JOURNAL OF CATALYSIS 4, 109–115 (1965)

# The Catalytic Decomposition of Methanol by Doped Zinc Oxide

P. FUDERER-LUETIĆ AND I. SVIBEN

*From the Institute of Physical Chemistry, Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia*

Received April 15, 1964

The catalytic activity of ZnO doped with $Li^+$ and $Al^{3+}$ ions, for the reaction $CH_3OH \rightarrow CO + 2H_2$ has been investigated. The aim was to study the influence of doping on the rate-controlling step of this catalytic reaction. It has been found that the presence of $Li^+$ ions causes a decrease, and that of $Al^{3+}$ ions a slight increase in activation energy of undoped ZnO. When both ions were present $Al^{3+}$ overshadowed the influence of $Li^+$ at temperatures above 333–335°C. At temperatures below 325–328°C $Al^{3+}$ had no marked influence on the effect caused by $Li^+$. In the same temperature interval, i.e. between 325° and 335°C a reversible change of activation energy and of activity occurred both for undoped ZnO and for all the samples of catalysts which contained either $Li^+$ or $Al^{3+}$. The rate-determining step for the overall reaction in the lower temperature interval seems to be the dissociative desorption of the surface complex, which at higher temperatures is in competition with an electron-accepting step.

## INTRODUCTION

The effect which the addition of cations with different valency exerts on adsorptive and catalytic properties of some oxides, which are typical semiconductors, has been investigated by several authors (*1–7*).

The addition of suitable ions to the semiconducting oxide changes its electrical conductivity and its catalytic properties, but a quantitative correlation between the change of these two properties in most cases does not seem to be possible (*3*).

ZnO is a typical *n*-type semiconductor with the donor level near the conductivity band. Trivalent cations incorporated in ZnO increase its concentration of quasi-free electrons, monovalent cations increase the number of positive holes (*8, 9*). It has been found that the increase of electron concentration caused by addition of $Ga^{3+}$ had a negative effect on the rate of adsorption of $H_2$ and CO on ZnO, whereas the increase of positive hole concentration, caused by addition of $Li^+$, had a positive effect (*3*). When $H_2$ and CO are adsorbed simultaneously it seems that the one gas creates sites for the adsorption of the other (*10*).

For the adsorption of primary alcohols on semiconductors, which are catalysts selective for dehydrogenation, Wolkenstein (*11*) postulates the following dissociative mechanism:

$$ROH + L \rightarrow RO\text{p}L + H\text{p}L$$

Investigations carried out on the dehydrogenation of different alcohols on metals (*12*) and of isopropyl alcohol on semiconductors (*4, 5*) seem to prove the hypothesis that the rate-determining step is the decomposition of the adsorbed complex, or the desorption of products (*13*).

## EXPERIMENTAL

### *Catalyst*

All the chemicals used were pA grade; water was redistilled in quartz apparatus. ZnO was prepared by decomposition of oxalate. This was precipitated with oxalic acid from a solution of $Zn(NO_3)_2$, and decomposed by heating it at 450°C for 10 hr. ZnO needed for all catalyst samples was prepared as one batch. The doping was carried out with solutions of $LiNO_3$ or $Al(NO_3)_3$ using the method of Cimino, Molinari, and Cipollini (*14*). These authors found that more than 90% of the amount of doping which was added was incorporated in ZnO. The method consists in wetting the dry powdered ZnO with approximately the same weight of aqueous solution which contains the wanted amount of doping salt. After that the samples were dried and heated again at 450°C for 10 hr. To induce the same eventual changes, due to wetting and heating in the samples of catalyst No. 1, which contained no doping, the samples of ZnO were wetted with water and further handled as the doped ones.

### *Apparatus and Procedure*

The determination of the reaction rate has been carried out in the vertical flow apparatus shown in Fig. 1.

Methanol (20 ml) was poured into the apparatus. Catalyst sample was placed in the tray, and the apparatus closed. Water was allowed to flow through the cooler, the catalyst heated to about 100°C, and the methanol heated to its boiling point. The air was expelled from the catalyst chamber with the vapor of methanol and the temperature of the catalyst was increased. The volume of gas evolved per minute was measured when the temperature had reached a constant value. The flow rate of methanol vapor through the catalyst zone was kept constant (about 1000 ml/min).

