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

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Received 7 April 2006; accepted 11 April 2006

Zinc oxide catalyses both methanol synthesis and the forward and reverse 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 2 O 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 2 O 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 attention 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 3 OH [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 3 OH [7–14].

A useful means of studying the mechanism of the synthesis of CH 3 OH 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 2 H 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 2 co-adsorption at 473 K [7], Tamaru and co-workers showed that the same formate species was formed by adsorbing CH 3 OH 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 3 OD Tamaru and co-workers claimed that the CO 2 was produced by the reaction

CD 3 OD + DCOO (a) → CD 3 O (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 3 OD 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 3 OH 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 at 450 K and above produced a formate species. The same formate was produced by the room temperature adsorption of HCHO and CH 3 OH. Temperature programmed decomposition of the adsorbed formate in vacuo produced coincident desorption of H 2 and CO at 580 K with a small amount (~ 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$_3$OH 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$_3$OH, 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 CO$_2$ synthesis, this rate decaying back to that produced by H$_2$ pretreatment as 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$_3$OH 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 (~1/17$^{\text{th}}$ of the CO peak) at 595 K. Chadwick and Zheng found that pre-adsorption of H$_2$O to a coverage of 1.7 × 10$^{-3}$ molecule cm$^{-2}$ prior to dosing CH$_3$OH, or co-adsorption of H$_2$O with CH$_3$OH followed by temperature programming, increased the amount of CO 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$_3$OH or some dehydrogenated intermediate reacted with the co-adsorbed H$_2$O to form CO$_2$ and H$_2$". Chadwick and Zheng [12] detected no H$_2$ evolution during H$_2$O adsorption, eliminating the possibility that H$_2$O 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$_2$O → 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$_2$O. This formate species decomposed principally (70%) back to CO and OH species in vacuo. In the presence of 4 × 10$^{-2}$ Pa of H$_2$O, however, this formate species decomposed entirely to CO$_2$ and H$_2$O. 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$_2$O.

In respect of the r-WGSR (CO$_2$ + H$_2$ → CO + H$_2$O), 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$_2$O. 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$_2$H on O-terminated ZnO(0001) 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$_2$H 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 more 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$_2$H 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$_3$OH 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$_3$OH 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).