The Mechanism of Dehydrogenation of Ethanol on Magnesium Oxide

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The mechanism of dehydrogenation of ethanol was studied over magnesium oxide. It was found that in the course of the reaction ethoxide and acetate are formed on the catalyst. The ethoxide is one of the intermediates of the dehydrogenation, whereas the acetate does not participate in the reaction. Hydrogen was produced by the decomposition of ethoxide but no acetaldehyde was evolved in the gaseous phase simultaneously with hydrogen. Acetaldehyde was formed in the presence of ethanol vapor but not in its absence.

In addition, it is demonstrated that the kinetic features of ethoxide on magnesium oxide are qualitatively from that on alumina.

INTRODUCTION

The decomposition of normal alcohol occurs primarily through its dehydration or dehydrogenation over metal oxides. The decomposition of ethanol has been extensively studied in connection with the selectivity and the mechanism of the decomposition (1–12). The kinetic behavior of the intermediate of the dehydration reaction has been elaborately studied in recent years with the help of spectroscopic methods and it was concluded that dehydration on alumina occurred through the decomposition of ethoxide (9,10). This was in accord with the mechanism which was proposed earlier by Topchieva et al. (6). On the other hand, it has not yet revealed how dehydrogenation occurs on metal oxides.

In view of the facts outlined above, the present work was undertaken to study the mechanism of dehydrogenation of ethanol over magnesium oxide which is highly selective toward dehydrogenation.

EXPERIMENTAL PROCEDURES

1. Materials

Catalyst. Magnesium oxide (10.2 g: Kishida Chemical Co. Guaranteed grade) used for the decomposition was pressed into pellets at a pressure of 10 kg/cm² and was prepared in a stream of oxygen at 450°C for 2 hr. The infrared spectra of adsorbed species were obtained on the catalyst in a form of thin wafer which was prepared in the same manner as that used for the preparation of the catalyst for decomposition.

Ethanol. Liquid ethanol (Nakarai Chemical Co. Guaranteed grade) used was dehydrated on dehydrated copper sulfate.

Nitrogen. Nitrogen in a cylinder was dehydrated over potassium hydroxide and molecular sieve 5 A.

2. Experimental Method

1. Infrared Spectra of Adsorbed Species

The catalyst in a form of thin wafer was supported in an infrared cell as used by

Hirota and co-workers (13). The cell was located at the inlet of the catalyst bed[1] and the spectra of adsorbed species were recorded with a Hitachi 215 infrared spectrophotometer. The amount of surface acetate formed in the course of the reaction was estimated from the intensity of the adsorption at 1580 cm^{-1} which is attributed to asymmetric stretching vibration of carboxylate

$$-C\overset{O}{\underset{O}{\diagup}} \quad (-).$$
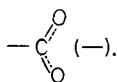
Prior to the experiment, the intensity of the absorption at a given reaction temperature was determined at various amounts of adsorbed acetic acid since acetate formed by the adsorption was stable under the present experimental conditions. The amount of ethoxide formed at 150°C was determined by the intensity of the C–O stretching vibration of ethoxide.[2] However, under the experimental conditions the amount of ethoxide was not simply determined since it was thermally decomposed. Therefore, after the intensity of the absorption band due to ethoxide had been measured in the absence of ethanol at the reaction temperature, the temperature was rapidly decreased to 150°C and the intensity was again measured. With the process of decreasing temperature, ethoxide was not converted into acetate. The intensity at the reaction temperature was therefore safely reduced to that at 150°C, where ethoxide was stable,[3] and the amount of ethoxide in the course of the reaction was successfully determined.

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[1] Some of the experiments were carried out in a system in which the cell was located at the outlet of the catalyst bed. The spectra obtained were practically the same as those obtained at the inlet of the catalyst bed.

[2] Ethoxide was stable at 150°C.

[3] The intensity of the absorption decreased with a rise in the temperature.

2. Decomposition Reaction

i. The decomposition under the steady state. The decomposition was carried out in a flow system. Dehydrated liquid ethanol was allowed to evaporate in a stream of prepurified nitrogen. Ethanol vapor was further dried on dehydrated copper sulfate and admitted through the catalyst bed with the nitrogen stream. The composition of gases at the inlet and the outlet of the catalyst bed was followed by means of gas chromatography, in which Porapak R and Q columns were employed.

