

**1132.** *Catalytic Dehydrogenation of Methanol over Zinc Oxide and Doped Zinc Oxide.*

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The effect of the mode of preparation on the surface area of zinc oxide has been studied, as well as the effects of an excess of zinc in the oxide and of small amounts of foreign ions in the lattice. These oxides have been used as catalysts in a study of the kinetics of the catalytic decomposition of methanol vapour. That reaction is predominantly one of dehydrogenation and obeys zero-order kinetics. Arrhenius plots are presented for reactions on twelve different catalysts. The incorporation of altrivalent ions, which changes the electronic properties of semiconductors such as zinc oxide, has little or no effect on the energy of activation for decomposition of methanol which in all cases lies in the range 36—39 kcal. mole<sup>-1</sup>. A mechanism for the reaction is discussed.

ACTIVATION energies covering the range 11—51 kcal. mole<sup>-1</sup> have been reported for dehydrogenation of methanol on zinc oxide catalysts prepared in various ways.<sup>1-3</sup> According to Menold,<sup>3</sup> the activation energy was lowered from *ca.* 44 kcal. mole<sup>-1</sup> over pure zinc oxide to 24.5 kcal. mole<sup>-1</sup> over zinc oxide doped with 0.4% of lithium oxide, both catalysts having been heated at 750° before use. A connexion between concentration of free charge carriers and catalytic activity was therefore postulated, though Wagner<sup>4</sup> found no evidence for this. Methanol is thought to decompose by way of formaldehyde in a two-stage process,<sup>1</sup> and Menold<sup>3</sup> has assigned activation energies of 24.5 and 44 kcal. mole<sup>-1</sup>, respectively, to the two reactions that make up the decomposition.

<sup>1</sup> Dohse, *Z. phys. Chem.*, 1930, **8**, 159.

<sup>2</sup> Shekhter and Moshkovskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 354; *Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 339; 1953, **89**, 1075.

<sup>3</sup> Menold, *Chem.-Ing.-Tech.*, 1960, **32**, 801.

<sup>4</sup> Wagner, *J. Chem. Phys.*, 1950, **18**, 69.

The results of doping catalysts with foreign ions in order to alter their semiconductivity have often been confusing, owing to the different relative importance of surface concentrations and lattice incorporation of the foreign ions.<sup>5</sup> The temperature at which the catalyst is prepared is a significant factor in this matter.<sup>6</sup> The present investigation is concerned with the effect, on surface area, of the mode of preparing zinc oxide and doped zinc oxide and with the use of these materials as catalysts for the dehydrogenation of methanol.

#### EXPERIMENTAL

*Apparatus.*—The static-type apparatus consisted of three interconnected sections: a purification and storage line for gases; a vacuum line leading through traps to a silicon-oil diffusion pump (Edwards Speedivac 203B) backed by a rotary oil pump; a reaction system made up of a Pyrex reaction bulb of capacity *ca.* 25 ml., connected by stopcocks to a gas burette, to a small bulb which was used for storage of reactants, for collection of products, or as a cold trap, and to two manometers, one of which could be used in conjunction with a cathetometer for low-pressure measurements. Pressures lower than  $10^{-4}$  mm., as indicated on a McLeod gauge, were achieved with this arrangement. The reaction bulb was heated in a small furnace whose temperature was controlled and measured by an electronic indicating controller (Foster Instrument Co. Ltd.) which incorporated an on-off attenuating control system. The instrument was calibrated accurately by the suppliers and also in this laboratory. The temperature of the furnace in the region occupied by the bulb could be controlled to  $<0.5^\circ$  and the variation in the catalyst bed was expected to be less than this.

*Materials.*—"AnalaR" methanol was distilled over quicklime and stored in a small evacuated bulb attached to the apparatus.

Carbon dioxide, oxygen, hydrogen, nitrogen (supplied by East African Oxygen Co. Ltd.), and methane (supplied by Thames Rea District Drainage Board), obtained from cylinders, were passed through concentrated sulphuric acid and aqueous potassium hydroxide and stored over phosphorus pentoxide. Carbon monoxide was prepared from "AnalaR" oxalic acid and was purified as above. "AnalaR" zinc oxide, zinc oxalate (prepared from "AnalaR" ammonium oxalate and zinc sulphate), aluminium nitrate, and lithium nitrate were used in the preparation of the catalysts.