## RESULTS

The reaction $CH_3OH \rightarrow CO + 2H_2$ was carried out over catalysts which consisted

TABLE 1
ADDED OXIDES IN CATALYST SAMPLES

| No. of the sample | Oxides added | ZnO (mole %) |
|---|---|---|
| 1 | — | — |
| 2 | $Li_2O$ | 0.5 |
| 3 | $Li_2O$ | 1.5 |
| 4 | $Al_2O_3$ | 0.5 |
| 5 | $Al_2O_3$ | 1.5 |
| 6 | $Li_2O + Al_2O_3$ | 0.5 + 0.5 |
| 7 | $Li_2O + Al_2O_3$ | 0.5 + 1.5 |
| 8 | $Li_2O + Al_2O_3$ | 1.5 + 0.5 |
| 9 | $Li_2O + Al_2O_3$ | 1.5 + 1.5 |

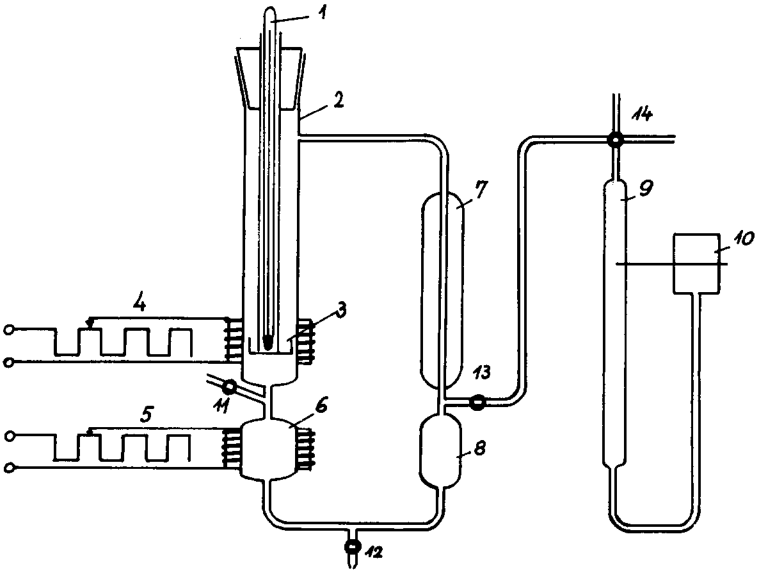

FIG. 1. Experimental apparatus: 1, thermometer; 2, catalyst chamber; 3, catalyst tray; 4,5, Variacs; 6, Methanol evaporator; 7, condenser; 8, methanol storage; 9, burette tube calibrated to 0.05 ml; 10, level bottle; 11, 12, 13, 14, stopcocks.

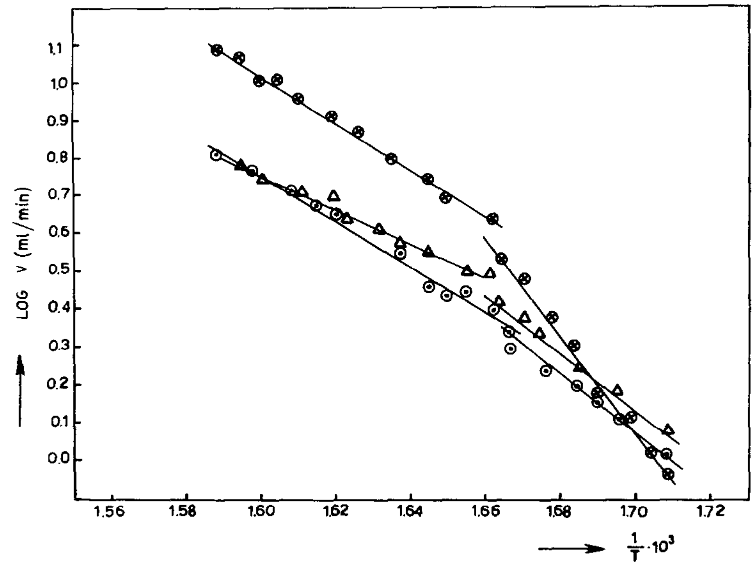

FIG. 2. Arrhenius plot for the methanol decomposition. Catalyst No. 1 (0.234 g), ⊕ ; No. 2 (0.227 g), ⊙; No. 3 (0.209 g), △.

of ZnO doped with the amounts of $Li^+$ and $Al^{3+}$ given in Table 1. The presence of $CH_2O$ in the exit reaction mixture could not be detected.

