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Studies on the Mechanism of Methanol Oxidation on Zinc Oxide by Dynamic Treatments of Chemisorbed Species under the Reaction Conditions

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The mechanism of methanol oxidation on zinc oxide was studied by quantitatively observing the dynamic behaviour of the surface species during the course of the reaction. It was concluded that the mechanism was similar to that of the decomposition reaction, with an additional step, the oxidation of the carbon monoxide formed. As a key step in the oxidation of methanol, the decomposition of adsorbed methoxide groups in the presence of oxygen at temperatures between 140 and 180 °C has been studied by infrared spectroscopy. The methoxide groups decompose to formate ions until a maximum surface concentration is reached. The rate of decomposition at first increases with methoxide concentration, then decreases as the surface coverage approaches saturation. The observed kinetics can be explained by a mechanism which postulates that negatively charged surface species repel electrons from the surface of the zinc oxide, thus inhibiting decomposition of the methoxide groups.

In order to elucidate the mechanisms of heterogeneous catalytic reactions, it is advantageous to be able to quantitatively observe the dynamic behaviour of the surface species during the course of the reaction.$^{1)}$ Infrared spectroscopy provides a means of achieving this, but progress has been limited, mainly because of experimental difficulties.$^{2)}$

Recently, a paper from this laboratory$^{3)}$ elucidated the mechanism of methanol decomposition on zinc oxide, by the use of simultaneous infrared and kinetic measurements. It was shown that methanol is adsorbed as methoxide and hydroxide groups. At temperatures above approximately 150 °C, the methoxide groups decompose to give formate ions, which at temperatures above 200 °C and in the absence of methanol vapour, decompose to give carbon monoxide.

Because of this successful application of quantitative infrared spectroscopy, it was felt that it would be profitable to extend this work to a detailed study of the individual reaction steps of a similar system. The oxidation of methanol was chosen because the presence of oxygen decreases the infrared absorption by zinc oxide. Experiments showed that the mechanism was similar to that of the decomposition reaction, with an additional step, the oxidation of the carbon monoxide formed. This paper reports on the decomposition of surface methoxide groups on zinc oxide in the presence of oxygen.

Experimental

The zinc oxide, Kadox 25, a product of the New Jersey Zinc Co., was the same as that used in the previous work,$^{3)}$ and had a B.E.T. surface area of 10 $m^2 g^{-1}$. It was pressed into self-supporting disks (ca. 0.1 g cm^{-2}) and a single disk placed in a previously described infrared cell,$^{4)}$ part of a conventional closed circulating system. The infrared spectrometer employed was a JASCO 402G Grating Spectrometer (Japan Spectroscopic Co.), and the spectra of the adsorbed species were studied within the 4000 to 900 cm^{-1} range.

Before each experiment, the catalyst disk was given the following outgassing treatment at 400 °C. Evacuation (*ca.* 10^{-5} Torr) for three hours, followed by 5 minutes in 1 cmHg of oxygen, a further 1 hour evacuation, 30 minutes in 1 cmHg of oxygen, and finally cooled to the reaction temperature (usually 150 °C) under oxygen. During the oxygen treatments, the gas phase was circulated through the infrared cell and a liquid nitrogen trap in order to remove any CO_2 that had desorbed from the catalyst surface. This treatment gave a highly oxidised catalyst, and the residual hydroxyl and carbon dioxide peaks were reduced to a satisfactory level.

The reactions were carried out in the absence of gas phase methanol, under 1 cmHg of oxygen. Methoxide groups are strongly bound to the zinc oxide surface, and at the temperatures studied, the rate of desorption was small, especially at lower coverages.

Results

Oxidation of Methanol and Decomposition of Methoxide Groups. The spectra observed for the methoxide, hydroxide and formate surface species on zinc oxide in the presence of oxygen, were the same as those reported by Ueno *et al.*$^{3)}$ on reduced zinc oxide, with the addition of a methoxide band overlapping the ZnO band at 1070 cm^{-1}, which is assigned to C–O stretching.

