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Temperature-programmed Desorption Studies of Alcohol Decomposition on Zinc Oxide

Propan-2-ol

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Temperature-programmed desorption (t.p.d.) has been used to investigate the nature of the interaction of propan-2-ol with the zinc oxide surface. Adsorption at pressures of 10 Torr resulted in an averaged saturation coverage of 2×10^{14} molecule cm^{-2} at 310 K. Temperature programming resulted in the desorption of propan-2-ol itself just above the adsorption temperature and a more strongly adsorbed intermediate species (an alkoxyl) decomposed at *ca.* 480 K to yield products of acetone, propene and hydrogen. It is proposed that these products derive from a sequential reaction scheme; first α-hydrogen elimination occurs, which yields acetone into the gas phase and an extremely reactive surface hydride. The latter then attacks remaining alkoxyl groups at a β-H position, the resulting transition state then decomposes to yield the alkene and hydrogen into the gas phase and shows a small temperature lag in the t.p.d. experiments.

In a previous paper in this series the results of a study of the decomposition of ethanol on reduced ZnO surfaces were reported.[1] Ethanol was adsorbed by the surface to produce a strongly bound intermediate which decomposed at 510 K to yield mainly ethylene, hydrogen and a small amount of acetaldehyde or ethylene oxide (which are difficult to distinguish in the mass spectrometer). Thus it appeared that the dehydration of ethanol was the dominant reaction route under the transient conditions used in temperature-programmed desorption (t.p.d.).

Akiba *et al.*[2] recently reported results of steady-state microreactor experiments for the decomposition of propan-2-ol on zinc oxide which showed only a dehydrogenation of the molecule to acetone and hydrogen. In view of our earlier results with ethanol this selectivity appeared surprising, and so the study described in the present paper was embarked upon in order to determine whether any products of dehydration (propene) could be detected. The technique we have used is the same as in the earlier paper,[1] namely temperature-programmed desorption.

EXPERIMENTAL

The apparatus used has been described in detail in a previous report.[3] Briefly, it consists of an adsorption chamber which can be filled with dosing gas to atmospheric pressure. The sample holder, containing 0.2 g of catalyst, was mounted on an FC38 conflat flange in this chamber. This holder consists of a quartz tube (8 mm o.d., 3.8 mm i.d.) within which the catalyst is packed and around which is wound a Pt–Rh wire for sample heating. The heating is provided from a programmable power supply and the heating rate can be varied; a typical heating curve has been reported in an earlier paper[4] and is linear above 400 K.

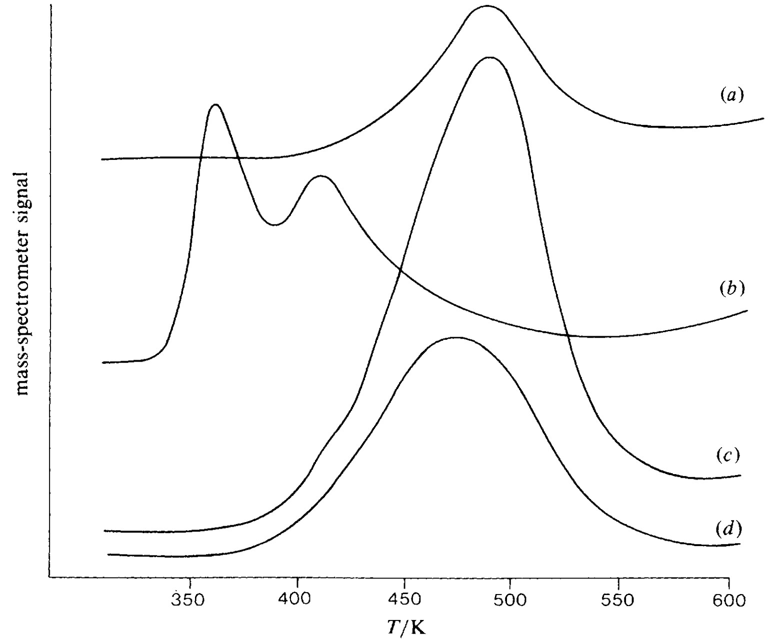


Fig. 1. Temperature-programmed desorption spectrum of products after the adsorption of propan-2-ol on ZnO at 310 K. The small contributions to any individual product peak from the other products has been subtracted for clarity and the desorption curves are offset vertically for the same reason. (*a*) Propene (*m*/*e* 41) × 3.3, (*b*) propan-2-ol (*m*/*e* 45) × 3.3, (*c*) hydrogen (*m*/*e* 2) × 1 and (*d*) acetone (*m*/*e* 58) × 10.