The rate of the reaction was followed by reading the volume of gases evolved per minute. This volume was maximally about 20 ml/min, so that the conversion of the methanol vapor did not exceed 0.6% approximately. The volume of gas was read at 20°C. It was assumed that the partial pressure of the methanol vapor was constant (saturated $CH_3OH$ vapor at 20°C) and that it was therefore not necessary to be taken into account.

When one set of readings was complete and the temperature of the catalyst reached about 360°C, the temperature was dropped and the experiment repeated. The results were the same as by the first readings. When the cooling and heating was repeated several times a slight decrease in activity could be detected.

Usually 0.2–0.25 g of catalyst was used. Only in two series of runs, with catalysts Nos. 1 and 9, was the weight of the catalyst samples varied from approximately 0.15 to 1 g. In this series of runs we wanted to establish the influence of the catalyst layer depth on the activation energy. For the sake of control an experiment was carried out without catalyst. In this experiment the evolution of gases did not take place until the temperature reached 340°C. In the range 340–360°C the evolution of gases was about 0.2–0.3 ml/min.

Logarithms of volume readings plotted versus reciprocal temperature give the Arrhenius plots which are represented in Figs. 2–5. As can be seen in almost all cases a break in Arrhenius plots occurs between 325° and 335°C. This break means a change of activation energy as well as of activity. The points of Figs. 2–5 represent the experimental values found with one

TABLE 2

APPARENT ENERGIES OF ACTIVATION

| No. of the sample | $E$ (average of several measurements) | |
|---|---|---|
| | Upper temp. range | Lower temp. range |
| 1 | 27.5 ± 0.6 | 61.0 ± 2.0 |
| 2 | 24.7 ± 1.1 | 36.7 ± 1.5 |
| 3 | 19.9 ± 0.3 | 34.2 ± 0.8 |
| 4 | 28.8 ± 1.3 | 64.5 ± 0.1 |
| 5 | 29.3 ± 1.3 | 66.4 ± 0.2 |
| 6 | 30.1 ± 1.2 | 38.0 ± 0.6 |
| 7 | 38.5 ± 0.4 | 38.5 ± 0.4 |
| 8 | 31.4 ± 0.4 | 34.6 ± 0.3 |
| 9 | 34.0 ± 0.8 | 34.6 ± 1.0 |