At temperatures above 150 °C in vacuum, ZnO slowly loses oxygen,$^{5)}$ giving an increase in the number of conduction electrons. This causes a marked decrease in the background transmission, and affects the optical density of the absorption bands due to adsorbed

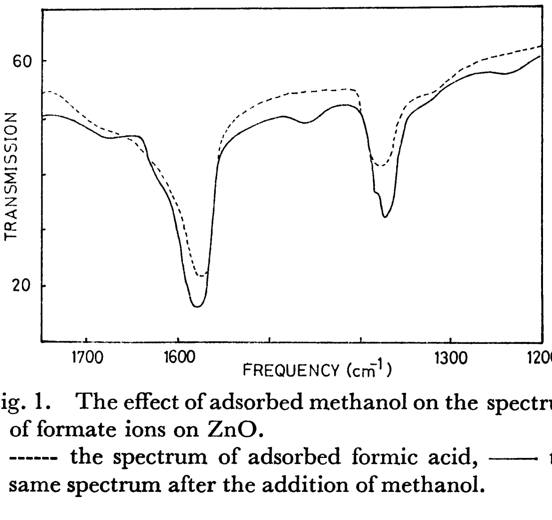


Fig. 1. The effect of adsorbed methanol on the spectrum of formate ions on ZnO.
----- the spectrum of adsorbed formic acid, —— the same spectrum after the addition of methanol.

species, especially those at lower frequencies. This loss of lattice oxygen appears to be enhanced by the adsorption of methanol. In the presence of oxygen, however, the background transmission is greatly improved, and the intense formate O–C–O asymmetric stretching band at 1570 cm^{-1} can be used for quantitative measurements.

It was found that the band shape and optical density of the formate 1570 cm^{-1} band were affected by the presence of other surface species as illustrated in Fig. 1. Therefore, for this band, the integrated optical density was used, as this was shown to be independent of the presence or absence of the other surface species occurring in this work.

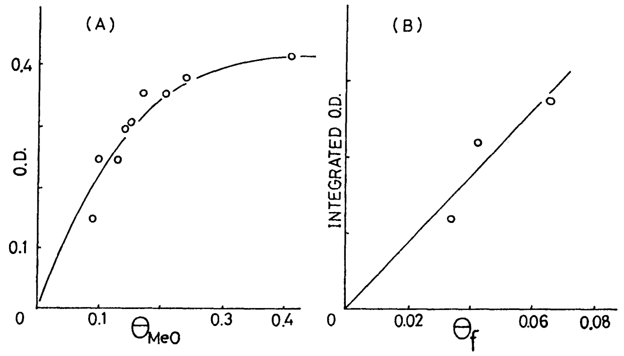


Fig. 2. Calibration curves. (A) Optical density of the 2830 cm^{-1} methoxide band *versus* methoxide group coverage. (B) Integrated optical density of the 1570 cm^{-1} formate ion band *versus* formate ion coverage.

The calibration curves for the methoxide group and formate ion shown in Fig. 2 were determined by measuring the 2830 and 1570 cm^{-1} bands when measured amounts of methanol and formic acid respectively were adsorbed at 100 °C. The concentration of surface sites on the zinc oxide was assumed to be 10^{15} cm^{-2}.

It is of significant interest to note that methanol oxidation proceeds in the presence of oxygen in a manner similar to that of methanol decomposition in the absence of oxygen, with an additional step, the oxidation of the carbon monoxide formed.

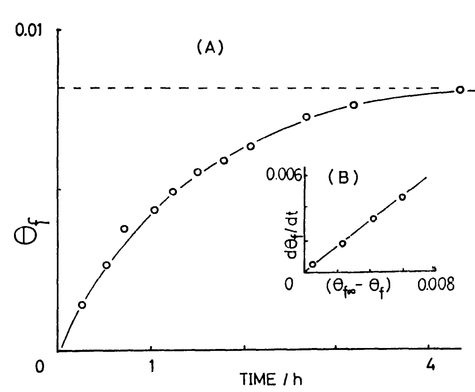


Fig. 3. Formate ion formation at 150 °C and $\theta_{MeO}=0.095$

When methanol was adsorbed on zinc oxide at 150 °C, the methoxide groups decomposed to give formate ions, until the surface formate ion coverage, θ_f, reached a saturation value, $\theta_{f\infty}$, which increased with increasing temperature. A typical result is shown in Fig. 3(A). It was found that the results, when plotted as $d\theta_f/dt$ against $(\theta_{f\infty}-\theta_f)$, as in Fig. 3(B), gave a straight line, and hence could be expressed as

$$d\theta_f/dt = k(\theta_{f\infty}-\theta_f).$$

Although the limited accuracy of the experimental results does not exclude other expressions, this form was found to be useful in defining a first order rate constant k, and in cases where the reaction was very slow, in estimating $\theta_{f\infty}$.

When formic acid was preadsorbed on the catalyst disk at 150 °C, to give a coverage of $\theta_f=0.01$, the integrated optical density of the 1570 cm^{-1} band remained constant with time, and did not change even when methoxide groups were introduced onto the surface. This showed that the methoxide groups did not decompose in the presence of this surface coverage of formate ions, and that the rate of formate ion decomposition at 150 °C is negligible.

