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OXIDATION OF ETHANOL BY OXYGEN OVER MAGNESIUM OXIDE

— Role of Surface Species —

By

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Abstract

The mechanism of ethanol oxidation was studied over magnesium oxide with the help of infrared spectrophotometric methods. It was shown that ethoxide and acetate were present on the catalyst in appreciable amount during the course of the oxidation. Either carbon dioxide or acetaldehyde was produced primarily through the oxidation of ethoxide. Acetate species participated in part in the reaction but played a very minor role in the reaction.

Introduction

When alcohol is brought into contact with metal oxides, alkoxide species are readily formed.[1~6] The infrared spectra of these species were found to be markedly influenced by the electronegativity of metal ion in the oxide.[7,8] This suggests that the nature of this species formed was strongly dependent upon that of oxide employed. Alkoxide formed on magnesium oxide was concluded to be more anionic than those on less ionic oxide such as alumina and silica. In the previous work, the dehydrogenation of ethanol[9] and the hydrogen transfer reaction[10,11] between ethanol and acetone were carried out over magnesium oxide. It was found by the infrared spectral observations that ethoxide and acetate were present during the course of these reactions. The ethoxide anion was found to participate effectively in these reactions and functioned as its intermediate. However, the acetate merely existed on the surface and was not involved in the reaction under the steady state. Recently, Miyata, Wakayama and Kubokawa[12] studied the oxidation of isopropoxide formed on magnesium oxide and nickel oxide. These authors found that isopropoxide was highly active toward oxgen and acetone was formed by the oxidation of this species while carboxylate which was transformed by the oxidation of isopropoxide was suggested to be involved in

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the carbon dioxide formation.

In connection with these results, it is, therefore, probable that either ethoxide or acetate is appreciably present on magnesium oxide and acts as an effective intermediate of a variety of reactions in which ethanol is involved. In the present work, experiments are carried out over magnesium oxide to study the role of these species in the oxidation of ethanol by oxgen under the steady state.

Experimental

The oxidation of ethanol was carried out over magnesium oxide (10.2 gr. Kishida Chemical Co., extra pure grade) at temperatures ranging from 256 to 340°C in a flow system. Ethanol vapor was admitted with a stream of oxgen or a mixture of oxgen and nitrogen into the catalyst bed. Total inflow was kept in the range of 120 to 450 cc/min for which the effect of the products upon the rate was practically negligible. Partial pressure of ethanol was kept at 11.8 torr, while that of oxygen was varied in the range of 40 to 760 torr. The reactants and the products were analyzed by means of gas chromatography. Peroxides were examined with iodie ion in 1.0 N sulfuric acid solution by use of starch indicator[13] but no peroxide was detected. An infrared cell in which a thin wafer of magnesium oxide was mounted was connected in series at the outlet of the reactor. The amount of adsorbed species was determined with the help of infrared spectrophotometric method. Gases used were purified in a manner similar to that in the previous work.[9]

Results and Discussion

I) Oxidation under the Steady State

Carbon dioxide, acetaldehyde and water were primarily formed by the oxidation under the steady state. Carbon monoxide, hydrogen and methanol were also observed as by-products but their amounts were negligible compared to those of the former three products. The gaseous composition in the outflow was found to be held unchanged irrespective of the postcatalytic volume. Therefore, no oxidation of the reactants and products occurred in homogeneous phase under the present experimental conditions. In the oxidation, the measured rates of acetaldehyde formation were at least 300 times as rapid as that in the dehydrogenation of ethanol $CH_3CH_2OH \rightarrow CH_3CHO + H_2$ which had been determined in the previous work.[9] The dehydrogenation was, therefore, negligible under the oxidation conditions. In Figure 1, the mole fractions of carbon dioxide and acetaldehyde in exit gases were