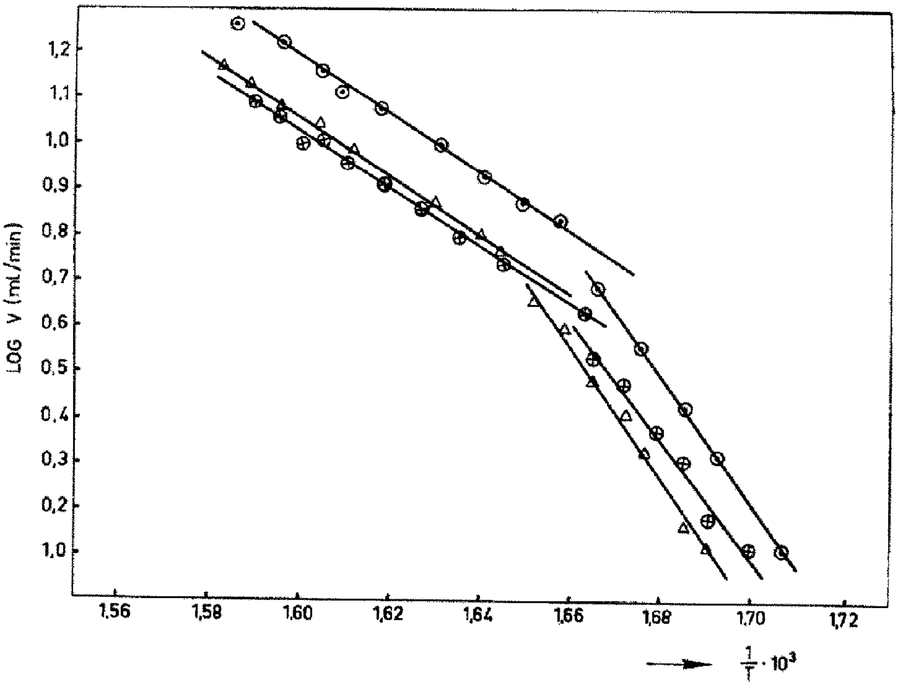

FIG. 3. Catalyst No. 1 (0.234 g), ⊕ (for comparison); No. 4 (0.268 g), ⊙; No. 5 (0.219 g), Δ.

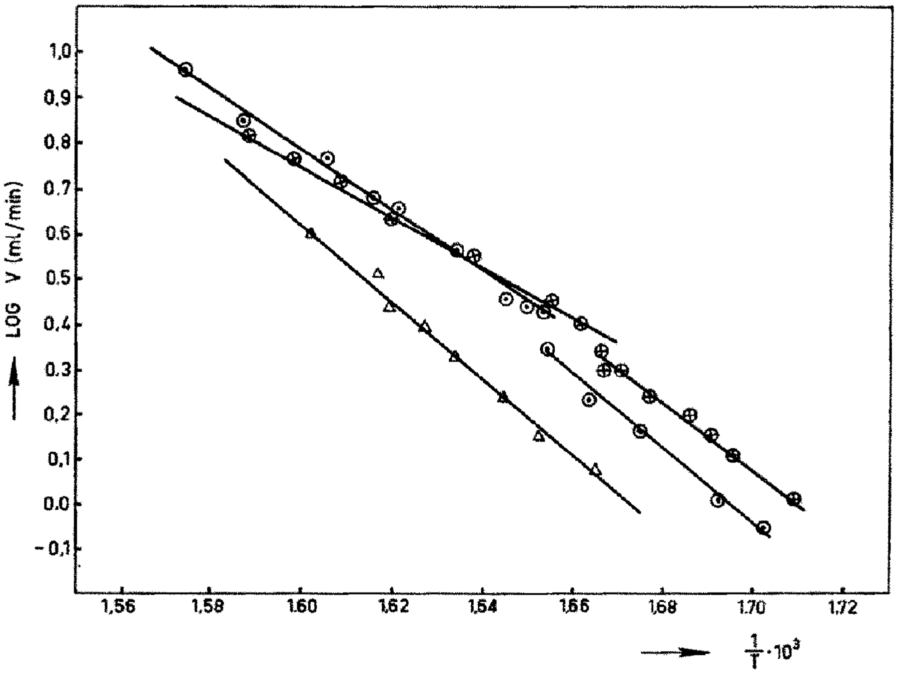

FIG. 4. Catalyst No. 2 (0.227 g), ⊕ (for comparison); No. 6 (0.250 g), ⊙; No. 7 (0.253 g), Δ.

