

전기전도도 측정에 의한 ZnO 상의 에탄올 산화반응 연구*

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한국과학원 화학 및 화학공학과

(1975. 8. 8. 접수)

Electrical Conductivity Studies of Ethanol Oxidation over Zinc Oxide*

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(Received Aug. 8, 1975)

요 약. 에탄올의 산화반응중의 칼륨을 dope 한 산화아연의 전기전도의 변화를 250~350 °C에서 측정하였다.

산화아연 상에서는 탈수소 및 탈수반응이 일어난다. 300 °C 이상에서 CO₂의 생성과 이에 따르는 전기전도의 증가를 보였는데 이것은 아세트알데히드의 분해에 의해 생긴 CO의 산화반응에 의한 것이 아닌가 본다.

에탄올에 산소를 가하면 아세트알데히드의 생성은 증가하나 에틸렌의 생성에는 변화가 없었다. 이것은 주로 O⁻로서 화학흡착 되어있는 산소가 에탄올 흡착과 이에 따른 탈수소 과정에 유리하게 작용하고 있는 것이 아닌가 한다.

ABSTRACT. Changes in the electrical conductivity of gallium doped zinc oxide during the dehydrogenative oxidation of ethanol between 250 and 350°C have been studied. Both dehydrogenation and dehydration of ethanol takes place on ZnO. At 300 °C and above formation of CO₂ was observed accompanied by an increase in the electrical conductivity. This seems to be due to oxidation of CO formed by the decomposition of acetaldehyde. Addition of oxygen to ethanol increases the amount of acetaldehyde formed, while no change is observed in ethylene formation. It may be that chemisorbed oxygen which is present primarily as O⁻ provides a favorable site for the adsorption of ethanol and for subsequent hydrogen subtraction.

INTRODUCTION

Dehydrogenative oxidation of alcohol on semiconductors has been studied by several investigators interested in possible correlations between

the electrical conductivity and the dehydrogenative activity.¹ Bielansky² has studied the dehydrogenation of ethanol on ZnO-Fe₂O₃ and has found a parallel correlation between the changes in electrical conductivity and activity for the acetaldehyde formation. Changes in the electrical conductivity are also observed for the decompo-

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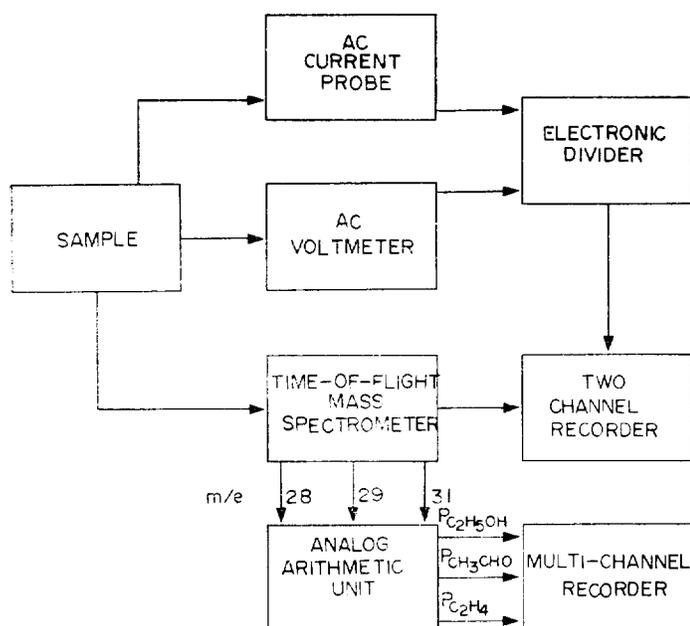


Fig. 1. Block diagram of the measuring system.

sition of methanol on zinc oxide³ and for the dehydrogenation of isopropyl alcohol on zinc oxide⁴.

Hall effect studies of the chemisorption of oxygen and the oxidation of carbon monoxide over doped zinc oxide have shown⁽¹⁾ that O^- is a predominant chemisorbed species that is also intimately involved in the oxidation reaction. Activation of oxygen at a solid surface by electron transfer from the solid plays an important role in the oxidation reaction. We have therefore investigated the possible role of chemisorbed oxygen in the dehydrogenative oxidation of ethanol.