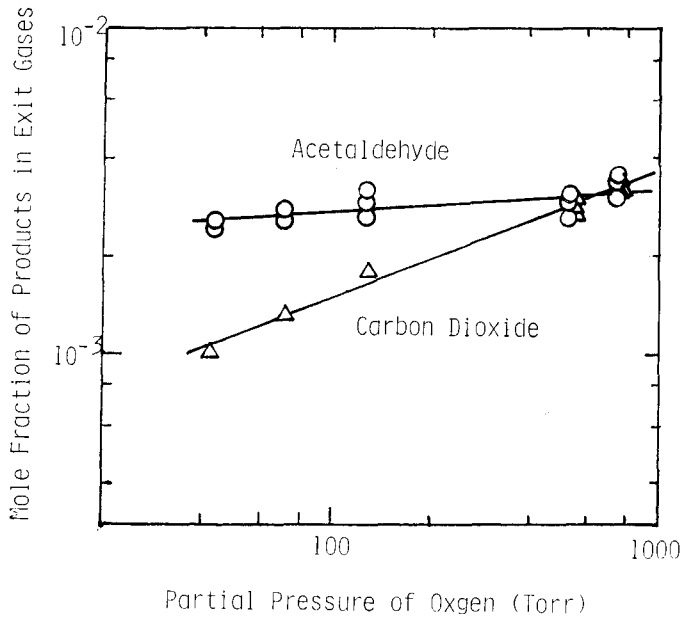

Fig. 1. Effect of Oxygen upon the Ethanol Oxidation.
Temperature: 290°C.
Total inflow: 200 ccSTP/min.
$P_{EtOH} = 11.8$ torr.

plotted against the partial pressure of oxgen. It shows that the formation of carbon dioxide proceeded in proportion to 0.45-s order in the partial pressure of oxygen, whereas that of acetaldehyde occurred practically independent of that of oxgen. The carbon dioxide and acetaldehyde formations were found to proceed with the activation energies of 34.4 and 17.6 kcal/mole, respectively.

II) Adsorbed Species

Figure 2 shows the infrared spectra of the surface species which formed in the oxidation. The absorption bands were observed at 1580, 1420, 1120 and 1060 cm^{-1}, indicating that acetate and ethoxide were formed in the course of the reaction. However, no absorption bands due to carbonate were observed. In Figure 3, the amounts of these species under the steady state are plotted against the reaction temperatures. The amount of acetate formed in the oxidation exceeded greatly that formed in the dehydrogenation.[9] However, that of ethoxide was practically unaffected by the presence of oxgen. Acetaldehyde which rapidly formed in the oxidation should trans-

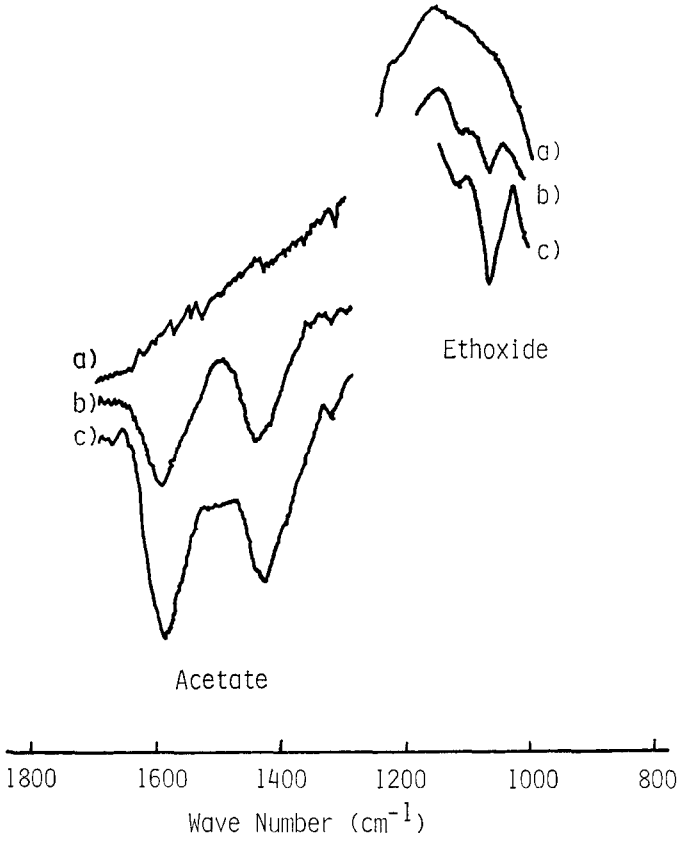

Fig. 2. Infrared Spectra of Surface Species present in the Course of the Ethanol Oxidation.
a) Background, b) 290°C, c) 162°C.

form in part into acetate according to the previous observations.[14] Acetate was, therefore, abundantly present in the oxidation.

