the Zn^{2+} species.) Since the polar faces are charged, a perfect face would have an infinite surface energy. These polar faces are therefore stabilised by having by having steps and kinks as shown in the figure. Figure 12 shows the Zn-terminated surface with a monodentate formate adsorbed on it. Figure 13 shows the Zn-terminated surface with a bidentate formate adsorbed on it.

4. Conclusions

(1) Co-dosing CO_2 and H_2 on to ZnO produces two different types of formate: (i) a bidentate formate which decomposes on temperature programming at 530 K to produce CO_2 and H_2 and (ii) a monodentate formate held on the surface of the ZnO at an anion vacancy; it decomposes to CO and H_2 at 580 K on temperature programming, the O atom from the formate healing the vacancy.

(2) Co-dosing CO_2 and H_2 at temperatures below 500 K produces the bidentate formate species predominantly. At temperatures above 500 K, the

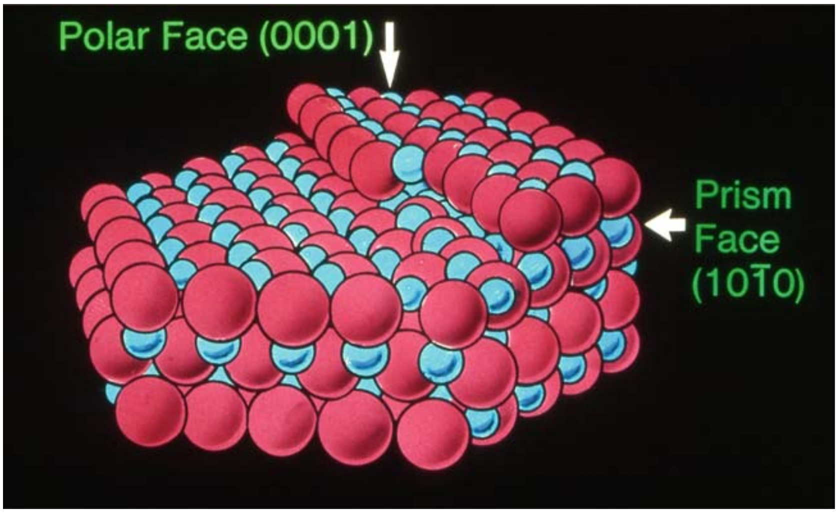


Figure 11. An ionic model of ZnO showing the Zn-terminated (0001) polar face and the(10$\bar{1}$0) prism face.

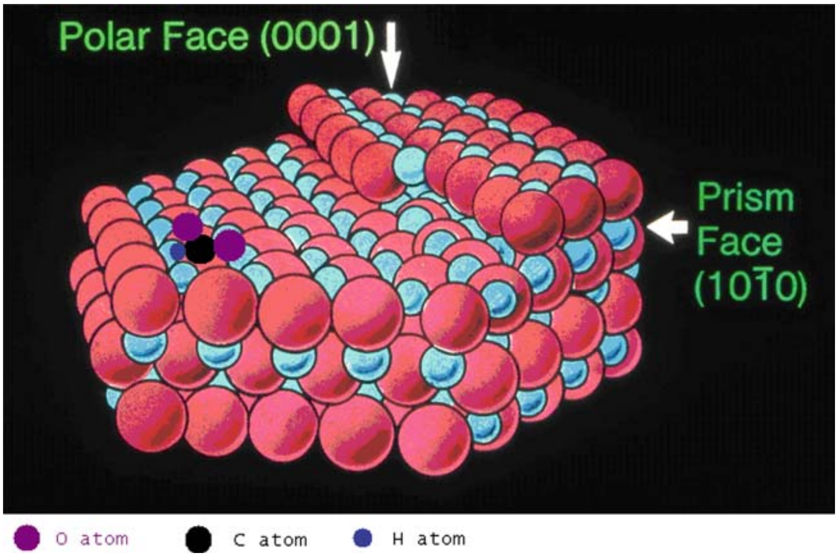


Figure 12. A model of CO_2 bonded to an anion vacancy on the Zn-terminated polar face with a vicinally adsorbed H atom ready to form an adsorbed formate.