The steady state of reaction was attained when the composition of gases remained unchanged at the outlet of the catalyst bed.

ii. The decomposition under transient state. The experiments were carried out in the same manner as had been done by Kobayashi and Kobayashi (14). Ethanol vapor was admitted through the catalyst bed with a nitrogen stream and the composition of gases at the outlet of the catalyst bed was followed with time until the steady state was attained. After the steady state had been attained, the inflow was switched over to a pure nitrogen stream and the change of the composition of gases in the outflow was followed. The amount of adsorbed species was followed by means of infrared spectroscopy.

RESULTS

Selectivity of the Reaction

Hydrogen and acetaldehyde were formed under the steady state of the decomposition with small amounts of ethylene and water. The selectivity of the dehydrogenation into hydrogen and acetaldehyde was estimated to be 91% at lowest. Figure 1 gives the ratio of acetaldehyde to hydrogen at various temperatures, showing the ratio equals unity. It is therefore concluded that under the
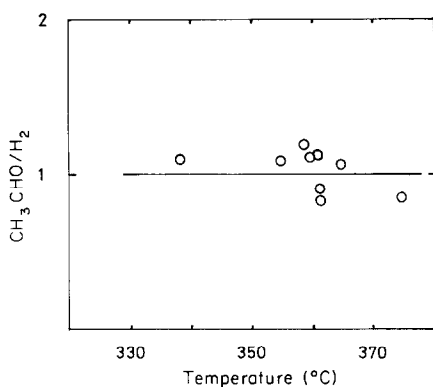
FIG. 1. The ratio of acetaldehyde to hydrogen under the steady state of the dehydrogenation of ethanol. $P_{EtOH} = 1.92 \times 10^{-2}$ atm; N_2 flow rate = 63 cc STP/min.

FIG. 2. Effect of the partial pressure of ethanol upon the rate of the dehydrogenation. N_2 flow rate = 63 cc STP/min.

steady state the reaction $C_2H_5OH \rightarrow CH_3CHO + H_2$ predominantly occurs on magnesium oxide.

Reaction Under the Steady State

i. The Decomposition and the Flow Rate of Carrier Gas

The mole fraction of hydrogen and acetaldehyde was determined at the outlet of the catalyst bed as a function of the flow rate of the carrier gas. The conversion of ethanol was less than 2% under the present experimental conditions so that the backward reaction was practically neglected. In addition, it was found that the mole fraction of the products is inversely proportional to the flow rate of the carrier. The forward rate is, therefore, independent of the partial pressures of the products.

ii. The Decomposition and the Partial Pressure of Ethanol

Figure 2 represents the effect of the partial pressure of ethanol upon the mole fraction of hydrogen at the outlet of the catalyst bed. It shows that the dehydro-
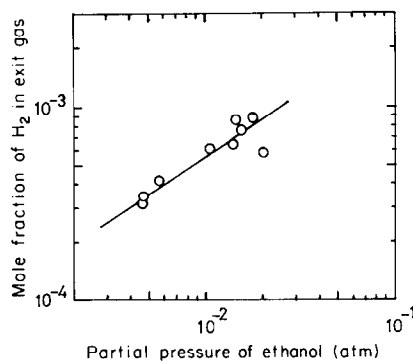
genation proceeds in proportion to 2/3-s order in the partial pressure of ethanol.

iii. The Temperature Dependence of the Rate

As can be seen from Fig. 3, the activation energy of dehydrogenation is estimated to be 29.3 kcal/mole.

Reaction Under the Transient State

After the catalyst had been kept in a nitrogen stream for a considerable period of time, the nitrogen flow was switched over to that containing ethanol vapor and the
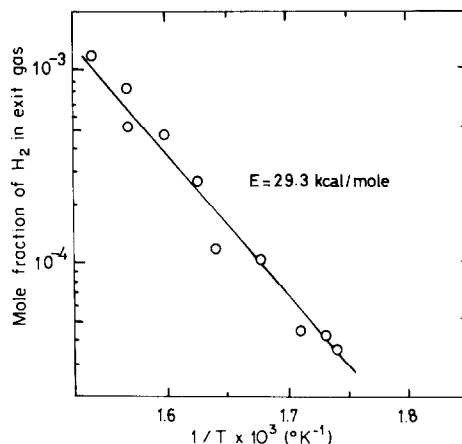

