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The importance of water in the mechanism of methanol decomposition on ZnO

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The decomposition of methanol on ZnO has been investigated by temperature programmed desorption. The main decomposition products were CO and H_2 with only a small amount of CO_2. The influence of water on methanol decomposition has been studied by a series of quantitative co-adsorption experiments. As the amount of coadsorbed water was increased, the CO yield decreased whereas that of the CO_2 increased and went through a maximum. This indicated that water and methanol competed for the same adsorption sites. The results suggest that methanol (or dehydrogenated intermediate) reacts with coadsorbed water to form CO_2 and H_2. Preadsorbed or residual water give similar results.

Keywords: Methanol; water; ZnO; TPD

1. Introduction

ZnO is an important constituent of the multi-component catalysts widely used for methanol and alcohol synthesis [1]. As a consequence, there have been many studies of the decomposition of alcohols over ZnO, especially using TPD and IR techniques. In the case of methanol, the main decomposition products observed in TPD are CO, CO_2 and H_2 occurring in the same temperature range [2–11] and it is generally proposed that the decomposition proceeds via the formation of surface methoxy species, which is transformed to a formate species and then decomposes to CO, CO_2 and H_2.

There are wide variations in the reported CO : CO_2 ratios from methanol decomposition on ZnO during TPD. For example, Roberts and Griffin [2,7] reported a CO_2 peak larger than CO; whilst Bowker et al. [3] found a CO peak larger than that of CO_2, with both studies proposing the same formate decomposition mechanism.

This raises the interesting question: how under TPD conditions can the formate intermediate ($HCOO_{(a)}$) decompose to different product ratios? The observed CO : CO_2 ratios have been explained in terms of the degree of reduction of the original ZnO surface [6] or the balance between type I or non-type I sites [2]. Chan and Griffin, who studied CH_3OH decomposition on a *c*-axis oriented ZnO thin film, reported that efforts to change the observed CO : CO_2 ratio by pre-oxidizing or pre-reducing the sample were unsuccessful, and that the ratio was independent of initial CH_3OH coverage and the number of TPD cycles performed [10].

The role of surface hydroxyls in methanol decomposition remains unclear. Previous studies of methanol decomposition have claimed that residual hydroxyls on ZnO were either displaced [4] or remained unaffected [2], and that coadsorbed water influenced the product distribution by site blocking [2]. Shlegel' et al. [12] found that an initial process of methanol decomposition over Cu/ZnO was reaction with surface hydroxyls on ZnO. Shido and Iwasawa [13] in a recent study of the water–gas shift reaction (WGSR) on ZnO have proposed a reactant promoted reaction mechanism where coadsorbed water influenced the rate of formate decomposition and product distribution. In view of the importance of CO_2 and H_2O in CH_3OH synthesis [4,14], it is of interest to explore the influence of water on methanol decomposition.

This study has investigated the decomposition of methanol on a low surface area ZnO by TPD and the effect of coadsorption of CH_3OH and H_2O. Close attention has been given to the quantitative variation in product distribution. In particular, we demonstrate that the CO : CO_2 ratio is quantitatively dependent on the presence of water.

2. Experimental

The TPD equipment used has been described previously [15]. 350 mg of ZnO (AR grade, BDH Chemicals, BET area = 4.6 m^2/g, particle range = 300–500 μm) was used in this study. The preparation of the catalyst as well as the experimental procedure and operating parameters were the same as reported previously [15]. The catalyst was preconditioned by heating in He flow from 300 to 825 K at 39 K min^{-1} and then cooled rapidly to room temperature. A series of mixed solutions were prepared by adding a required amount of purified H_2O into CH_3OH, with H_2O mole fraction, X_{H_2O}, ranging from 0 to 30 mol%. In a typical coadsorption experiment, a CH_3OH and H_2O mixed solution was injected up stream of the ZnO at 300 K. The injected adsorbates were monitored by the mass spectrometer and methanol breakthrough was taken as an indication that the ZnO surface was saturated. After the excess amount of absorbate(s) were flushed away by He carrier gas over a period of 2 to 3 min, the TPD experiment was commenced and desorption spectra taken.