*Methods.*—(a) Solutions of aluminium and lithium nitrates of required concentration were mixed with samples of zinc oxide or zinc oxalate and these were dried overnight at  $110^\circ$  before being fired at higher temperatures. Samples AZ, AL, and AA consisted of ZnO, ZnO + 1 mole % of  $\text{Li}_2\text{O}$ , and ZnO + 1 mole % of  $\text{Al}_2\text{O}_3$ , respectively, prepared from "AnalaR" zinc oxide; similar samples, OZ (ZnO), OL (ZnO + 1 mole % of  $\text{Li}_2\text{O}$ ), and OA (ZnO + 1 mole % of  $\text{Al}_2\text{O}_3$ ), were prepared by heating zinc oxalate and its mixtures with lithium and aluminium nitrates, respectively. Sets of samples were prepared by heating at  $850^\circ$  and  $1000^\circ$  for various times. Those employed in the dehydrogenations were prepared by heating at  $1000^\circ$  for (i) 1 hr. and (ii) 5 hr.

(b) Surface areas of the samples were measured by the B.E.T. method, with nitrogen absorbed at  $-184^\circ$ . An area of  $16.2 \text{ \AA}^2$  was assumed for the nitrogen molecule.

(c) Excess zinc contents of some zinc oxide samples (0.5 g.) were measured by a method similar to Secco and Moore's,<sup>7</sup> but end-points of titrations were determined by an amperometric technique.<sup>8</sup>

(d) The catalysed dehydrogenation of methanol vapour was studied by observing the increase of pressure with time in the static apparatus between  $200^\circ$  and  $400^\circ$ . The initial methanol pressures,  $P_1$ , varied from 10 to 35 mm., though in most cases  $P_1$  was *ca.* 25 mm. Before a series of runs, a catalyst was outgassed at  $400^\circ$  for 2 hr. After some reaction at  $385^\circ$ , reproducible results could be obtained at this temperature and at lower temperatures. The evacuation periods between runs were standardised to 15 min. at a temperature which was  $20^\circ$  above that of the previous run, together with evacuation whilst cooling to the reaction temperature. Variation of this procedure within quite wide limits had a negligible effect on the reproducibility of rates.

<sup>5</sup> Stone, *Adv. Catalysis*, 1962, **13**, 36; Parravano and Boudart, *ibid.*, 1955, **7**, 71.

<sup>6</sup> Bevan, Shelton, and Anderson, *J.*, 1948, 1729.

<sup>7</sup> Secco and Moore, *J. Chem. Phys.*, 1957, **26**, 942.

<sup>8</sup> Evans and Simmons, *J. Soc. Chem. Ind.*, 1944, **63**, 29.

## RESULTS

*Surface Areas.*—Table 1 sets out the results obtained for catalysts heated at 850° and 1000°. Incorporation of Li<sup>+</sup> and Al<sup>3+</sup> ions affects the surface area of zinc oxide in different ways. In general, areas of samples prepared from zinc oxalate are larger than those prepared from "AnalaR" zinc oxide.

TABLE 1.

Prep. temp. Time of heating (hr.) Sample	B.E.T. areas (m. <sup>2</sup> g. <sup>-1</sup> ).					
	850°		1000°			
	0.5	1	0.5	1	2	5
AZ .....	0.72	0.62	0.24	0.14	0.07	0.07
AL .....	0.16	0.04	v. low	—	—	—
AA .....	2.66	2.24	1.16	0.75	0.70	0.45
OZ .....	0.88	0.58	0.42	0.31	0.30	0.10
OL .....	0.40	0.23	0.22	0.15	0.18	0.09
OA .....	5.20	1.77	1.42	0.81	0.93	0.53

TABLE 2.

Method of prepn.	Excess zinc in zinc oxide (p.p.m.).	
	"AnalaR" ZnO	ZnO from oxalate
As received .....	8—14	
Heated at 1000° for 1 hr. ....	20—24	0
Heated at 1000° for 2 hr. ....	30—33	0
Heated at 1000° for 5 hr. ....	47—50	6—8

*Excess Zinc Content.*—The results are summarised in Table 2.