FIG. 3. Temperature dependence of the rate of the dehydrogenation. $P_{EtOH} = 2.05 \times 10^{-2}$ atm; N_2 flow rate = 63 cc STP/min.
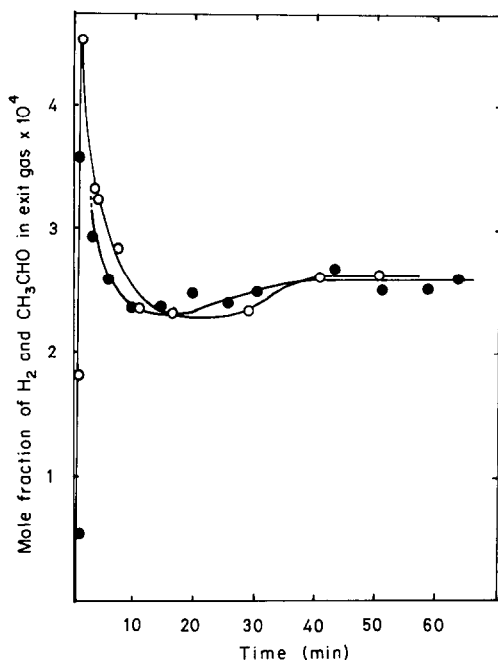
FIG. 4. The change in the concentration of products under the transient state (I). (●) Hydrogen; (○) acetaldehyde; reaction temp, 342°C; N_2 flow rate = 63 cc STP/min.

gaseous composition was followed with time at the outlet of the catalyst bed. As illustrated in Fig. 4, the formation of hydrogen and acetaldehyde reached the maximum at the initial period of the reaction, followed by the decrease of these species and finally increased to steady values. During the course of the reaction, adsorbed species were determined by the measurement of infrared absorption spectra. In Fig. 5, the spectra obtained after the removal of gaseous species are illustrated. The absorption bands were observed at 1580, 1420, 1120 and 1060 cm^{-1}. The former two bands have been assigned to

$$ -\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{C}}}\; (-) $$
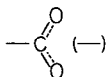
stretching vibration of surface acetate (15), and the latter two bands have been assigned to C–O stretching vibration of surface ethoxide (16) since the C–O
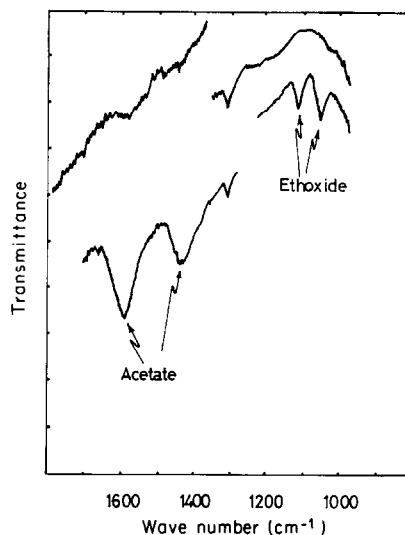

FIG. 5. Infrared spectra of the adsorbed species at 364°C. Upper spectrum: background spectra; lower spectra: adsorbed species in the course of the reaction at the partial pressure of ethanol = 2.05 × 10^{-2} atm.

stretching vibration occurred at 1123 and 1070 cm^{-1} in magnesium ethoxide (17). Figure 6 represents the time variation of the amount of surface acetate which shows that the acetate increased monotonically at the initial stage and then approached a steady value.[4]

After the reaction had reached the steady state, the inflow of ethanol vapor was switched over to a nitrogen stream. Figure 7 illustrates the resulting change in the gaseous composition at the outlet of the catalyst bed. Acetaldehyde and ethanol were rapidly decreased after the inflow of ethanol had been cut off. The mode of the decrease in aldehyde is much the same as that in ethanol. Hydrogen, on the other hand, decreased slowly and its formation lasted for a long time, even after the evolution of ethanol and acetaldehyde ceased. The results indicate that hydrogen was not