3. Results

3.1. ADSORPTION AND DECOMPOSITION OF METHANOL

A typical TPD spectrum obtained after a saturation dose of methanol onto ZnO dehydroxylated as described in the experimental section is presented in fig. 1. CH_3OH mainly decomposed to form H_2, CO and CO_2. Other masses corresponding to CH_4, Zn and O_2 were monitored, but were not found in the TPD processes. The decomposition of adsorbed CH_3OH to CO and H_2 was found to be the main reaction (14×10^{18} and 30×10^{18} molecules/g respectively). The desorption feature of CO consisted of two overlapped peaks with peak temperatures $T_m = 610$ and 625 K and a very small shoulder at 680 K. Four overlapped, but distinguishable, H_2 peaks evolved at 515, 550, 580 and 610 K. A small CO_2 peak was observed at 595 K (0.8×10^{18} molecules/g), indicating that methanol oxidation on ZnO during TPD was a relatively minor pathway in comparison to that of decomposition to CO. The observed CO : CO_2 ratio was about 17 : 1. The T_{515K} and T_{550K} H_2 peaks were not accompanied by the desorption of any significant amount of carbon containing species. This H_2 desorption has been suggested by Roberts and Griffin to be derived from the transformation of adsorbed methanol (in the form of methoxy) into dehydrogenated intermediates [2]. In contrast, the T_{580K} and T_{610K} H_2 peaks occurred with the approximate coincident desorption of CO, consistent with the decomposition of the dehydrogenated intermediate(s). Consequently, there appear to be two sites for methanol decomposition on the present ZnO, with successive dehydrogenation occurring on each site.

A small amount of CH_3OH (0.4×10^{18} molecules/g) desorbed in a wide double

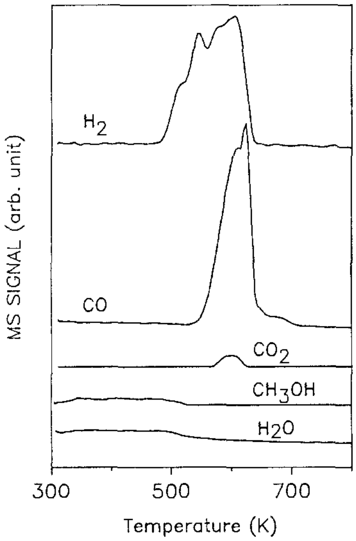

Fig. 1. Methanol TPD spectrum obtained from a saturation coverage of methanol on ZnO.

peak within the temperature range of 330–540 K. This desorption feature is very similar to that reported previously for a polycrystalline ZnO sample [2] and for a ZnO single crystal [16]. An ill-defined and very small $m/e = 18$ desorption feature was observed in the same temperature range of 330–550 K. This arises from the cracking fraction of methanol and possibly some H_2O. No other desorption states of H_2O were found for temperatures higher than 550 K. Methyl formate was not detected in the desorbed products.

The methanol TPD spectrum in fig. 1 differs from those obtained previously, although the main characteristics are close to that reported by Bowker et al. [3]. They also observed the main products to be CO and H_2, and if the fine peak structure in the present data is ignored, the peak temperatures of CO and H_2 obtained by Bowker et al. are close to the present measurements. Both studies agree that the desorption temperature of CO_2 was lower than that of CO with a much lower yield. The CO_2 desorption temperature was some 40 K higher in the present results. The present data contrasts with that of Roberts and Griffin [2] who reported a smaller CO peak than that of CO_2. Bowker et al. [3] found a small amount of H_2O desorbed with the CO and H_2, which was not observed in the present study.

3.2. METHANOL AND WATER COADSORPTION

To determine the role of H_2O in the decomposition of CH_3OH, a series of experiments were performed in which CH_3OH and H_2O were coadsorbed on ZnO. The amount of weakly held CH_3OH desorbing below 550 K varied only slightly with increasing X_{H_2O} and was essentially the same as in the case of "pure" CH_3OH TPD. The desorbed quantity of CH_3OH was very small and constituted only a minor process in the TPD.