After dosing the sample with gas and pumping the ambient away, the temperature was ramped and the products desorbed were measured in a Vacuum Generators QX200 quadrupole mass spectrometer which could be programmed to select four individual mass peaks for one run. Thus several dosing experiments were performed in order to gather complete cracking patterns for the various products desorbing from the surface.

The propan-2-ol used was analytical-reagent grade (99.5% pure) and was subjected to pumping cycles to remove any impurities more volatile than propan-2-ol itself; the purity of alcohol was confirmed by *in-situ* mass-spectral analysis.

RESULTS

The ZnO sample was initially treated in the same way as described in the earlier papers,[1,3,4] *i.e.* it was heated to 700 K to remove desorbable impurities (0.25% carbonate being the major quoted impurity) and was then reduced at 550 K in order to prescribe a constant initial surface state of the zinc oxide. After this pretreatment the propan-2-ol was dosed onto the catalyst at 10 Torr* for 900 s in a closed system with the sample *ca.* 310 K. The remaining gas was then pumped away to a base pressure of *ca.* 10^{-6} Torr and temperature programming was begun. The resulting desorption product distribution is shown in fig. 1. The detectable products were propan-2-ol, acetone, propene and hydrogen. Fig. 1 shows experimental curves obtained for four individual masses which are considered as representative of the four

* 1 Torr = 101 325/760 Pa.

products seen. Many other mass peaks were also monitored to verify the correctness of the interpretation, although most other masses had significant fragments from two or more of the products. The double-peaked nature of the propan-2-ol desorption is an artefact of the heating method: the ramp takes some time to linearise and is only truly linear above *ca.* 400 K.[4] Nevertheless the integral under the desorption curves is still proportional to the surface coverage of the zinc oxide by propan-2-ol. Monitoring mass 18 during the desorption sequence showed that no water was evolved during heating.

The major features of the desorption were similar to the earlier results for ethanol,[1] namely that intact alcohol was desorbed just after heating was begun (360–430 K), whereas a more strongly adsorbed species appeared to be left after such treatment, which, on desorbing, yielded the alkene and ketone products with a peak rate at 480 K.

Although the decomposition peaks for propan-2-ol appeared in the same temperature range, the lineshapes for propene and acetone were different, the latter being much broader (87 K *vs* 57 K for propene at half the peak maximum intensity) and peaking 12 K earlier than propene. The hydrogen desorption appears to be of intermediate lineshape but with a peak maximum temperature coincident with that of propene. Reduction of the catalyst between each desorption experiment was found to be unnecessary, since the desorption was quite reproducible even without such treatment.

The coverage of the sample by the adsorbed alcohol was calculated from the time–intensity integral of the desorption spectra using the pumping speed of the chamber and the sensitivity of the mass spectrometer to the various products. The formula used for such a calculation is

$$n = \frac{BLN_r I}{SR}$$

where n is the surface coverage by adsorbate (in molecule cm^{-2}), L is the pumping speed of the system for the product concerned (in dm^3 s^{-1}), N_r is Avogadro's number per Torr per dm^3, I is the integral under the desorption spectrum measured at the mass spectrometer (in A s) and B is a correction factor to account for the fact that only a part of the material desorbed comes through from the adsorption chamber to the detector. S is the sensitivity of the machine in A Torr^{-1} and R is the total surface area of the sample. The factor B in the present work was 5.3, while L was 1 dm^3 s^{-1}. The sensitivity S depends upon the peak analysed, but for mass 43 for acetone, for instance, it has a value of 3 A Torr^{-1}. The surface area of the sample was 0.6 m^2 (3 m^2 g^{-1}). Using this method the total coverage of the surface by propan-2-ol-derived species (*i.e.* propan-2-ol, acetone and propene derived from individual adsorbed propan-2-ol molecules) was 2.2×10^{14} molecule cm^{-2}. In product terms this comprised 8×10^{13} molecule cm^{-2} of propan-2-ol which were desorbed intact, 9×10^{13} molecule cm^{-2} of acetone and 5×10^{13} molecule cm^{-2} of propene. The surface density of Zn and O atoms depends on the particular plane exposed, and the analytical-reagent ZnO which we have used can be approximately described as being composed of particles of hexagonal cylindrical shape. The ends of these cylinders are polar $(000\bar{1})$ and (0001) planes, while the six coaxial faces are prism planes; from previous SEM/TEM studies the polar planes constitute *ca.* 20% of the total surface area. The density of Zn and O atoms on the prism faces is 1.4×10^{15} atom cm^{-2}, while on the polar faces the density is 1.1×10^{15} atom cm^{-2}. Thus, the averaged surface coverage by adsorbate is *ca.* 0.2 of a monolayer.