[4] The amount of ethoxide was not determined under the steady state since the positions of the absorption bands of ethoxide overlapped with those of ethanol vapor. However, the spectra showed a discernible shoulder near 1120 cm^{-1} which was ascribed to surface ethoxide.
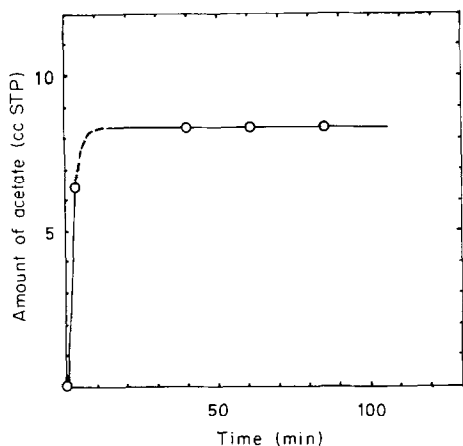
FIG. 6. The change in the amount of surface acetate. Reaction temp, 364°C; N_2 flow rate = 63 cc STP/min.

FIG. 8. The change in the amount of surface acetate and ethoxide under the transient state (II). (●) Acetate; (○) ethoxide.

evolved in gaseous phase simultaneously with aldehyde. It is particularly noted that 1,3-butadiene was formed with the rapid decreases in ethanol and acetaldehyde. These results suggest the aldehyde was formed from intermediate only in the presence of ethanol whereas in its absence butadiene was formed. Figure 8 shows the
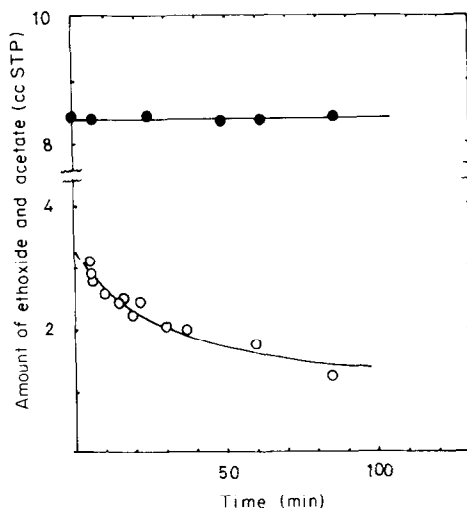

FIG. 7. The change in the concentration of the gaseous components under the transient state (II). (◐) Hydrogen; (○) ethanol; (◕) acetaldehyde; (●) 1,3-butadiene; reaction temp, 364°C; N_2 flow rate = 63 cc STP/min.

change in the amount of the adsorbed species when the gaseous composition was changed as represented in Fig. 7. Surface acetate remained unchanged whereas surface ethoxide decreased slowly. Ethanol was recharged on the catalyst but the amount of surface acetate still remained unchanged. Therefore, it is concluded that acetate is not an intermediate of the dehydrogenation.

In Fig. 9, the amount of acetate and ethoxide under the steady state of the reaction was plotted against the reaction temperature.[5] As shown in Fig. 9, no acetate is formed below or at 150°C. The amount of acetate increases with a rise in the temperature above 150°C. On the other hand, ethoxide is observed in the whole temperature range covering 25 to 370°C, and its amount decreased with increasing temperature. Since in the wave number 1150 to 1000 cm^{-1} the absorption bands due to ethoxide was overlapped with those of ethanol vapor, the amount of ethoxide was not simply determined under the steady state. The amount shown in Fig. 9 was estimated by extrapolating the
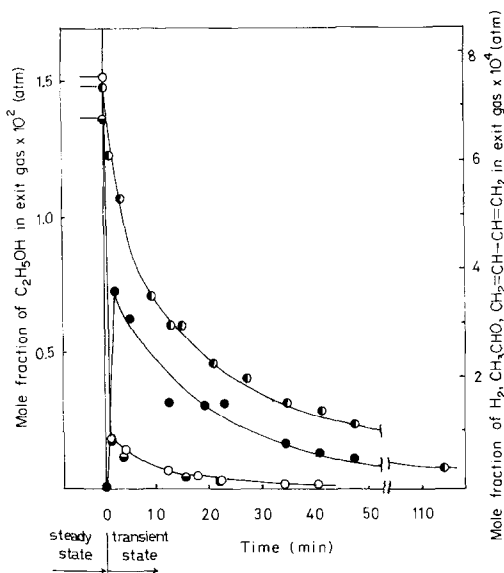
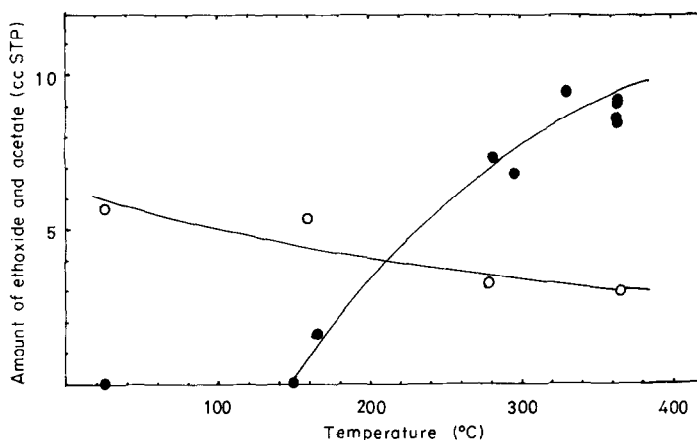[5] No reaction occurred below 300°C.

