A New Dynamic Approach for Elucidating the Mechanism of Catalytic Reactions. The Mechanism of the Decomposition Reaction of Methyl Alcohol on ZnO

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(Received May 2, 1970)

Many reports[1] have been published on the infrared spectra of the species on the catalyst surface, but most of them have dealt only with the kind or with the structure of the species when no catalytic reaction takes place. The importance of observing the amounts and the dynamic behavior of the chemisorbed species on the catalyst surface in the course of the reaction in order to elucidate the mechanism of the catalytic reaction was previously emphasized by one of the present authors.[2] Accordingly, the mechanism of the H_2-D_2 exchange reaction,[3] the decomposition of formic acid,[4] and the water-gas shift reactions[5] on zinc oxide have been elucidated by means of a new dynamic approach, measuring the infrared spectra of the surface species.

The mechanism of the decomposition reaction of methyl alcohol on ZnO was studied by means of a new dynamic treatment. When CD_3OD was introduced to ZnO at 200°C, the CD_3O(a), OD (a), and DCOO(a) chemisorbed were observed by means of infrared spectroscopy, but CD_3OD(a) was not. The behavior of these surface species as well as that of the ambient gas and the overall reaction rates were simultaneously examined under various reaction conditions, including non-stationary conditions.

D_2, CO_2 and CO were formed by the decomposition of CD_3OD on ZnO at 200°C, but when CD_3OD was trapped out of the system by a dry ice-methanol mixture or in the absence of an ambient methanol vapour, the evolution of D_2 and CO_2 stopped correspondingly, though that of CO from the surface species continued during the trapping. The amount of CD_3O(a) on the catalyst decreased, but that of DCOO(a) increased, during the trapping. The decrease in the CD_3O(a) was nearly equal to the total increase in DCOO(a) and CO(g). Most of the CD_3O(a) on the surface disappeared during the trapping at 240°C, though DCOO(a) still remained on the catalyst, whereas the evolution of CO(g) was uninfluenced and continued at a rate comparable to the overall rate. When the CD_3OD collected in the trap was released into the gas phase, the amounts of D_2 and CO_2 were increased rapidly, but that of CO continued to increase without any change. It was, consequently, concluded that the CO was produced mainly from the decomposition of DCOO(a) on ZnO, and that the D_2 and CO_2 resulted from the interaction between the CD_3OD in the ambient gas and the surface DCOO(a). The results are shown in Fig. 1.

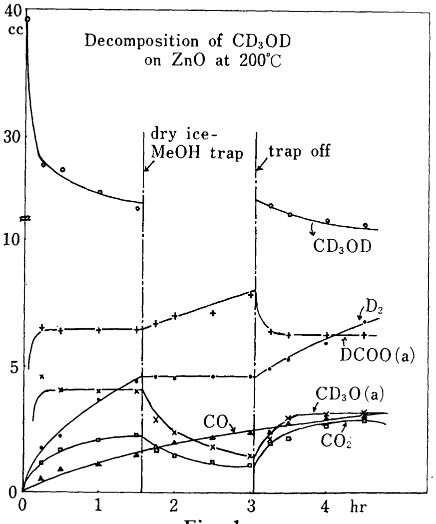
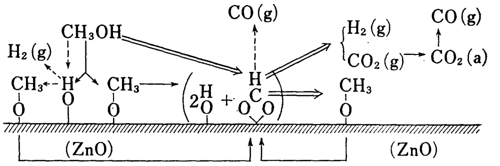


Fig. 1.

When CH_3OD was introduced onto the catalyst, the surface of which had been covered by OD(a), the hydrogen produced contained overwhelmingly more deuterium than protium. It was, accordingly, demonstrated that CH_3OD reacted not only with the surface formate, but also with the hydroxide on the surface of ZnO. It was, consequently, concluded that the mechanism of the decomposition of methyl alcohol on ZnO is shown as follows:



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