In their study of propan-2-ol decomposition Akiba *et al.*[2] proposed that the propanol forms a very strongly bound intermediate which they believe to be the enol tautomer of acetone. Therefore as a test of whether adsorbed acetone would produce

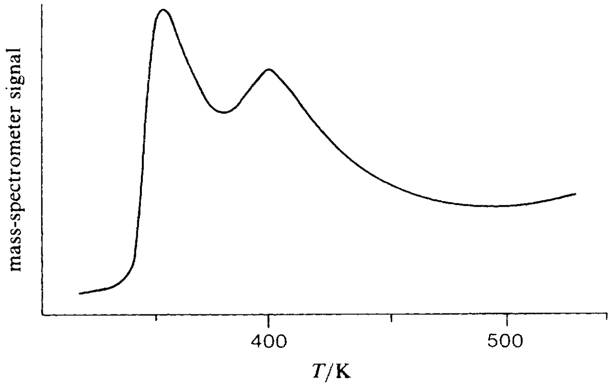


Fig. 2. T.p.d. spectrum for acetone adsorption on ZnO at 310 K [(*m*/*e* 43) × 3.3].

the enol tautomer or might be responsible for the products seen in fig. 1 at *ca.* 490 K, the sample was dosed with acetone at 320 K (40 Torr for 300 s resulted in saturation coverage, 1.4×10^{14} molecule cm^{-2}) and the subsequent t.p.d. spectrum is shown in fig. 2. These indicate that a strongly adsorbed complex was not formed, the adsorbed acetone being desorbed intact in the low-temperature region.

DISCUSSION

The results described above are grossly similar to the previous results obtained for the lower alcohol, ethanol;[1] the alcohol is adsorbed in a relatively weakly bound state which is desorbed in the low-temperature range as the parent alcohol, and forms a more strongly bound intermediate which only leaves the surface at higher temperatures. The mechanism of the interaction with the surface can be written in a similar way to that for ethanol, *i.e.* initial adsorption probably takes place as follows:

$$C_3H_7OH(g) \rightarrow C_3H_7OH(a) \tag{1}$$

$$C_3H_7OH(a) + O_s \rightarrow C_3H_7O(a) + OH(a) \tag{2}$$

$$C_3H_7OH(a) + OH(a) \rightarrow C_3H_7O(a) + H_2O(g) + V_0 \tag{3}$$

where (a) and (g) refer to adsorbed and gas-phase species, respectively, s refers to the lattice sites and V_0 is an anion vacancy. The nature of the equipment we have used precludes an analysis of the propanol adsorption process (the mass spectrometer is shut off from the adsorption chamber during dosing, because of the relatively high pressures used) so that there is no direct evidence for the mechanism of steps (2) and (3), *i.e.* water production. However, several features point to this mechanism being operative. First, no water is produced in the desorption process shown in fig. 1, even though a dehydration product of propan-2-ol, *i.e.* propene, is produced during the desorption. If no water were produced during adsorption the surface would become 'saturated' with oxygen after one or two desorption experiments owing to this conversion, and the propensity of the surface for the dehydration reaction would diminish.

This was found not to be the case. The surface seems to maintain a constant state during repeated experiments, without the necessity for re-reduction. Thus water must be lost from the surface during the adsorption process to maintain this reproducibility, and so steps (2) and (3) are included. Furthermore, earlier experiments on single-crystal Cu(110) doped with surface oxygen showed that alcohols interact with the surface in just this way to produce water which is lost from the sample below room temperature.[5]