FIG. 9. The amount of ethoxide and acetate under the steady state. (●) Acetate; (○) ethoxide.

curves illustrated in Fig. 7 back to $t = 0$ at various temperatures.

Thermal Decomposition of Ethoxide

Thermal decomposition of surface ethoxide was carried out in order to study how it participates in the reaction. When the catalyst was exposed to a flow of nitrogen and ethanol mixture at 150°C, the partial pressure of ethanol at the outlet of the catalyst bed was initially small due to the occurrence of the adsorption of ethanol. It increased with time monotonically and finally the outflow of ethanol become

steady. Thereafter, ethanol flow was changed to nitrogen so that physically adsorbed ethanol was desorbed. The outflow of ethanol was monotonically decreased and finally became practically zero. The amount of irreversibly adsorbed ethanol was successfully estimated from these two response curves (*14*). It was found that 2.1 cc of ethanol was retained on the surface in the form of ethoxide as revealed by the infrared spectra. The temperature was raised at a rate of 5°C/min and the thermal decomposition of ethoxide was carried out in the nitrogen stream. In Fig. 10, the mole fraction of the products at the outlet of the catalyst bed was plotted against the temperatures. Ethanol began to desorb at 165°C and its mole fraction reached the maximum at 256°C, followed by its decrease with a continuing rise of the temperature. The total amount desorbed as ethanol was estimated to be 0.22 cc. Hydrogen began to desorb at 284°C and it increased until the temperature reached 370°C. It is remarkable that butadiene was formed in the decomposition of ethoxide instead of the formation of acetaldehyde. The results clearly indicate that, in the absence of ethanol, ethoxide is decomposed into hydrogen and butadiene.
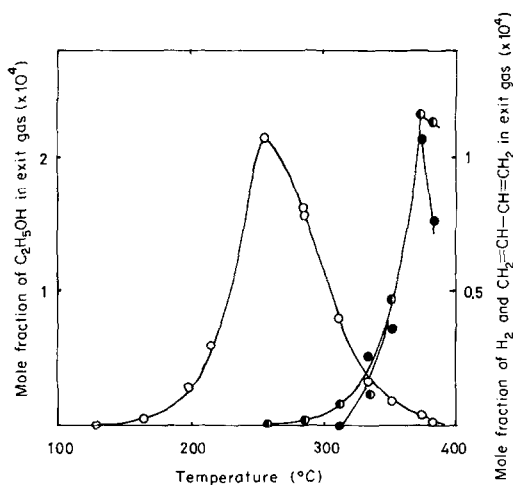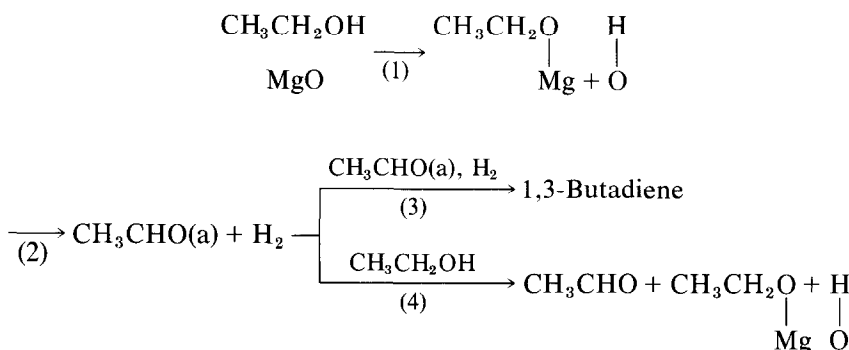