*Catalysed Dehydrogenation of Methanol Vapour.*—Heterogeneous decomposition of methanol occurred over zinc oxide and doped zinc oxides at temperatures above 200°. The net reaction was predominantly dehydrogenation of the methanol, as indicated by an analysis of the final

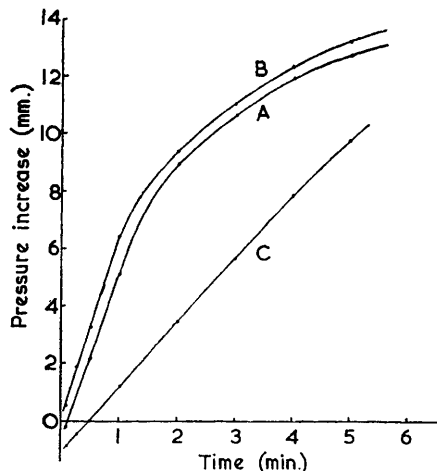


FIG. 1. Rates of pressure increase for methanol decomposition on zinc oxide at 385°: the effect of pretreatment of the catalyst with oxygen and air. (A) Catalyst sintered in air at 1000°; (B) "used" catalyst; (C) catalyst pretreated with oxygen for 15 min. at 400°. (Outgassing period in each case, 1 hr. at 400°.)

products:  $\text{CH}_3\cdot\text{OH} = \text{CO} + 2\text{H}_2$ . Above 330°, there was evidence of carbon dioxide formation (ca. 10% of the products at 385°) over a zinc oxide catalyst. After a few runs on a fresh catalyst at these higher temperatures a deposit of metallic zinc was observed near the entrance to the reaction bulb, and the catalyst became darker. These effects could not be reproduced by holding a fresh oxide sample under a vacuum for 2 days. This indicates reduction of the oxide catalyst by carbon monoxide to zinc with carbon dioxide formation.

The pressure increase at any time was therefore taken as being equal to twice the amount of methanol vapour decomposed; this is discussed below.

The rates of catalysed dehydrogenation of methanol vapour alone showed no significant

variation from those determined for mixtures of methanol vapour with each of the possible products (carbon monoxide, hydrogen, carbon dioxide, formaldehyde vapour, water vapour, methane; each at about 20 mm.) or with products from a previous experiment. Only brief

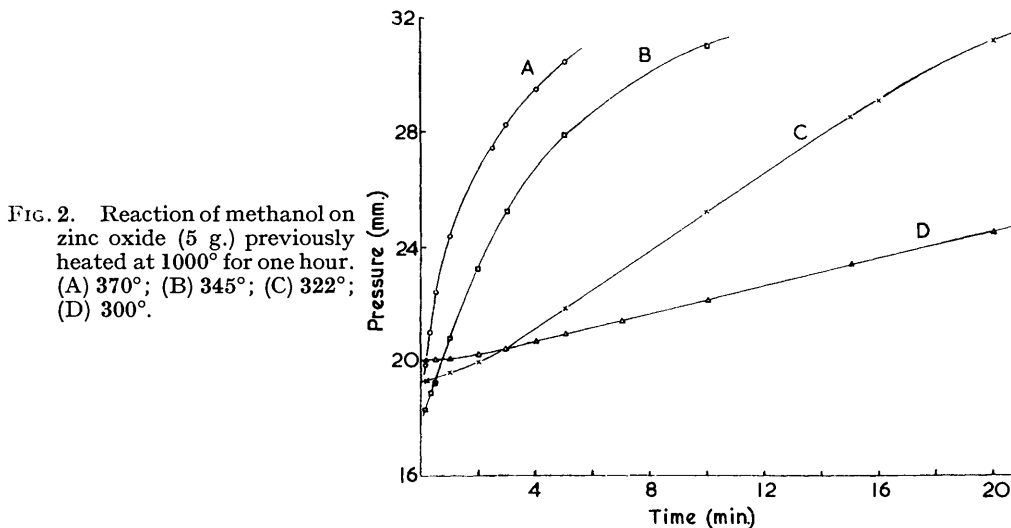


FIG. 2. Reaction of methanol on zinc oxide (5 g.) previously heated at  $1000^{\circ}$  for one hour. (A)  $370^{\circ}$ ; (B)  $345^{\circ}$ ; (C)  $322^{\circ}$ ; (D)  $300^{\circ}$ .