EXPERIMENTAL

A digital oscillator having a frequency range of 10 to 1 megacycle (Hewlett-Packard 4204A) was used as a signal source. The voltages are measured with an AC voltmeter (Hewlett-Packard 400F) and the current with an AC current probe (Hewlett-Packard 456A) that clamps

around the current carrying wire. No frequency dependence of the electrical conductivity was observable for the present sample up to 500 kcps; the measurements were made at 1 kcps. An electronic divider (Philbrick 23-M2P) divides the output current by the voltage to give an output that is directly proportional to the electrical conductivity. A premixed mixture of ethanol and oxygen (5:1) or ethanol vapor was passed to the catalyst through a variable leak and the gas mixture was continuously analyzed with a time-of-flight mass-spectrometer. One analog channel of the mass spectrometer continuously scans the mass range between 12 and 50

and its output is recorded on a two channel recorder (Hewlett-Packard 7100) together with the electrical conductivity output from the electronic divider. Three other analog channels of the mass spectrometer monitor masses 28, 29 and 31 which are the parent peaks for ethylene, acetaldehyde and ethyl alcohol, respectively. The output for the latter three channel are fed into the analog arithmetic unit where they are divided by the sensitivity of the instrument to the individual gas and the background is subtracted. The outputs of the analog unit are recorded on a multichannel recorder. A block diagram of the measuring circuit is given in Fig. 1.

The sample was made from powder prepared by impregnating spectroscopically pure zinc oxide with gallium-nitrate solution and contained approximately $1.1 \times 10^{18} \text{ cm}^{-3}$ gallium as determined by spectrographic analysis. A Hall effect measurement on a sample made from the same preparation gave a donor concentration of $1.0 \times 10^{18} \text{ cm}^{-3}$. The sample was subsequently sintered

at 850 °C.

We have determined the carrier mobility from the simultaneous measurement of Hall effect and electrical conductivity of an indium doped sample. These mobility values were used in the present work to obtain the carrier concentration of the sample from the conductivity measurements. The sample has a dimension of $2.6 \times 0.9 \times 0.1$ cm and surface area of $0.85 \text{ m}^2/\text{g}$ as determined by the BET method using the adsorption isotherms of krypton at liquid nitrogen temperature.

RESULTS and DISCUSSION

Oxidation of ethanol was studied between 200 and 350 °C by passing ethanol or a mixture of ethanol and oxygen (5 to 1) over the gallium-doped zinc oxide. The reaction products observed were ethylene, acetaldehyde and carbon dioxide. Fig. 2 shows the formation of ethylene and acetaldehyde at 250, 300 and 350 °C. The formation of ethylene is about the same for all temperatures used. The formation of acetaldehyde, however, increases markedly with increasing temperature. At 350 °C the formation of carbon dioxide becomes rather appreciable. Fig. 3 shows the changes in the carrier concentration that occur during the course of the reaction: the concentration usually decreases but at 350 °C it showed an increase beyond the starting level, after an initial decrease.

To see the effect of oxygen on the dehydrogenative oxidation, measurements were carried out on ethanol alone and ethanol with oxygen (5 to 1) at 250 and 300 °C. Fig. 4 and 5 show the formation of ethylene and acetaldehyde at 250 and 300 °C, respectively. It can be seen that the formation of ethylene is not affected by the presence of oxygen. The formation of acetaldehyde however, is appreciably increased by the addition of oxygen. To investigate factors respon-