Selective TPD spectra showing the effect of coadsorbed H_2O on CH_3OH decomposition are presented in fig. 2. As X_{H_2O} was gradually increased, the CO profile became smaller and narrowed to a single peak (fig. 2a). From $X_{H_2O} = 0–20$ mol%, the amount of desorbed CO_2 increased slowly with the peak becoming broader, but remaining as a single peak (fig. 2b). When X_{H_2O} was increased from 20 to 30 mol%, the CO_2 yield decreased and the TPD profile became two peaks – a main peak at 612 K and a shoulder at 675 K (fig. 2b).

The quantitative variation in the yields of CO, CO_2 and H_2O with X_{H_2O} is shown in fig. 3. The CO yield is seen to decrease and that of CO_2 increase linearly as X_{H_2O} is increased from 0–20 mol%. We note that the rate of decrease in the CO yield with increasing X_{H_2O} was approximately twice that of the increase in the yield of CO_2 for $X_{H_2O} = 0–20$ mol%. The CO_2 yield reached a maximum at $X_{H_2O} = 20$ mol% and then decreased as X_{H_2O} was further increased (fig. 3c). The general trend of the dependence of the yield of H_2 on X_{H_2O} was that H_2 production was reduced as X_{H_2O} was increased (not shown).

As X_{H_2O} was increased from 0–30 mol%, an insignificant amount of desorption was seen at $m/e = 18$ from 300–500 K, arising from methanol and water. Our stu-

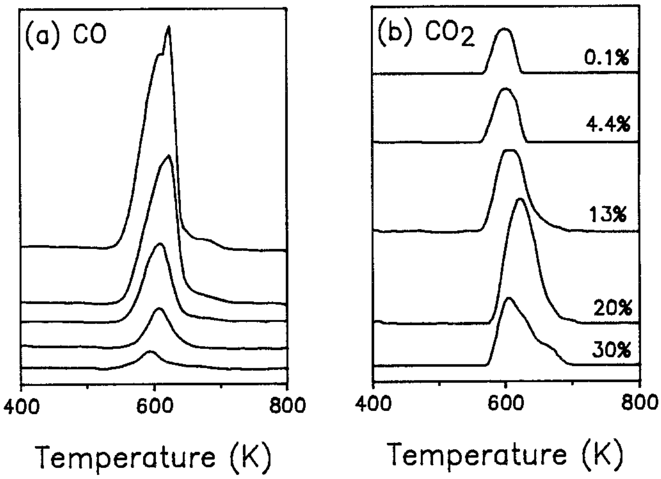

Fig. 2. TPD spectra from CH_3OH and H_2O coadsorption. (a) CO; (b) CO_2 desorption states. The stated values refer to the H_2O concentration in mol%.

dies of H_2O adsorption on ZnO have shown that, at low coverage, H_2O would be desorbed only when the temperature was raised above 550 K [17]. As an example, a typical H_2O desorption spectrum at low H_2O coverage ($\sim 8 \times 10^{18}$ molec/g) is shown in fig. 4a in which the main H_2O desorption state was at $\sim$ 750 K, with no desorption states observed below 550 K. Consequently, in the present $CH_3OH + H_2O$ study and at low X_{H_2O}, the coinjected H_2O would be expected to be adsorbed on ZnO and desorb at temperatures higher than 550 K. In contrast to expectation, as X_{H_2O} was gradually increased from 0 to 20 mol%, there was no H_2O desorbed at temperatures higher than 550 K. H_2O desorption at temperatures higher than 550 K was only observed when X_{H_2O} was raised beyond 20 mol%, when the CO_2 yield began to fall. The H_2O desorption profile at $X_{H_2O} = 20$ mol% is shown in fig. 4b where the amount of H_2O desorbed at $\sim$ 750 K was very small.

The failure to observe an increase in the total amount of H_2O desorbed, and particularly the lack of high temperature H_2O desorption above 550 K as X_{H_2O} was increased from 0–20 mol%, raises a question regarding the fate of the H_2O coinjected with CH_3OH. There are three possibilities:

(1) CH_3OH has a much higher sticking probability than H_2O and a higher heat of adsorption so that coinjected CH_3OH was preferentially adsorbed and, therefore, no H_2O desorption was found in the TPD process.

(2) H_2O was adsorbed on the ZnO surface and reacted with oxygen vacancies to liberate hydrogen.