FIG. 10. Thermal decomposition of surface ethoxide. (○) ethanol; (◐) hydrogen; (●) 1,3-butadiene; N_2 flow rate = 63 cc STP/min.

DISCUSSION

It was shown in the previous section that under steady state the reaction

$CH_3CH_2OH \rightarrow CH_3CHO + H_2$ takes place predominantly over magnesium oxide. When the inflow of ethanol had been stopped in the course of the reaction, acetaldehyde formation was rapidly decreased but hydrogen formation lasted for a long time. Butadiene, on the other hand, began to appear with decreases in ethanol and acetaldehyde. This is strikingly different from the results of the steady reaction. The amount of the surface acetate formed in the course of the decomposition remained unchanged whereas that of ethoxide was slowly decreased. In the thermal decomposition of ethoxide, it was found that hydrogen and butadiene were formed but no acetaldehyde was observed. On the basis of these facts, it was concluded that acetaldehyde was formed only when ethanol was present in gaseous phase. Hydrogen formation occurred whenever ethoxide was present on the surface. It does not require the presence of ethanol vapor. Since it has been known that butadiene is produced through the dimerization of acetaldehyde (1), we conclude that ethanol is dehydrogenated by the following scheme:

fore the adsorbed aldehyde may be initially accumulated due to the continuous occurrence of step (2). This brought about the initial increase in the partial pressure of butadiene produced through step (3) as was evident from the results in Fig. 7. Hydrogen is produced by step (2) and is consumed in part by step (3) when butadiene is formed. In Fig. 11, the results in Fig. 7 and 8 are replotted in which the sum of the rates of the formation of hydrogen and butadiene[6] under the transient state is shown with the corresponding rate of the decomposition of ethoxide. These rates are fairly in accord with each other although the results at the initial period are not given since ethanol vapor interfered with the determination of the amount of ethoxide. In Fig. 12 the rate of the ethoxide decomposition shown in Fig. 11 is plotted as a function of the amount of ethoxide. The rate r can be expressed by the Elovich equation (18) as $r = ke^{hv}$, where k and h are constants and v is the amount of ethoxide. When the decomposition was carried out at 364°C under the partial pressure of ethanol of 5×10^{-3} atm, 1.95 cc of ethoxide was present under the steady

$$CH_3CH_2OH \xrightarrow[\quad(1)\quad]{} \begin{array}{cc} CH_3CH_2O & H \\ | & | \\ Mg + O \end{array}$$
$$MgO$$

$$\xrightarrow[(2)]{} CH_3CHO(a) + H_2 - \left[\begin{array}{l} \overset{CH_3CHO(a),\ H_2}{\underset{(3)}{\xrightarrow{\hspace{2cm}}}} \text{1,3-Butadiene} \\ \overset{CH_3CH_2OH}{\underset{(4)}{\xrightarrow{\hspace{2cm}}}} CH_3CHO + \begin{array}{cc} CH_3CH_2O & H \\ | & | \\ Mg & O \end{array} \end{array} \right.$$

where $CH_3CHO(a)$ is adsorbed acetaldehyde, the structure of which is not revealed in the present experiments.