III) Reactivity of Adsorbed Species

Both ethoxide and acetate were also formed when ethanol-nitrogen mixture had been admitted into the catalyst bed. When the stream of the mixture was switched over to that of nitrogen at 290°C, ethanol in gaseous phase rapidly diminished and the ethoxide was gradually decreased while the acetate remained unchanged. When the stream was again switched over to that of oxgen or oxgen-nitrogen mixture, the ethoxide decreased at fairly rapid rate,*) and carbon dioxide and acetaldehyde were formed. Formation

*) The oxidation occurred practically with ethoxide (see later).

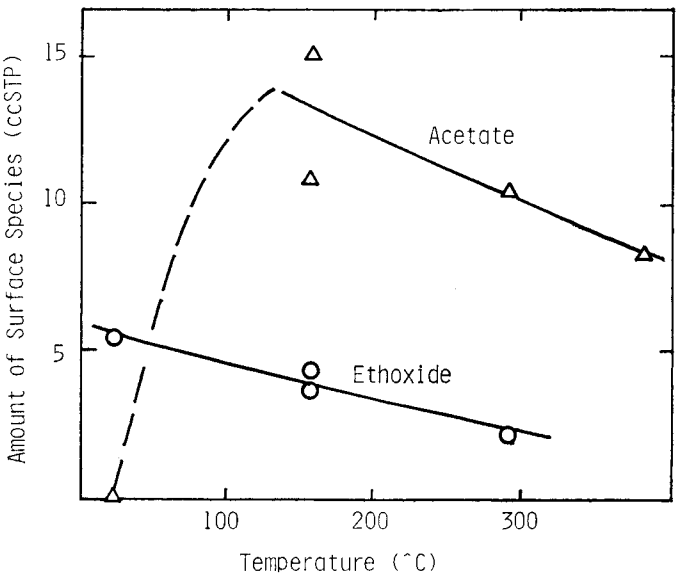

Fig. 3. The Steady Amount of Ethoxide and Acetate formed during the Course of the Ethanol Oxidation.
$P_{EtOH}=11.8$ torr, $P_{O_2}=760$ torr.

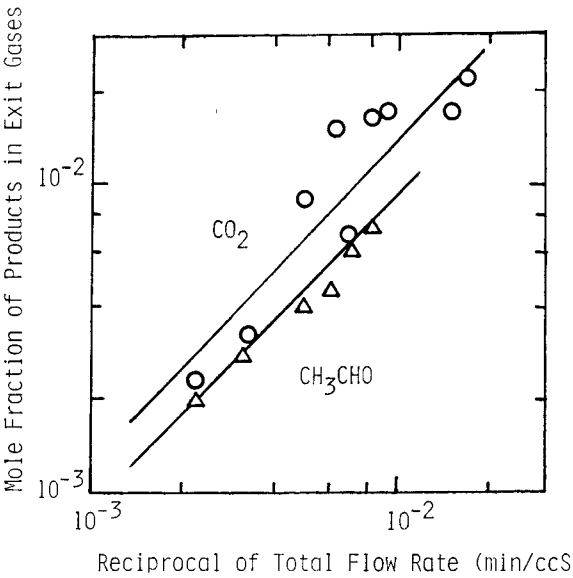

Fig. 4. Effect of Total Inflow upon the Oxidation of Surface Species.
Acetate: 7.3 cc STP, Ethoxide: 2.8 cc STP, Temperature: 290°C, $P_{O_2}=760$ torr

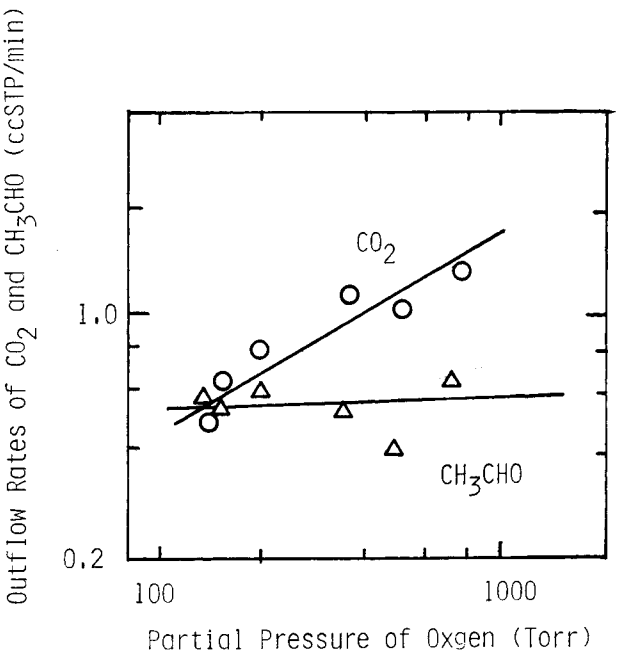

Fig. 5. Effect of the Partial Pressure of Oxygen upon the Oxidation of Ethoxide.
Acetate : 7.3 cc STP, Ethoxide : 2.64 cc STP.