However, this mechanism must only apply to that fraction of the surface which subsequently produces propene. The acetone production must proceed through a dehydrogenation mechanism which does not evolve water from the surface, probably by the recombination of dissociated hydrogen atoms during the adsorption (Griffin and Yates[6] have shown that such a process can occur below 300 K on zinc oxide):

$$C_3H_7OH(a) \rightarrow C_3H_7O(a) + H(a) \qquad (4)$$

$$2H(a) \rightarrow H_2(g). \qquad (5)$$

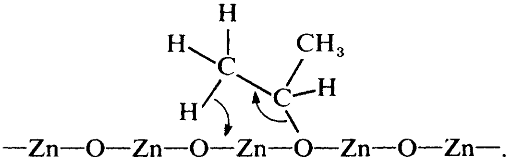
These processes leave a surface populated by 2-propoxyl and adsorbed alcohol species. The alcohol desorption at low temperatures is either due to recombination of adsorbed alkoxyl and hydrogen atoms [the reverse of step (4)] or, more likely, to the desorption of intact propan-2-ol molecules bonded to the surface by relatively weak, oxygen lone-pair interactions with the surface:[5]

$$C_3H_7OH(a) \rightarrow C_3H_7OH(g). \qquad (6)$$

This then leaves the surface covered with two types of adsorbed alkoxyl species, those with the usual nearest-neighbour oxygens and those with anion vacancies produced by step (3). They then decompose at a similar temperature to produce quite different reaction products. The alkoxyl species, which is associated with an anion vacancy in the zinc oxide lattice, decomposes in a way which removes the vacancy, thus:

$$C_3H_7O(g) + V_0 \rightarrow C_3H_6(g) + H(a) + O(s) \qquad (7)$$

and so balances out the loss of surface oxygen shown in step (3). The deprotonation presumably takes place at adjacent sites on the zinc oxide by β-H removal, as proposed for ethanol:[1]



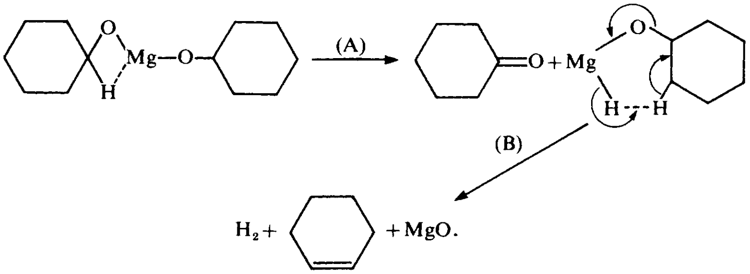
The dehydrogenation reaction probably takes place at different sites: either at stoichiometric ZnO sites, as proposed by Fahim *et al.*[7] for propan-2-ol decomposition on ceria, or on the Zn-dominated (0001) polar face of the sample (which constitutes *ca.* 10% of the total area):

$$C_3H_7O(a) \rightarrow C_3H_6O(g) + H(a) \qquad (8)$$

$$2H(a) \rightarrow H_2(g). \qquad (9)$$

The possibility that this reaction occurs on the more metal-like polar face is attractive, since the noble metals dehydrogenate in this way[5] and the amount of material desorbing as acetone (9×10^{13} molecule cm^{-2}) seems to correspond reasonably well with the total Zn polar-face sites (*ca.* 11×10^{13} atom cm^{-2} of total catalyst area).

However, one feature of the data which does not seem to fit well with the simple mechanism outlined above is the similarity of the decomposition temperature for the two products from two such different sites. Usually, in t.p.d. experiments, the evolution of products in coincident peaks is taken to indicate that the products evolve from an adsorbed intermediate which is common to them all. By this token the products we observe would be derived from some kind of dimeric surface complex, but without spectroscopic equipment the existence of such an intermediate cannot be proved. A more likely explanation for the behaviour observed may, however, be found in the work of Ashby *et al.*,[8] who studied the decomposition of a variety of magnesium and zinc dialkoxides and alkyl alkoxides. They found that for the dialkoxides, for instance, a generalised mechanism can be written by reference to the decomposition of dicyclohexyloxymagnesium:



This, then, seems to explain all the products seen in the above experiment. Furthermore, it could explain both the similarity of peak desorption temperatures for acetone and propene and the fact that acetone slightly precedes the latter. Clearly the whole mechanism depends on the occurrence of step (A) (α-hydrogen elimination) which also produces an hydride species. If this reaction occurs on a particular site of the ZnO surface, this hydridic species must be mobile in order to 'seek out' other alkoxide species with which to react; it is not likely that, for a zinc ion bound to a substrate, two alkoxide species could be attached to the same ion in the way shown above for metal alkoxide molecules. This hydridic, and presumably cation-bound, entity then deprotonates an alkoxide to produce propene in a β-elimination reaction [step (B)]. However, this second step does involve a further small activation energy barrier which results in a temperature shift of the alkene product. Furthermore, it is possible that, as described above, some recombination of hydrogen from step (A) can take place which results in $< 50\%$ evolution of propene. Indeed, if the decomposition were as shown in steps (7) and (8) above, the hydrogen-desorption envelope should simply be a convolution of the acetone and propene curves, which it clearly is not from the averaged normalised lineshapes shown in fig. 3. (It is skewed towards the propene curve.) Furthermore, if the mechanism were exactly like that of Ashby *et al.*[8] the lineshape should be coincident with the propene, whereas the halfwidth is between the two. This, together with the fact that there are unequal amounts of the two organic products, indicates that some hydrogen-atom surface recombination takes place corresponding with the lower amount of alkene production by hydride-induced β-elimination.