According to the mechanism described above, step (4) occurs only in the presence of ethanol vapor. When the inflow of ethanol is stopped in the course of the reaction, step (4) should be stopped and there-

state of the decomposition. With reference to the results in Fig. 12, the decomposition of ethoxide occurred at a rate of 0.016 cc STP/min. It is therefore revealed that the rate is fairly in accord with the steady rate

[6] The rate of the formation of hydrogen or butadiene was calculated by multiplying the partial pressure of hydrogen or butadiene by the total flow rate.
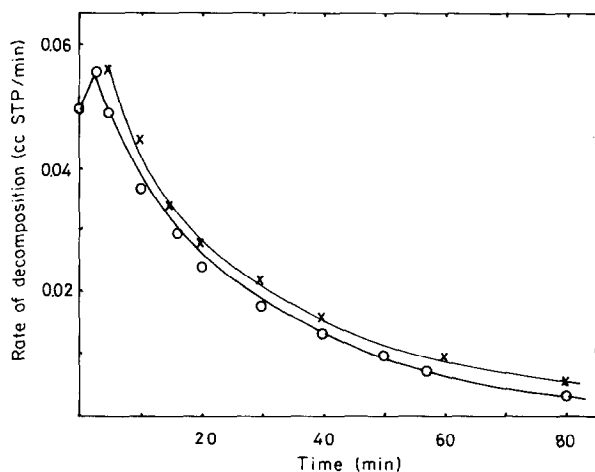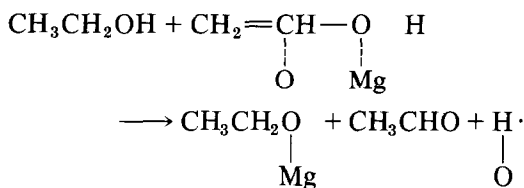
FIG. 11. The rate of hydrogen evolution. The results in Figs. 7 and 8 are replotted. (O—) The sum of the rates of hydrogen and butadiene formation; (X—) The rate of the decomposition of ethoxide.

of hydrogen formation of 0.012 cc STP/min. On the basis of these results, we conclude that ethoxide is an intermediate of the dehydrogenation of ethanol and surface hydroxyl group participates in the hydrogen production.

Since the steady decomposition proceeded in proportion to 2/3-s order in the partial pressure of ethanol, step (2) could be rate-determining. In the present work, it is not elucidated how step (4) proceeds. Adsorbed acetaldehyde in enolic form is possibly reacted with ethanol vapor by the process:

$$CH_3CH_2OH + CH_2{=}CH{-}\underset{\underset{Mg}{|}}{\overset{\overset{H}{|}}{O}}$$

$$\longrightarrow CH_3CH_2\underset{\underset{Mg}{|}}{O} + CH_3CHO + H \cdot \underset{\underset{O}{|}}{}$$

However, no direct evidence was given for the presence of enolic form of acetaldehyde.

Relevance to Other Work

The kinetic behavior of adsorbed species was recently investigated with the aid of infrared spectroscopy (10). It was
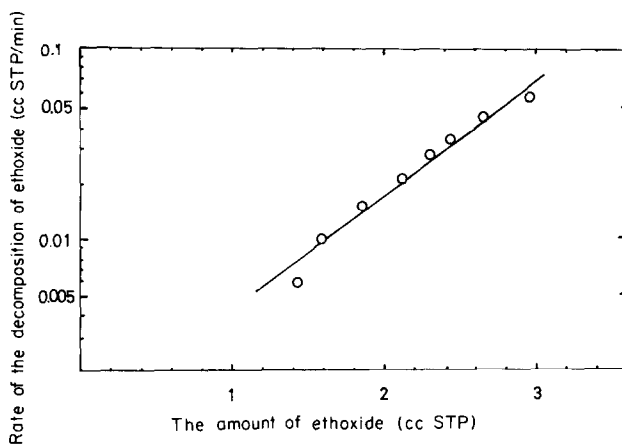

FIG. 12. The amount of ethoxide versus the rate of the decomposition of ethoxide. Temp 364°C.

concluded that the dehydration of ethanol occurred through the decomposition of surface ethoxide on alumina. The ethoxide was decomposed into water and ether or ethylene in the course of the dehydration. Arai et al. (9) confirmed that the ethoxide was decomposed into such species by the thermal desorption experiments. In the present study, we showed that ethoxide was also an intermediate of the dehydrogenation reaction. However, the process was not simple as found in the dehydration.

In previous studies, we concluded that ethoxide formed on the oxides of electropositive metal is more anionic (19,20). Therefore, ethoxide on magnesium oxide was more anionic compared to that on alumina. This suggests that a different reaction could be expected even when the intermediate is similar in structure. The charge of species should be considered in study of the kinetic features of adsorbed species.

ACKNOWLEDGMENT

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