(3) H_2O was adsorbed on the ZnO surface, but was consumed in the TPD process to form CO_2 and, therefore, no H_2O desorption was observed.

The first possibility can be ruled out, since it would not only mean that the coinjected H_2O would have no effect on CH_3OH TPD process, which is clearly not the case, but also H_2O breakthrough should have been observed following injection

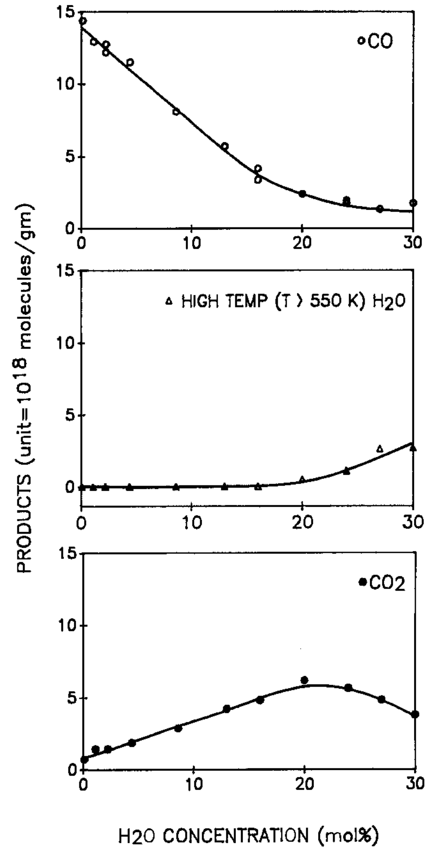

Fig. 3. Quantitative variations in TPD product yields from methanol and water coadsorption as a function of water concentration. (a) CO; (b) high temperature H_2O and (c) CO_2.

of the mixtures during the adsorption sequence. No such H_2O was observed for X_{H_2O} below 20 mol%. Again, no H_2 was detected during adsorption and so we can eliminate the second process as being a major factor. Moreover, when X_{H_2O} was higher than 20 mol%, H_2O was seen to desorb above 550 K in an increasing amount as X_{H_2O} was raised. This leads to the conclusion that the coinjected H_2O was adsorbed on the dehydroxylated ZnO surface and subsequently consumed in the TPD process to form CO_2, as proposed in (3) above.

3.3. H_2O PREADSORPTION FOLLOWED BY CH_3OH ADSORPTION

To clarify further the reactivity of adsorbed H_2O with CH_3OH TPD studies were performed following a sequential adsorption experiment where H_2O was preadsorbed on ZnO followed by CH_3OH adsorption. A small quantity of H_2O was first injected into He stream to produce a low water coverage on ZnO. No H_2O breakthrough was observed during the adsorption process. H_2 was also monitored,

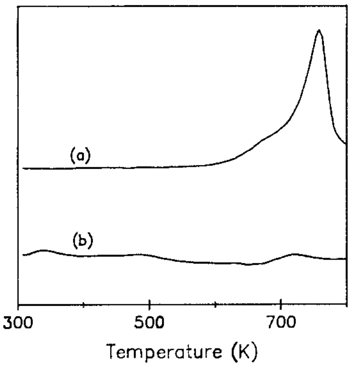

Fig. 4. Water desorption: (a) a low coverage of ~ 8 × 10^{18} molec/g H_2O; (b) from $CH_3OH + H_2O$ coadsorption at X_{H_2O} = 20 mol%.

but was not found. The desorbed H_2O (~ 6.5 × 10^{18} molec/g) was characterized by the profile shown in fig. 5a. H_2O was again adsorbed on ZnO using the identical procedure followed by CH_3OH injection to saturation coverage. During the CH_3OH dosing process, the H_2O signal was continuously monitored. Desorption of H_2O was not observed indicating that, under the prevailing experimental and temporal conditions, the preadsorbed H_2O was not displaced by CH_3OH and remained adsorbed on ZnO surface. The subsequent TPD spectrum is shown in fig. 5b. The amount of CO desorbed was relatively small (2.7 × 10^{18} molec/g) with a peak at 600 K, while 5.1 × 10^{18} molec/g CO_2 desorbed at ~ 610 K. The presence of the preadsorbed H_2O caused a broadening of the desorption spectrum.