From their transmission infrared measurements Koga *et al.*[9] conclude that an enol-type intermediate is formed from either propan-2-ol adsorption and heating to 363 K, or acetone adsorption at room temperature, yet in the present work the same intermediate certainly was not formed from acetone. As fig. 2 shows, there was little evidence of strong adsorption of acetone at all. The source of the difference between these results and those of Tamaru and coworkers[2, 9] in this respect is not clear, though it is possible that residual OH groups on the ZnO in Tamaru's work contributed to acetone adsorption and reaction. However, several points of similarity between the present results and Tamaru's are noteworthy. First, the specific rate of acetone

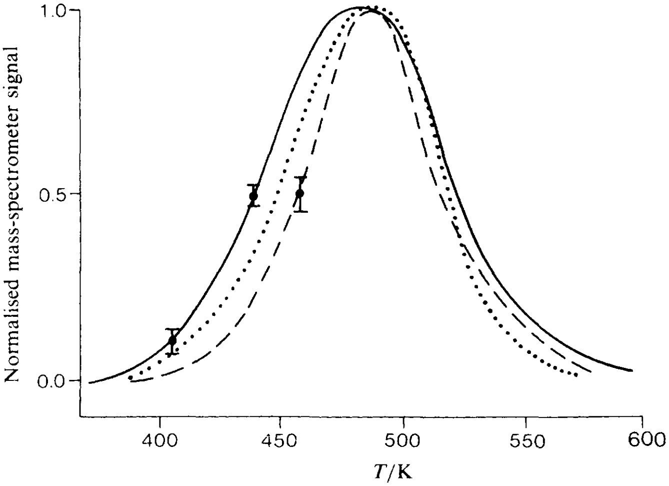


Fig. 3. Normalised desorption peaks for propan-2-ol decomposition on ZnO. The solid line is acetone desorption, the dashed line is propene and the dotted line is hydrogen. The curves are the averaged result of four experiments for each product, and mean deviations of signal are indicated on the figure.

formation from the latter work[2] at saturation surface coverage (1.5×10^{10} molecule cm^{-2} s^{-1} at 363 K) is very similar to the rates of acetone formation (at the leading edge of the acetone desorption, *ca.* 1.2×10^{10} molecule cm^{-2} s^{-1} at 370 K) shown in fig. 1. Secondly, at the low temperatures which they used, these authors observed the build-up of a species (which they designate as an enol) which is inactive for acetone production in the absence of gas-phase alcohol; this species may well correlate with the propene production shown in fig. 1, the rate of which, at the low-temperature desorption edge, is very much slower than that of acetone. This appears to support the two-species aspect of the model described above. The major difference between these two works is the large amount of propene production seen in the present work. The difference seems to be explicable in terms of (i) the much faster production of acetone at low temperatures, even though the total temperature-integrated product ratio is very similar, and (ii) the fact that the 'inactive' species of Tamaru's work can be converted into acetone by the presence of propan-2-ol in the gas phase, thus preventing its build-up and subsequent blockage of acetone production.

In conclusion then, temperature-programmed desorption experiments have shown that propan-2-ol interacts strongly with the ZnO surface to produce adsorbed alkoxyl-type species. These decompose to produce acetone and propene with a peak rate at 480 K. The source of the two products is considered to be two different adsorption sites, those with and those without adjacent anion vacancies, respectively. The alkene is produced by the interaction of hydridic species (generated from the alkoxyl decomposing to yield the ketone) with the more strongly bound anion vacancy associated alkoxyl, which results in β-hydrogen elimination/abstraction. However, the generality of these observations will be examined by further experiments using the adsorption of other alcohols on ZnO in combination with these techniques and will be reported upon completion.

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