(*ca.* 1 min.) outgassing of an oxide sample was necessary for reproducibility of pressure-time plots. Desorption studies indicated that the products formed on the surface were easily displaced by reactant molecules.

Pretreatment of the catalysts with oxygen considerably retarded the reaction, as shown in Fig. 1 (curve C); the previous activity (curve B) was regained after two more runs at  $385^{\circ}$ .

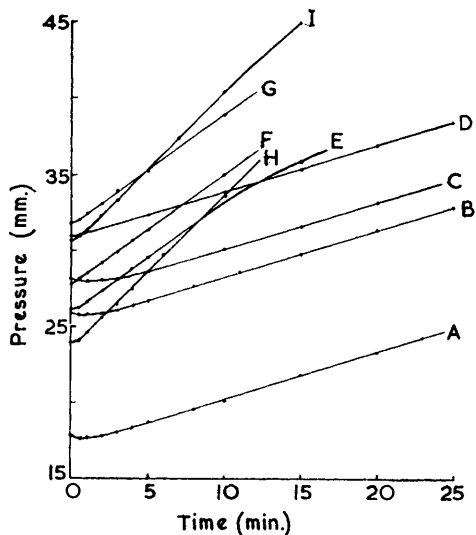


FIG. 3. Effect of initial pressure on the reaction of methanol over zinc oxide catalysts.

Runs at  $260^{\circ}$  with catalyst OL (prepared at  $1000^{\circ}$  for 5 hr.), with initial pressure (A) 17.8 mm. (run 13), (B) 25.9 mm. (run 12), (C) 28.3 mm. (run 26), and (D) 30.9 mm. (run 15).

Runs at  $270^{\circ}$  with catalyst OA (prepared at  $1000^{\circ}$  for 1 hr.), with initial pressure (E) 26.1 mm. (run 23), (F) 27.8 mm. (run 21), and (G) 31.8 mm. (run 22); and at  $272^{\circ}$  with initial pressure (H) 24.0 mm. (run 18), and (I) 30.7 mm. (run 19).

However, there was little difference in the rates of reaction over freshly sintered and used catalysts.

The temperatures at which reaction commenced within reasonable time follow the order,  $\text{ZnO} + 1 \text{ mole } \% \text{ of } \text{Al}_2\text{O}_3 < \text{ZnO} < \text{ZnO} + 1 \text{ mole } \% \text{ of } \text{Li}_2\text{O}$ ; they are slightly lower for "O" samples than for the corresponding "A" samples. In the lower part of the temperature range, 200–400°, instantaneous reversible adsorption of methanol occurred, followed by a further slow uptake. The coverage was estimated to be *ca.* 10% at  $280^{\circ}$  on AA and AL samples

sintered at 1000° for one hour, it being assumed that a methanol molecule effectively covers an area of 16.5 Å<sup>2</sup>. A slow reaction followed, for which plots of pressure against time were linear for long periods. At higher temperatures the initial reaction rates increased considerably and, because of simultaneous adsorption, they were not measurable. At this stage the plots are curved (Fig. 2). However, the equation,

$$\text{Rate of reaction, } dx/dt = \text{a constant, } k, \quad (1)$$

represents the initial kinetics of the reaction over much of the temperature range investigated. Variation of the initial pressure of reactant produced no significant effect on the linear plots (see Fig. 3), in accordance with equation (1).

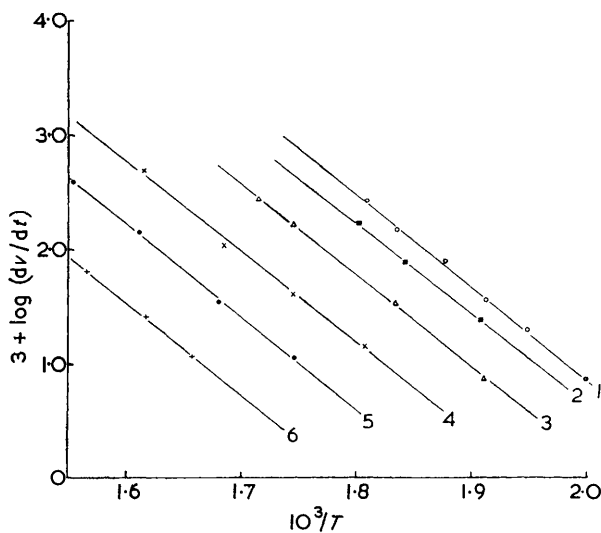


FIG. 4.