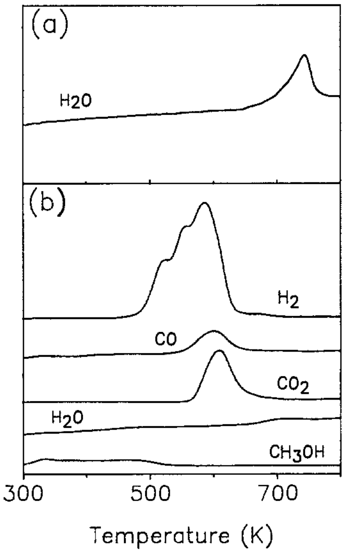

Fig. 5. (a) H_2O desorption from a low coverage of ~ 6.5 × 10^{18} molec/g; (b) TPD spectrum obtained following preadsorption of a low coverage of H_2O and CH_3OH adsorption to saturation coverage.

The H_2O desorption spectra in fig. 5 show clearly that CH_3OH adsorption to a saturation coverage onto the ZnO surface containing preadsorbed H_2O resulted in a drastic reduction in the amount of H_2O desorbed. Comparison with the TPD of "pure" methanol, fig. 1, shows that the existence of the preadsorbed water increases the CO_2 yield at the expense of CO. Furthermore, the CO_2 yield in the sequential adsorption experiment is approximately equal to the estimated net loss of desorbed water. This leads to the conclusion that the preadsorbed H_2O was consumed in the TPD process and resulted in increased CO_2 desorption. Further experiments indicated that when residual H_2O was allowed to build up as a consequence of accumulation from the He carrier gas, the results were very similar to the above deliberate sequential adsorption experiments. Thus, under our experimental conditions, there was little difference as to whether H_2O was preadsorbed, coadsorbed with CH_3OH, or was present in residual form. The results showed clearly that adsorbed H_2O takes part in the mechanism of CH_3OH decomposition on ZnO with the end reaction products being CO_2 and H_2.

4. Discussion

The first point for discussion is the variation in the CO_2 yield with water content in the coadsorption experiments and the relationship to the CO yield. In the $CH_3OH + H_2O$ coadsorption experiments, the CO_2 yield reached a maximum (at $X_{H_2O} \approx 20$ mol%). For CO_2 yields below the maximum, no water desorption occurred above 550 K whereas water was observed to desorb above 550 K in an increasing amount as the CO_2 yield started to decrease, fig. 3. This suggests that for the water concentration greater than 20 mol%, there was an excess amount of adsorbed H_2O present on the ZnO surface, which could not be consumed in the formation of CO_2 and desorbed as water. The quantitative variation in CO, CO_2 and H_2O yield can be understood if adsorbed H_2O occupied sites which otherwise would be the sites for methanol adsorption and when CH_3OH was adsorbed alone (i.e., without H_2O coadsorption), each adsorbed CH_3OH decomposed to CO and H_2. Thus, when CH_3OH and H_2O were coinjected, methanol coverage would be decreased by the amount of adsorbed H_2O. If adsorbed hydroxyls reacted with adsorbed CH_3OH to give CO_2 and H_2, then this would result in two former methanol adsorption sites producing only one molecule of CO_2 and associated H_2. In this way, the rate of decrease in CO production as X_{H_2O} was increased from 0–20 mol% would be twice the rate of increase in CO_2 yield. This is illustrated in fig. 6 where the ratio of the two slopes is 2.3, close to the expected value of 2. Here the terms "adsorbed methanol" and "reaction" are used in a general sense and are not intended to imply a direct reaction between molecularly adsorbed methanol and water. The precise nature of adsorbed methanol and water, and the reaction, is not important in the above argument. The competition between methanol and