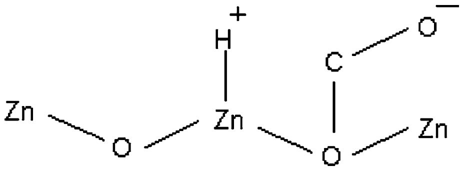


Figure 13. A model of CO_2 bonded as a bidentate carbonate to the Zn-terminated polar face with a vicinally adsorbed H atom ready to form an adsorbed bidentate formate.

monodentate formate is the predominant species formed. This is because at the higher temperatures the H_2 in the H_2/CO_2 mixture produces an increased number of anion vacancies on the ZnO.

(3) The bidentate formate is the intermediate for the f- and r-WGSR on ZnO.

(4) The monodentate formate held at an anion vacancy is the intermediate for CH_3OH synthesis on ZnO from CO_2/H_2 feeds.

(5) The activation energy for methanol synthesis on ZnO obtained in this work is 104 kJ mol^{-1} while that for r-WGS reaction is 73 kJ mol^{-1}. This provides additional corroborative evidence for the method synthesis reaction and the f- and r-WGS reaction occurring through different intermediates.

References

[1] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) 263.

[2] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, J. Chem. Soc. Faraday Trans. 1 83 (1987) 213.

[3] Hadden RA, Vandervell HD, Waugh KC and Webb G (1988) aa. Proc 9th Int Cong Catal, 1835.

[4] E. Colbourn, R.A. Hadden, H.D. Vandervell, K.C. Waugh and G. Webb, J. Catal. 130 (1991) 514.

[5] A.J. Elliott, M.J. Watson, B.H. Sakakini, J. Tabatabaei, F.W. Zemichael and K.C. Waugh, Catal. Let. 79 (2002) 1.

[6] G Natta, "Catalysis", vol 3, ed. P H Emmett (Reinhold, New York, 1955).

[7] A. Ueno, T. Onishi and K. Tamura, Trans. Faraday Soc. 66 (1970) 756.

[8] A. Ueno, T. Onishi and K. Tamura, Trans Faraday Soc. 67 (1971) 3585.

[9] M. Bowker, H. Houghton and K.C. Waugh, J. Chem. Soc. Faraday Trans, 1 1(77) (1981) 3023.

[10] M. Bowker, J.N.K Hyland, H.D. Vandervell and K.C. Waugh, *Proc 8th Int Cong Catal* (Verlag Chemie, Weinheim FDR, 1984) 35vol II.

[11] M. Bowker, H. Houghton, K.C. Waugh, T. Giddings and M. Green, J. Catal. 84 (1983) 252.

[12] D. Chadwick and K. Zheng, Catal. Lett. 20 (1993) 231.

[13] T. Shido and Y. Iwasawa, J. Catal. 129 (1991) 343.

[14] T. Shido and Y. Iwasawa, J. Catal. 140 (1993) 575.

[15] A. Ludviksson, R. Zhang, C.T. Campbell and K. Griffiths, Surf. Sci. 313 (1994) 64.

[16] A. Ludviksson, K. H Ernst, R. Zhang and C.T. Campbell, J. Catal. 141 (1993) 380.

[17] J. Yoshihara and C.T. Campbell, Surf. Sci. 407 (1998) 256.

[18] J.M. Vohs and M.A. Barteau, Surf. Sci. 176 (1986) 91.

[19] R.R. Gray, M.H. Nodine, V.E. Henrich, H.J. Ziegler and E.I. Solomonaa.., J. Am. Chem. Soc. 102 (1980) 6752.

[20] W.T. Petrie and J.M. Vohs, Surf. Sci. 245 (1991) 315.

[21] S. Akhter, K. Lui and H.H. Kung, J. Phys. Chem. 89 (1985) 1958.

[22] S. Akhter, W.H. Cheng, K. Lui and H.H. Kung, J. Catal. 85 (1984) 437.

[23] K.C. Waugh, App. Cat. 43 (1988) 315.