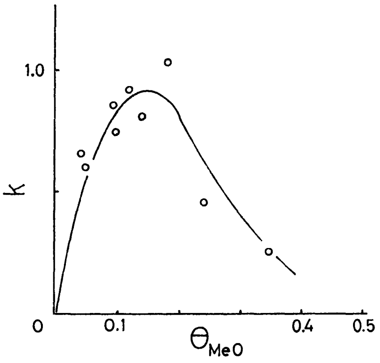


Fig. 4. The dependence of k on the methoxide group coverage.

Figure 4 shows the dependence of k on the methoxide surface coverage, θ_{MeO}. As $\theta_{f\infty}$ was always small compared to θ_{MeO}, the methoxide coverage was approximated as being constant during each run, although the gradual desorption of methanol may lead to errors of up to 10% in the value of θ_{MeO} at higher coverages. The results from Fig. 4 suggest that the rate equation for the reaction could be written as

$$d\theta_f/dt = k'(\theta_{f\infty}-\theta_f)\theta_{MeO}^{x}(1-\theta)^{y}$$

where θ is the total surface coverage. Although the scatter of the experimental points cannot justify putting exact values to x and y, it seems probable that $y \geq x \approx 1$.

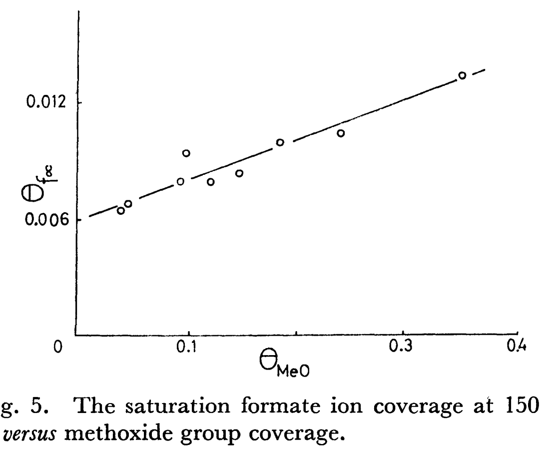


Fig. 5. The saturation formate ion coverage at 150 °C *versus* methoxide group coverage.

Support for the $(1-\theta)^y$ term was given by the results of an experiment in which the methoxide coverage was increased in the middle of a normal run. θ increased from 0.27 to 0.75 and the rate of formate ion formation was drastically reduced. As shown in Fig. 5, $\theta_{f\infty}$ depends linearly on θ_{MeO}.

It was found that there was no measureable dependence of either $\theta_{f\infty}$ or k on oxygen pressure in the range 1 to 12 cmHg. At oxygen pressures of less than about 0.5 cmHg, the zinc oxide appeared to lose oxygen, and the formate ion coverage was impossible to measure quantitatively.

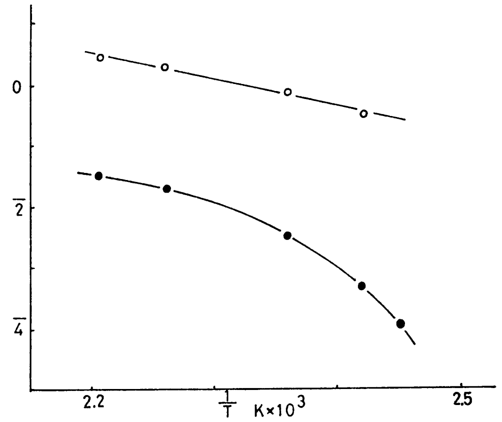


Fig. 6. Arrhenius plots of k —●—, and the initial rate of formate ion formation —○—.

Arrhenius plots of k and the initial rate of formate formation, for constant $\theta_{MeO}=0.16$, are shown in Fig. 6. The slope of the straight line given by $\log_{10} k$ against $1/T$ is equivalent to an activation energy of 85 kJ·mol^{-1}.

Preadsorbed Carbon Dioxide. The effect of CO_2 on the rate of the formate ion decomposition and on $\theta_{f\infty}$ was also investigated. CO_2 was admitted onto the zinc oxide in the presence of oxygen at 150 °C, then the circulated gas phase was trapped with liquid nitrogen. Figure 7 shows the spectrum immediately after the CO_2 was removed from the gas phase, and after a further 40 min trapping. The addition of methanol caused a large proportion of the remaining carbon dioxide to desorb.