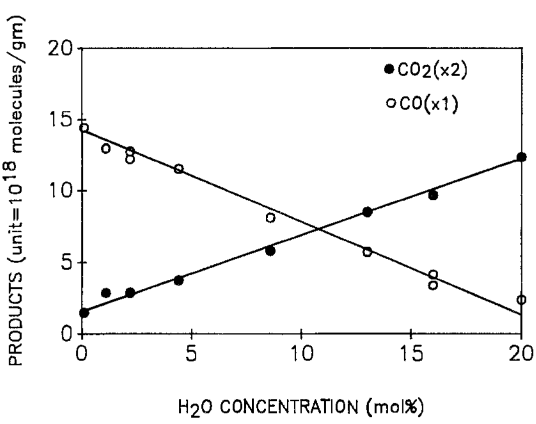

Fig. 6. Comparison of the dependence of CO_2 and CO TPD yields from methanol and water coadsorption for water concentrations 0–20 mol%.

water for the same adsorption sites also explains the decrease in H_2 yield with the increasing X_{H_2O}.

In a previous study of H_2O, CH_3OH and $H_2O + CH_3OH$ adsorption on ZnO by Roberts and Griffin using combined IR and TPD techniques [2], CH_3OH adsorption on type I sites was shown to be blocked by preadsorbed water, and this behaviour is similar to that observed in the present study. However, they concluded that preadsorbed water was not incorporated in CO_2 formation which was produced on non-type I sites. The role of adsorbed water was viewed as reducing the CO yield by influencing the relative availability of type I and non-type I sites. This conclusion was based on a number of factors, one of which was the similarity of the CO_2 yield when preadsorbed water was either present or absent. However, we have shown that for the present ZnO surface, the same CO_2 yield can be obtained in TPD with different CO : CO_2 ratios at two water coverages, fig. 3, as a consequence of the competition of methanol and water for the same adsorption sites.

The process by which adsorbed methanol and water yield CO_2 may involve the water–gas shift reaction (WGSR) over ZnO in which CO originating from the decomposition of CH_3OH may react with surface hydroxyls. Experiments were performed in which pulses of CO were injected into a He stream saturated with H_2O in the temperature range of 500–660 K (within the CO desorption temperature range). We did not find any significant CO_2 production over the ZnO catalysts in this temperature range. This would appear to rule out the possibility that the CO_2 produced in TPD was by reaction between gas phase or readsorbed CO (from CH_3OH decomposition) with surface hydroxyls.

Roberts and Griffin [2] assigned a 3618 cm^{-1} OH band to residual surface hydroxyls, which were assumed to take no part in methanol decomposition on ZnO. However, examination of the published IR spectra suggests that when the

CH_3OH dosed catalyst was heated from 300 to 530 K, this hydroxyl band decreased in intensity whilst IR bands belonging to formate species were simultaneously observed. These intensity changes might be explained by the reaction between surface hydroxyls and adsorbed CH_3OH although Roberts and Griffin did not arrive at this conclusion. Edwards et al. [4], who studied CH_3OH decomposition on Cu/ZnO and $Cu/ZnO/Cr_2O_3$, reported a concurrent disappearance of the IR hydroxyl bands at 3666 ± 5 and 3620 ± 2 cm^{-1} (assigned to hydroxyls on ZnO sites) and at the same time the appearance of formate and gaseous CO_2 IR bands during methanol adsorption at 190–200°C. The disappearance of these bands was viewed by Edwards et al. [4] as the evidence of the displacement of the adsorbed hydroxyls by methanol to form adsorbed methoxy and H_2O. However, this could be interpreted in terms of the reaction of adsorbed methanol with surface hydroxyls. Recently, Shlegel' et al. [12] have suggested that an initial process in methanol decomposition on $Cu–Zn–Al_2O_3$ catalysts was the reaction of methanol with strongly bound residual hydroxyls on ZnO to give CO_2 and H_2. Combined with the present data, this suggests that formate is an intermediate involved in a reaction of adsorbed methanol and surface hydroxyls to produce CO_2 and H_2.