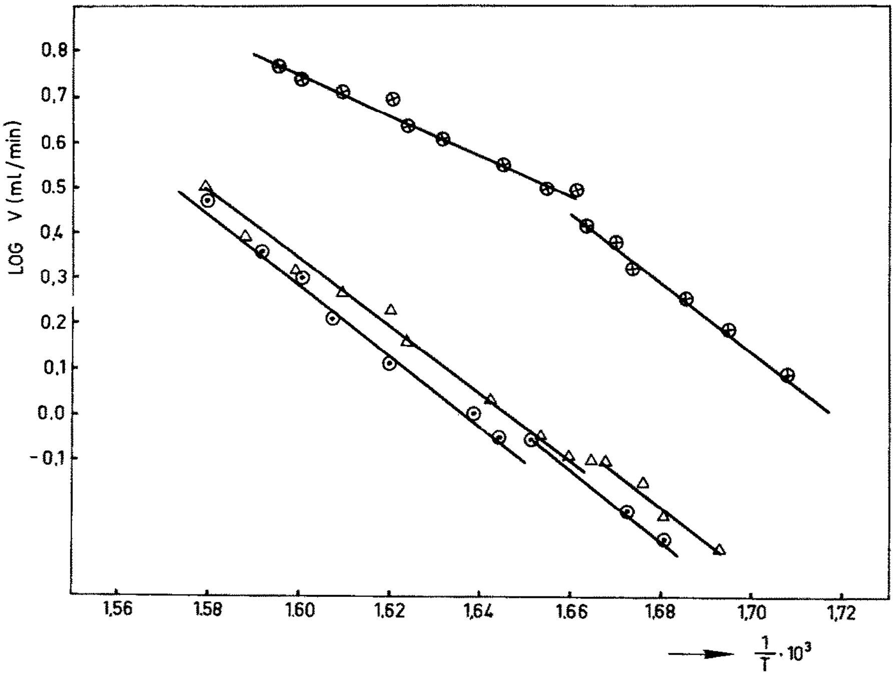

Fig. 5. Catalyst No. 3 (0.209 g), ⊕ (for comparison); No. 8 (0.200 g), ⊙; No. 9 (0.230 g), △.

sample of the catalyst. The apparent activation energies, given in Table 2, are calculated from such plots for three samples of each catalyst.

In experiments carried out with different amounts of catalysts the volume of gases evolved at a given temperature was proportional to the weight of the catalyst, at least when the weight of the sample was higher than 0.2 g (Fig. 6).

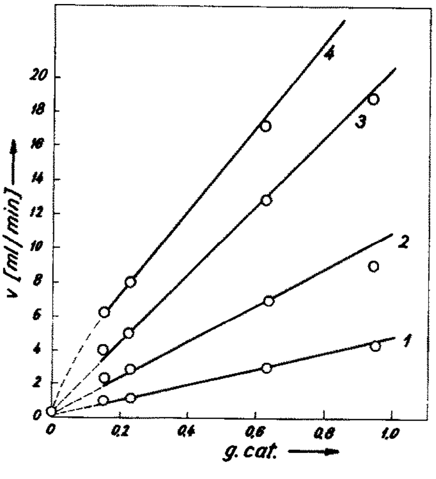

Fig. 6. Volume of gases evolved per minute over different weight of ZnO. 1. $T = 315°C$, 2. $T = 326°C$, 3. $T = 333°C$, 4. $T = 344°C$.

As the depth of the catalyst layer was proportional to its weight it follows that the whole catalyst layer takes part in the reaction, and that the diffusion into the catalyst layer does not influence the shape and the slope of the Arrhenius plots.

In the case of catalysts Nos. 1–5 a compensation effect occurs. The values of log $v_{T\infty}$ for 0.1 g of catalyst are given in Table 3. These values represent the average for

TABLE 3
The Equivalent of Frequency Factor for 0.1 g of Catalyst

| No. of the sample | log $v_{T\infty}$ Upper temp. range | log $v_{T\infty}$ Lower temp. range |
|---|---|---|
| 1 | 9.4 ± 0.2 | 22.0 ± 0.9 |
| 2 | 8.3 ± 0.3 | 13.8 ± 0.6 |
| 3 | 6.7 ± 0.1 | 11.8 ± 0.4 |
| 4 | 9.8 ± 0.3 | 22.4 ± 1.4 |
| 5 | 10.1 ± 0.1 | 24.0 ± 0.5 |

three samples of each catalyst. The plot of log $v_{T\infty}$ values from both columns versus $E$ consists of only one straight line, which can be represented by the equation:

$$\log v_{T\infty} = (E/2.6) - 1.08$$

In the case of catalysts doped with two cations the compensation effect is not pronounced.