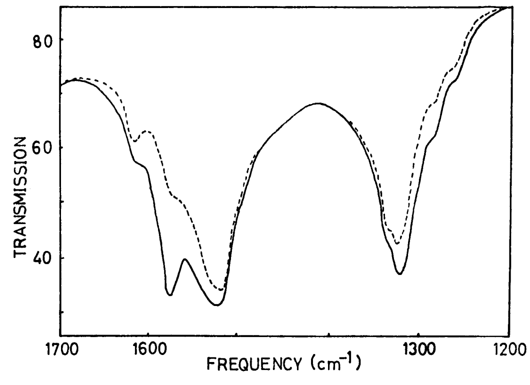
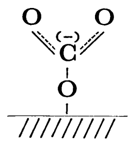
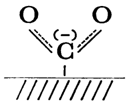


Fig. 7. The spectrum of CO_2 adsorbed on ZnO at 150 °C.
—— immediately after trapping the gas phase CO_2.
---- after 40 minutes trapping.

Despite a considerable amount of literature, the assignment of the infrared bands of CO and CO_2 adsorbed on metals and metal oxides remains very uncertain.[2] However, it seems probable that the two strong bands at 1530 and 1325 cm^{-1} should be assigned to the asymmetric and symmetric O–C–O stretching vibrations of



because of the close correlation with the spectrum of $Na_2[Cu(OCO_2)_2]\cdot 3H_2O$, which has bands at 1529 and 1326 cm^{-1}.[6] The unstable species absorbing at 1575 and probably 1325 cm^{-1} is possibly.[7]



Although it is difficult to determine exactly the amount of chemisorbed carbon dioxide species, it was found that the chemisorption of an estimated θ_{CO_2} of 0.02 halved the formate ion coverage at saturation. This effect is obviously too great to be attributed solely to the $(1-\theta)^y$ term.

Discussion

It appears unlikely that the apparent saturation of the formate ion is caused by its simultaneous decomposition, because the rate of decomposition of formate ions was shown to be negligible at 150 °C, and because this explanation would predict a linear Arrhenius plot for the initial rate.

A possible explanation for the results arises from the observation that negatively charged surface ions such as adsorbed CO_2 and formate ions appear to inhibit the decomposition of the methoxide groups. If the methoxide group must capture an electron from the zinc oxide before it can decompose,

$$CH_3O(a) + e \rightleftharpoons CH_3O^-(a) \qquad (1)$$

$$CH_3O^-(a) + \text{free surface sites} \longrightarrow HCOO^-(a) + 2OH(a) \qquad (2)$$

and it is assumed that the concentration of $CH_3O^-(a)$ is small, and that the latter reaction is rate controlling, we can write

$$d\theta_f/dt = k''(1-\theta)^a[CH_3O(a)][e_s]K \qquad (3)$$

where e_s is the concentration of free electrons at the surface of the zinc oxide and K is the equilibrium constant for Eq. (1). The concentration of electrons at the surface can be written as[8]

$$[e_s] = N_c \exp\{-(\mu+eQ^2/2N_d\varepsilon\varepsilon_0)/kT\} \qquad (4)$$

where N_c is the number of free electrons, μ is the energy difference between the Fermi level and the bottom of the conduction band in the bulk, N_d the donor density, ε the dielectric constant of the ZnO, ε_0 the permittivity of the ambient gas, and eQ^2 the surface charge arising from charged surface species ($HCOO^-(a)$, $CO_2^-(a)$, and $O^-(a)$). Substitution of this term into Eq. (3) gives a rate equation similar to the experimentally derived rate equation, except that the $(\theta_{f\infty}-\theta_f)$ term has been replaced by an expression for the surface electron concentration which is exponential in $-eQ^2$. It is very unlikely that the experimental results could distinguish between these two forms, especially in view of the approximations of constant θ_{MeO} and θ, and the lack of information about chemisorbed oxygen. The proposed mechanism therefore suggests that the slowing down of the reaction is caused by the negatively charged layer of surface formate ions (or adsorbed CO_2^-) repelling electrons from the surface.

The increase of $\theta_{f\infty}$ with increasing temperature and increasing θ_{MeO} can be explained by their effects on the amount of chemisorbed O^-. Both would tend to decrease $[O^-(a)]$ thus decreasing the number of negatively charged species at the surface. Although no oxygen pressure dependence was found at oxygen pressures above 1 cmHg, it is possible that the surface is virtually saturated with $O^-(a)$ below this pressure. In support of this, increasing the oxygen pressure from 1 to 12 cmHg had little effect on the background ZnO infrared absorption. Further, values of $\theta_{f\infty}$ (ignoring formate ion decomposition) in the absence of gas phase oxygen, calculated from the results of Ueno *et al.*[3] are approximately 10 times larger than those found in this work.

Doping of the zinc oxide should also affect $\theta_{f\infty}$, though not to the same extent as changes in the surface charge, and this may help to explain the direct relationship between the electrical conductivity of zinc oxides and their activities for the decomposition of methanol.[9]

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