The decomposition of CH_3OH on ZnO is commonly envisaged to proceed via a surface formate ($HCOO_{(a)}$) intermediate [2–8,18], whose decomposition results in the approximate coincident desorption of CO, CO_2 and H_2. The formation of the formate ion requires a surface lattice oxygen [6]. Consequently, decomposition of the formate to CO_2 involves the removal of ZnO surface oxygen and the creation of oxygen vacancies [2,8,11,16,19]. In a study of methanol decomposition over a reduced ZnO catalyst, Ueno et al. [6] showed that formate decomposed almost entirely to CO and H_2. Similarly, Bowker et al. explained the low CO_2 yield from methanol TPD and the reproducibility of the data in terms of the defective state of the ZnO surface [3]. In the present study, it could be that the dehydroxylation procedure leaves the ZnO surface in a reduced state such that CO and H_2 are the preferred products of formate decomposition. The desorption of CO_2 (and hydrogen) from methanol decomposition occurs close to the temperature we observed for the decomposition of formate produced by the reaction of CO_2 and H_2 at 475 K on the same ZnO [20]. That is, formate yields CO_2 and H_2 when its genesis and decomposition does not involve the permanent removal of lattice oxygen from the dehydroxylated surface. In the presence of water, formate can be produced by the reaction of methoxy (or a further dehydrogenated species) with adsorbed H_2O, as discussed above, which decomposes to CO_2 and H_2. Since there is always a small amount of water in methanol or in the "dried" carrier gas, the CO_2 desorbed in "pure" methanol TPD could arise from reaction with residual hydroxyls. The reaction with hydroxyls could occur either directly, i.e., between the adsorbed species, or indirectly where CO_2 production involves lattice oxygen and adsorbed water. Alternatively, Saussey et al. [21,22] claimed evidence for the existence of a formyl species on a heat treated ZnO, produced from the reaction of CO and H_2. One might speculate that for the dehydroxylated surface the decomposition of methanol to CO and H_2 may involve a formyl intermediate, while decomposition to CO_2 and H_2 occurs via formate. However, in a later study of methanol decomposition over ZnO/Al_2O_3 using chemical trapping techniques, it was concluded that formyl played no role in the decomposition mechanism [23].

In order to fully understand CO_2 production from methanol decomposition, we have attempted to adjust the stoichiometry of the dehydroxylated surface. Experiments were carried out in which the ZnO was first dehydroxylated and then annealed in oxygen or hydrogen. However, the affinity of the dehydroxylated surface for water is such that we have found it impossible to prevent the reintroduction of surface hydroxyls. Desorption of these prior to methanol adsorption probably regenerates the original dehydroxylated surface which then gave data identical to that obtained without H_2 or O_2 treatment.

Recently, Shido and Iwasawa [13] reported a reactant promoted reaction mechanism for the WGSR over ZnO in which CO reacts with hydroxyls (on-top adsorption on Zn^{2+}) to produce both bidentate and monodentate formates. They found that the formates decomposed 70% to CO and 30% to CO_2. We have demonstrated that in the case of methanol decomposition, when there is an excess of adsorbed methanol (X_{H_2O} less than 20 mol%), each adsorbed water results in the desorption of a CO_2 molecule, so that there is no water desorption from the surface and the "excess" methanol apparently decomposes almost exclusively to CO and H_2. Shido and Iwasawa [13] observed that the presence of excess water promoted the decomposition of formate to CO_2 via an intermediate unidentate carbonate. In the present study, when H_2O is in excess on the surface and the CO_2 yield is falling as X_{H_2O} increases, a second CO_2 desorption peak is developed at higher temperature. This additional CO_2 feature may involve carbonate and be a consequence of the process described by Shido and Iwasawa [13].

It has been shown that methanol is synthesized mainly from hydrogenation of CO_2 over Cu/ZnO catalysts [4,14,24,25]. The present results imply that the reverse reaction of methanol synthesis from CO_2 and H_2, namely the reaction of methanol and water, is possible over ZnO catalysts and probably takes place via a formate intermediate.

5. Conclusions

CH_3OH adsorption on dehydroxylated ZnO decomposed mainly to CO and H_2 during TPD. As the amount of coadsorbed water was increased, the CO yield decreased almost monotonically whereas that of the CO_2 increased and went through a maximum. A quantitative analysis of this behaviour has established that water and methanol compete for the same adsorption sites and that production of CO_2 and H_2 probably arises from a reaction between adsorbed methanol (or a dehydrogenated intermediate) and surface hydroxyls. In a sequential adsorption experiment, it was demonstrated that preadsorbed water was incorporated in CO_2

production. It is suggested that the intermediate in this process is probably formate, although carbonate may be involved at the higher water concentration.

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