rates of these species were initially rapid and decreased with time. In Figure 4, the mole fractions of these species in the exit gases at the initial stage of the oxidation of surface species are plotted against the reciprocal of the total flow rate. It shows that the mole fractions are proportional to the latter parameter. The initial rates of formations of these species were, therefore, practically independent of the total flow rate, so that the formations of these species were unaffected by the products. Figure 5 shows the plots between the initial rates of the acetaldehyde and carbon dioxide formation and the partial pressure of oxgen. It is seen that the formation of acetaldehyde is practically independent of the partial pressure of oxgen whereas that of carbon dioxide is found to proceed in proportion to 0.6-s order in the partial pressure of oxgen.

When nitrogen was allowed to flow over the catalyst on which ethoxide and acetate were present, the former species decreased, while the latter species remained unchanged. When oxgen was admitted over the catalyst on which only acetate was present, it reacted slowly with the acetate. As illustrated in Figure 6, the acetate initially decreased at a rate of 0.055 cc

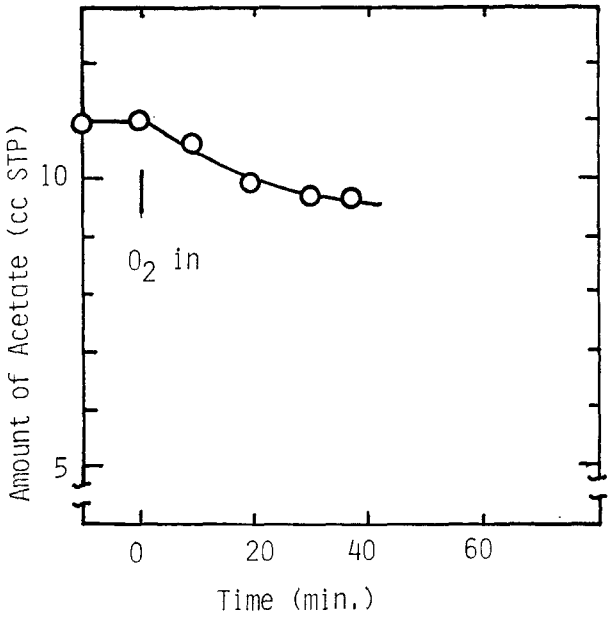

Fig. 6. The Oxidation of Acetate formed during the Course of the Ethanol Oxidation.

Temperature: 290°C, $P_{O_2}=760$ torr.
Initial amount of Acetate=11.1 cc STP. No ethoxide was present.

STP/min at 290°C when 11.1 cc STP of acetate was brought into contact with oxgen at 760 torr. The corresponding rate of carbon dioxide formation was estimated to be 0.11 cc STP/min. Under the conditions described in Figure 5, ethoxide was, therefore, highly active towards oxgen, while acetate reacted sluggishly with oxgen.

IV) Reaction Intermediate

As Figure 3 shows, 2.5 cc STP of ethoxide exists on the surface together with 11.1 cc STP of acetate under the steady state of ethanol oxidation at inlet partial pressures of $P_{EtOH}=11.8$ torr and $P_{O2}=760$ torr and 290°C. The steady rate of carbon dioxide formation under these conditions was found to be 0.68 cc STP/min whereas that of acetaldehyde was 0.64 cc STP/min. When oxgen stream was passed over the catalyst on which 2.5 cc STP of ethoxide was present, carbon dioxide and acetaldehyde were formed at rates of 0.76 and 0.50 cc STP/min, respectively. These values are practically in accord with those obtained under the steady state. In these respects, it is, therefore, concluded that both acetaldehyde and carbon dioxide were mostly

formed by the oxidation of ethoxide under the steady state of ethanol oxidation. However, acetate formed during the course of the reaction played a very minor role in the reaction. The kinetic feature of acetate formed in the ethanol oxidation is very different from that of carboxylate formed by the oxidation of isopropoxide for which the carboxylate was suggested to participate in the carbon dioxide formation.[12] Since it was shown that isopropoxide was oxidized in part into acetate and formate,[12] the latter species would be an effective intermediate for carbon dioxide formation from isopropoxide.

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