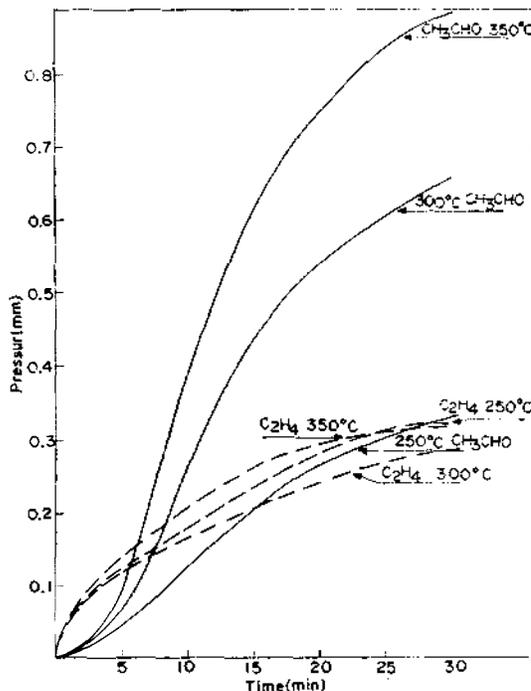


Fig. 2. Formation of acetaldehyde and ethylene over ZnO.

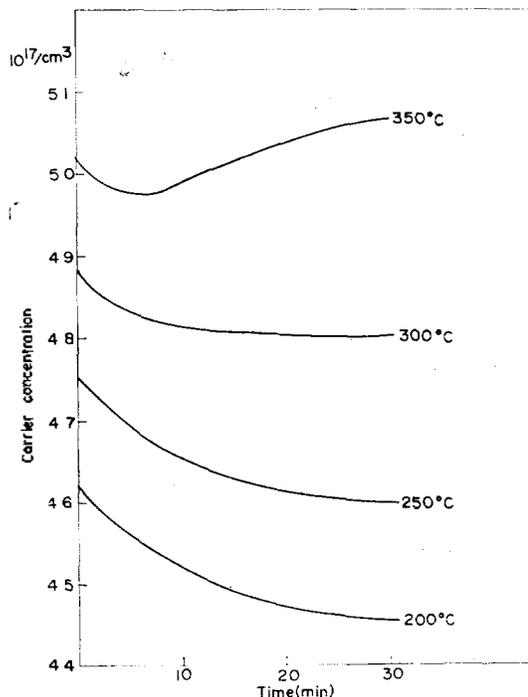


Fig. 3. Changes in the carrier concentration of ZnO during the reaction.

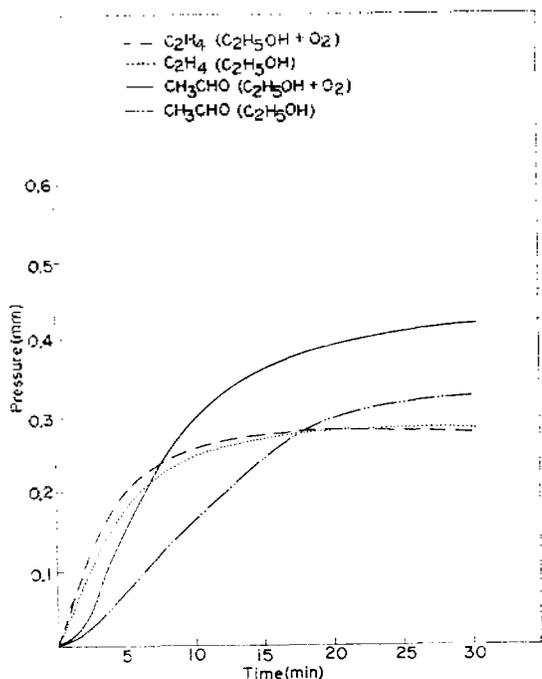


Fig. 4. Formation of acetaldehyde and ethylene over ZnO at 250 °C.

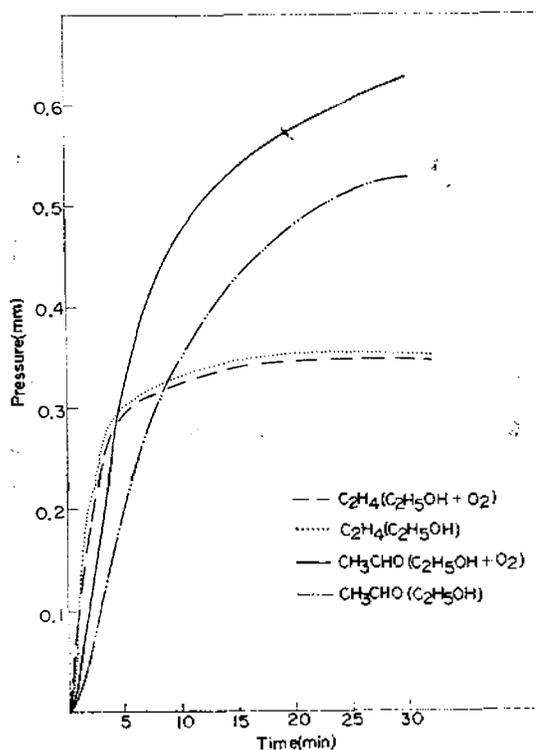


Fig. 5. Formation of acetaldehyde and ethylene over ZnO at 300 °C.