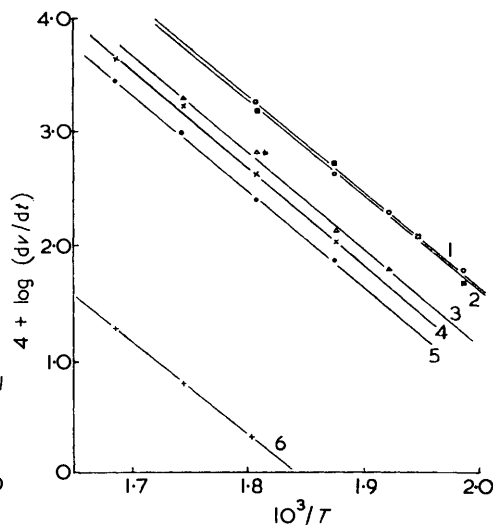


FIG. 5.

Figs. 4 and 5. Arrhenius plots for methanol decomposition on zinc oxide and doped zinc oxide, prepared by heating at 1000° for one hour (Fig. 4) or for five hours (Fig. 5).

( $v$  is the volume of products reduced to S.T.P.; catalyst weight = 7.0 g.)

(1) ZnO + 1 mole % of Al<sub>2</sub>O<sub>3</sub> ("O" sample from oxalate). (2) ZnO + 1 mole % of Al<sub>2</sub>O<sub>3</sub> ("A" sample from "AnalaR" ZnO). (3) ZnO (O). (4) ZnO + 1 mole % of Li<sub>2</sub>O (O). (5) ZnO (A). (6) ZnO + 1 mole % of Li<sub>2</sub>O (A).

Determination of the initial rates yielded values for the velocity coefficient,  $k$ . Arrhenius plots of these values are shown in Figs. 4 and 5, obtained by the method of least squares. Table 3 lists the energies of activation,  $E$ , calculated from the slopes of these plots. The scatter in values in each set is within the limits of experimental error. The average  $E$  for each set is

TABLE 3.

Sample	Set I (Heated at 1000° for 1 hr.)			Set II (Heated at 1000° for 5 hr.)		
	$E$ (kcal. mole <sup>-1</sup> )	$10^{-7}A'$ (mole min. <sup>-1</sup> g. <sup>-1</sup> cat.)	$10^{-7}A'/s$ (mole min. <sup>-1</sup> m. <sup>-1</sup> cat.)	$E$ (kcal. mole <sup>-1</sup> )	$10^{-9}A'$ (mole min. <sup>-1</sup> g. <sup>-1</sup> cat.)	$10^{-9}A'/s$ (mole min. <sup>-1</sup> m. <sup>-2</sup> cat.)
AZ .....	37.2	0.29	2.1	38.5	0.14	2.0
AL .....	36.1	0.062	(1.5)	37.8	0.001	—
AA .....	35.9	12	16	38.2	0.88	1.9
OZ .....	36.6	4.2	14	39.0	0.31	3.1
OL .....	36.2	1.1	7.3	39.1	0.22	2.4
OA .....	37.2	22	27	38.5	0.94	1.8

$36.5 \pm 1.0$  kcal. mole<sup>-1</sup> and  $38.5 \pm 1.0$  kcal. mole<sup>-1</sup>, respectively. Estimation of the frequency factors,  $A$ , of the Arrhenius equation:

$$k = A \exp (-E/RT), \quad (2)$$

depends on a lengthy extrapolation and the results are very sensitive to small errors in the slope. Extrapolations were therefore made from an arbitrary ordinate erected in the middle of the experimental temperature range,<sup>9</sup> and the average value of the slope in each set given above was used. These yielded only relative values of the frequency factors ( $A'$  in Table 3) which, however, could be tested for influence of surface area. Table 3 shows that values of  $A'/s$  (where  $s$  = original surface area) for set I increase in the order  $\text{ZnO} + \text{Li}_2\text{O} < \text{ZnO} < \text{ZnO} + \text{Al}_2\text{O}_3$ , being higher for "O" than for corresponding "A" catalysts. This is also the order of increasing surface area. The values are smaller and approximately constant for catalysts of set II.