## Discussion

The results obtained show the following features:

1. The break in Arrhenius plots in the temperature range 325–335°C. At this temperature in all cases but one a decrease of activation energy, and for all catalysts containing only one, or no foreign cation, an increase in activity occurs.
2. For catalysts which do not contain $Li^+$ the activation energy in the upper and lower temperature range differs considerably.
3. The addition of $Li^+$ causes a decrease in activation energy. This is larger in the lower than in the upper temperature range. In the lower temperature range a small quantity of $Li^+$ (0.5 mole %) already has a considerable influence [($E$ on cat. 1) — ($E$ on cat. 2) = 24.5 kcal $mole^{-1}$]. Addition of more $Li^+$ causes only a small further decrease.
4. The addition of $Al^{3+}$ causes a moderate increase of $E$ in the lower, and has no influence in the upper, temperature range.
5. The performance of catalysts which contain $Li^+$ and $Al^{3+}$ in the lower temperature range is the same as when $Al^{3+}$ was not present at all, whereas in the upper temperature range the same $Al^{3+}$ overshadows the presence of $Li^+$.
6. In the series ZnO and ZnO with one added cation there exists a compensation effect. All the values of log $v_{T\infty}$ plotted versus $E$ fall on a single straight line.

It seems that the breaks in Arrhenius plots cannot be attributed to diffusion. The catalysts were used in the form of fine powders. The depth of the catalyst layer had no influence either on the change of the position of the break, or on the activation energy. The points log $v_{T\infty}$ versus $E$ fall on the same straight line for both temperature ranges. In some cases the values of $E$ are higher in the upper than in the lower temperature range. Therefrom it can be concluded that either a change in semiconductive properties of the catalysts or a change in the controlling step of the over-all reaction occurs.

The adsorption of methanol does not seem to be essentially different from the adsorption of other primary alcohols. It has been found that for the chemisorption of alcohols two surface sites are necessary (*11, 13*). One is connected with the presence of a free electron in the surface layer of the catalyst, at which the fragment $CH_3$–O . . . becomes attached and the other is a defect site on which H atoms are adsorbed by a weak bond (*10*). It is evident that the positive holes or electron traps, connected with the addition of $Li^+$, facilitate the rate-determining step in the lower temperature range. Therefore it can be assumed that in this temperature range the dissociative desorption of the $CH_3OeL$ complex is the rate-determining step. For this step the activation energy is lower when the concentration of free electrons in the catalyst is lower. The results from the upper temperature range can be explained by assuming that here a process with lower activation energy, which is connected with the availability of free electrons in the surface layer, becomes the rate-determining one. This concept seems to be in agreement with the appearance of the compensation effect, which in this case can be explained as the result of the competitive influence of sites available for adsorption and the ease of desorption.

## References

*1.* Chaplin, P., Chapman, P. R., and Griffith, R. H., *Nature* **172,** 77 (1953).
*2.* Hauffe, K., *Advan. Catalysis* **7,** 213 (1955).
*3.* Cimino, A., Molinari, E., and Cipollini, E., *Gazz. Chim. Ital.* **90,** 79 (1960).
*4.* Garcia de la Banda, J. F., *J. Catalysis* **1,** 136 (1962).

*5.* Garcia de la Banda, J. F., and Kremenic-Orlandini, G., *Anales Fis. Quim.* **54,** 97 (1958); **54,** 115 (1958).

*6.* Butler, J. D., and Weston, B. G., *J. Catalysis* **2,** 8 (1963).

*7.* Giordano, N., Cavaterra, E., and Zema, D., *Chim. Ind.* (*Milano*) **45,** 15 (1963).

*8.* Schwab, G. M., and Block, J., *J. Chim. Phys.* **51,** 664 (1954).

*9.* Morrison, R., *Advan. Catalysis* **7,** 257 (1955).

*10.* Nagarjunan, T. S., Sastri, M. V. C., and Kuriacose, J. C., *J. Catalysis* **2,** 223 (1963).

*11.* Wolkenstein, T., *Advan. Catalysis* **12,** 189 (1960).

*12.* Fuderer-Luetić, P., and Brihta, I., *Croat. Chem. Acta* **31,** 75 (1959).

*13.* Wicke, E., *Z. Elektrochem.* **53,** 279 (1949).

*14.* Cimino, A., Molinari, E., and Cipollini, E., *Gazz. Chim. Ital.* **90,** 91 (1960).