sible for the increase in the carrier concentration during the reaction the changes in carrier concentration were followed with oxygen, ethylene+oxygen, acetaldehyde, acetaldehyde+oxygen, ethanol and ethanol+oxygen admitted, at 300 °C. The results are shown in Fig. 6. Changes in the carrier concentration of the catalyst for the mixture of ethylene and oxygen are the same as for oxygen alone. The changes for the mixture of acetaldehyde and oxygen and the mixture of ethanol and oxygen are the same. In both cases the decrease in the carrier concentration is less pronounced compared to the decrease when oxygen alone was present. Increase in the carrier concentration was observed for both ethanol and acetaldehyde.

Chemisorption of oxygen on zinc oxide is associated with a transfer of electrons from zinc oxide to chemisorbed oxygen, which explains the observed decrease in the carrier concentration.

Adsorption of ethylene has no effect on the carrier concentration of the sample. The facts that (a) CO_2 formation was observed at 300 and 350 °C both from ethanol and acetaldehyde, and (b) a parallel increase in carrier concentration is observed for both ethanol and acetaldehyde suggest that the increase is associated with the formation of CO_2 , possibly from the oxidation of CO that was formed from the decomposition of acetaldehyde. From Hall effect studies on ZnO we have shown previously that oxygen is chemisorbed primarily as O^- above some 180 °C and CO reacts with chemisorbed oxygen according to $\text{CO} + \text{O}^- = \text{CO}_2 + e^-$, thereby increasing the carrier concentration

Both dehydrogenation and dehydration of ethanol take place on zinc oxide. Addition of oxygen to ethanol increased the formation of acetaldehyde

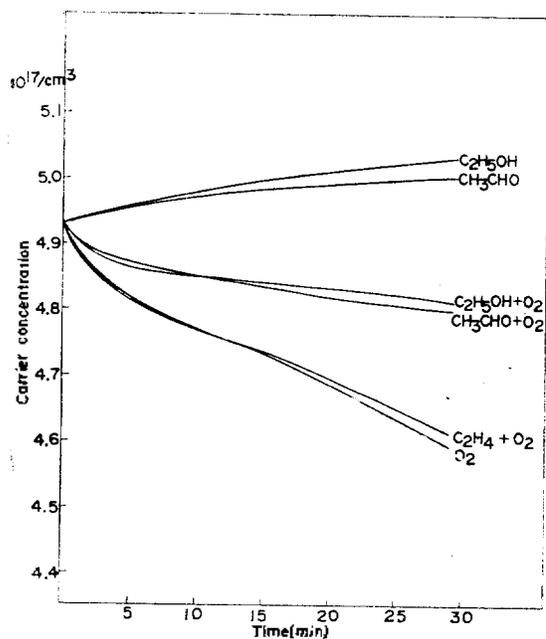


Fig. 6. Changes in the carrier concentration of ZnO during the adsorption of gases.

while no change in the formation of ethylene was observed. The fact that the formation of acetaldehyde was increased by the presence of oxygen suggests that the chemisorbed oxygen

may play a role in the dehydrogenation of ethanol. It may be that the chemisorbed oxygen which is present primarily as O^- provides a favorable site for the adsorption of ethanol and subsequent hydrogen subtraction. In their studies of methanol oxidation over ZnO+Ag, Schwab and Koller⁵ also suggest that the adsorbed oxygen forms adsorption center for methanol. Methanol molecules are added by formation of hydrogen bridges. They point out that atomic distance H—H in the organic molecules and Zn—O are of comparable order of magnitude.

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