#### DISCUSSION

Small amounts of foreign ions have a relatively large effect on the surface area of zinc oxide, in contradiction to the assumption of Hauffe *et al.*<sup>10</sup> The decrease of surface area caused by incorporation of lithium contrasts with the results of other workers<sup>11</sup> for samples sintered at lower temperatures and of somewhat higher lithium content. This may reflect the predominance of surface effects over bulk incorporation in the latter cases. Sintering at 1000° should produce a more uniform oxide structure, though the actual foreign-ion concentrations, especially of lithium ions, are likely to be smaller than the calculated amounts because of volatility.<sup>12</sup> It is evident from Table 1 that many factors are involved, and no simple correlation can be attempted. However, sintering would be expected to be greater for samples in which the concentration of lattice defects had been reduced by incorporation of lithium in the lattice,<sup>13</sup> as found in the present case. The results given in Table 1 explain the trend of  $A'/s$  values quoted for samples of set I in Table 3. Komarov *et al.*<sup>14</sup> found that the surface area of zinc oxide was lowered by heating at 320–440° in the presence of ethyl alcohol. If similar sintering occurred during dehydrogenation of methanol on the present catalysts, it would be expected to be greatest for lithium-doped catalysts and least for aluminium-doped catalysts. The values of  $A'/s$  would lie closer if allowance were made for this effect. Samples of set II were extensively sintered during preparation, and exposure, when heated, to methyl alcohol would be expected to produce little further change in the surface area. The smaller values of  $A'$  than of those for set I, and the approximate constancy of  $A'/s$ , indicate that the variation of  $A'$  values is largely a result of the difference in surface areas of the various catalysts.

The values of excess zinc content found for "AnalaR" zinc oxide as received correspond to those found by Allsopp and Roberts.<sup>15</sup> Sintering in air at 1000° increases these values for AZ samples, whereas those for OZ samples remained low. These results agree with those of other workers,<sup>16</sup> though Allsopp and Roberts<sup>15</sup> report low values of excess zinc for single crystals of zinc oxide when sintered in air at 1300° for 0.5 hour. The very different effects on the rate of decomposition of methanol caused by preheating the catalyst in air at 1000°, and in oxygen at 400° (where the oxygen uptake is near its maximum value<sup>17</sup>) therefore indicate that the reproducible reaction involves the participation of zinc sites at the surface. The appearance of a zinc mirror during the first few runs of a series implies a reaction such as:  $\text{CH}_3\cdot\text{OH} + \text{ZnO} = \text{CO}_2 + \text{Zn} + 2\text{H}_2$ . Thereafter the

<sup>9</sup> Schwab and Schwab-Agalladis, *J. Amer. Chem. Soc.*, 1949, **71**, 1806.

<sup>10</sup> Hauffe, Glang, and Engell, *Z. phys. Chem.*, 1952, **201**, 223.

<sup>11</sup> Enikeev, Ya Margolis, and Roginskii, *Doklady Akad. Nauk S.S.S.R.*, 1959, **129**, 372; Zhabrova, Vladimirova, and Vinogradova, *ibid.*, 1960, **133**, 1375.

<sup>12</sup> Dry and Stone, *Discuss. Faraday Soc.*, 1959, **28**, 192.

<sup>13</sup> Hauffe and Vierk, *Z. phys. Chem.*, 1950, **196**, 160; Heckelsburg, Clarke, and Bailey, *J. Phys. Chem.*, 1956, **60**, 559.

<sup>14</sup> Komarov, Drozdova, and Chernikova, *Zhur. fiz. Khim.*, 1949, **23**, 1141.

<sup>15</sup> Allsopp and Roberts, *Trans. Faraday Soc.*, 1959, **55**, 1386.

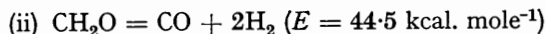
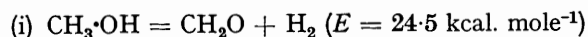
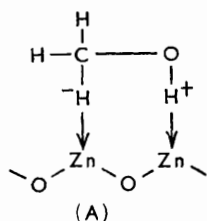
<sup>16</sup> Hahn, *J. Appl. Phys.*, 1951, **22**, 855; Miller, *Phys. Rev.*, 1941, **60**, 890.

<sup>17</sup> Morrison and Miller, *J. Chem. Phys.*, 1956, **25**, 1064.

products are predominantly carbon monoxide and hydrogen, and the zinc oxide does not appear to be further reduced at 200—330°.

Alteration of the Fermi level of zinc oxide catalyst by the incorporation of altrivalent ions did not affect the energy of activation of dehydrogenation of methanol in these experiments. Thus, once zinc sites at the surface are available for adsorption of methanol, the activity of the catalyst does not depend on the Fermi level of the catalyst in a rate-controlling step. Menold,<sup>3</sup> however, found that addition of lithium lowered the activation energy from *ca.* 44 kcal. mole<sup>-1</sup> for pure zinc oxide to 24.5 kcal. mole<sup>-1</sup> for ZnO + 0.4 mole % of Li<sub>2</sub>O, the oxides being prepared by heating at 750° for 2 hours. This temperature is below that needed for incorporation of foreign ions in the lattice,<sup>6</sup> and it is therefore likely that in Menold's work the alteration of activation energy was due to surface effects only, and not to a change in Fermi level in the oxide.

The zero-order kinetics indicate that the adsorption of methanol is not rate-controlling. Eucken and Heuer,<sup>18</sup> and Wicke,<sup>19</sup> postulate an adsorption step (A). This is followed by breakdown of the adsorbed alcohol to formaldehyde and adsorbed hydrogen atoms. Formaldehyde then yields carbon monoxide and hydrogen in a step which may involve desorption of adsorbed aldehyde or of its decomposition products from the surface of the oxide catalyst. The energies of desorption of carbon monoxide<sup>20a</sup> and of hydrogen<sup>20b</sup> from zinc oxide are *ca.* 40 and 10—31 kcal. mole<sup>-1</sup>, respectively. The energies of activation found in these experiments lie close to the value for desorption of carbon monoxide, suggesting the latter as a rate-controlling step in the dehydrogenation. However, the molecule is considered to be adsorbed as CO<sup>+</sup> on zinc oxide,<sup>21</sup> and thus the activation energy for desorption would be expected to vary with incorporation of foreign ions in the oxide catalyst. This is contrary to the evidence. The rate-controlling steps, therefore, probably involve loss of hydrogen atoms from the adsorbed alcohol or decomposition of formaldehyde. A value of 24.5 kcal. mole<sup>-1</sup> has been assigned to the activation energy involved in the most energetic of the former steps.<sup>3</sup> The energy of activation for decomposition of formaldehyde in the gas phase<sup>22</sup> is 44.5 kcal. mole<sup>-1</sup>. Comparison with the results of the present work shows that the energies of activation obtained can be explained by assuming either decomposition of adsorbed formaldehyde with an activation energy lower than that for the gas-phase decomposition, or that the two stages:



yield an overall activation energy of 36—39 kcal. mole<sup>-1</sup> when rate constants are determined over a limited temperature range. This implies that formaldehyde is formed in the gas phase in the early stages of the reaction, before breakdown to the final products. The initial presence of formaldehyde, in small amounts, was indicated by pumping out the products after partial reaction had occurred, and passing them through a solution containing chromotropic acid; the solution became blue-violet. Since formaldehyde had no retarding effect on the reaction, it is likely that the determined energy of activation is a composite one, as discussed above.

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<sup>18</sup> Eucken and Heuer, *Z. phys. Chem.*, 1950, **196**, 40.

<sup>19</sup> Wicke, *Z. Elektrochem.*, 1949, **53**, 279.

<sup>20</sup> Kubokawa, *Bull. Chem. Soc. Jap.*, 1960, **33**, (a) 555, (b) 546.

<sup>21</sup> Hart and Sebba, *Trans. Faraday Soc.*, 1960, **56**, 551; Roginskii, *Doklady Akad. Nauk S.S.S.R.*, 1959, **126**, 817; 1960, **130**, 122.

<sup>22</sup> Fletcher, *Proc. Roy. Soc.*, 1934, *A*, **146**, 357.