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Decomposition of Methanol on Zinc Oxide Pelleted at Various Pressures

F. MORELLI, M. GIORGINI, AND R. TARTARELLI

Institute of Industrial and Applied Chemistry, Pisa University, Italy

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The effect of the compacting pressure of catalysts containing zinc oxide for the methanol decomposition has been investigated previously by Takamizawa *et al.* (*1*) and Ogino and Nakajima (*2*). According to Takamizawa *et al.*, the activity of a catalyst containing ZnO, Cr_2O_3, CuO, and graphite decreased with the compacting pressure as a whole, but it passed through a maximum at approximately 5000 kg/cm². Corresponding anomalies were observed in the curves of the surface area, the total pore volume, and the average pore radius against the compacting pressure, which caused in addition little variation in the lattice spacings of the catalyst. The anomaly in activity has been explained by the pore radius changes. Ogino and Nakajima, studying the effect of compression on the activity of a ZnO–Cr_2O_3 catalyst, found a maximum of activity and a minimum of activation energy at the compacting pressure of 2500 kg/cm², at which a minimum of the lattice distance of $ZnCr_2O_4$ has been revealed too. The variation in catalytic activity has been attributed to the variation in lattice distance.

As early remarked by Dohse (*3*) and successively by Wicke and Brotz (*4*), Fuderer-Luetić and Sviben (*5*), and Wencke and Heise (*6*), the Arrhenius plot for the methanol decomposition on catalysts containing ZnO may show a variation in the activation energy. That has been attributed to the consecutive steps

$$CH_3OH \underset{(I)}{\rightarrow} CH_2O + H_2 \underset{(II)}{\rightarrow} CO + 2H_2$$

of which the first is rate limiting at higher, the second at lower temperature, to either a change in the controlling step of the overall reaction or a change in catalyst semiconductivity (*5*), and to diffusional resistances within the catalyst (*4*, *6*). In addition, in the methanol decomposition on zinc oxide, diffusion effects within the catalyst pellets have been cited by Weisz and Prater (*7*) and a relation between the effective diffusion coefficient and the conversion rate has been established by Alder (*8*).

Because some discrepancies on the interpretations, often not well supported, of the break on the Arrhenius plot still exist, we have limited the present investigation on the compacting pressure effect on the pure ZnO behavior to the lower temperature range where undoubtedly inter- and intraparticle diffusion resistances could be excluded.

EXPERIMENTAL

Catalyst. The zinc oxide was prepared by thermal decomposition of oxalate (zinc nitrate and ammonium oxalate molar solutions) (*9*). The zinc oxalate precipitate, washed until free of nitrates, had been calcined for 14 hr in a current of nitrogen and the zinc oxide powder had been sintered at 300°C for 3 hr under various compacting pressures ranging from 235 to 4000 kg/cm². Details of the apparatus for the compression are reported elsewhere (*10*). Four types of ZnO have been employed:

ZnO(I)—pelleted at 235 kg/cm²;
ZnO(II)—pelleted at a pressure the exact

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value of which could not be measured owing to an accidental trouble of the compression apparatus, but which must have ranged from 235 to 1975 kg/cm^2;

ZnO(III)—pelleted at 1975 kg/cm^2;

ZnO(IV)—pelleted at 4000 kg/cm^2.

The catalyst pellets were crushed and separated by DIN 1171 series sieves into a number of size fractions. Before employment, the catalyst was activated at 400°C in the reactor for 9 hr in a current of hydrogen (flow rate = 1.2 liter/hr).

The surface area (BET) of the catalyst was measured by a Carlo Erba Sorptomatic apparatus. The pore volume was measured by the helium–mercury method.

The crystallography was investigated by X-ray powder patterns with a Philips diffractometer. The (100), (002), and (101) diffractions were measured by Cu$K\alpha$ radiation with wavelength 1.5418 Å; the (213) diffraction by Cu$K\alpha_1$ radiation with wavelength 1.5405 Å. The position of the peaks was measured by the step scanning operation of the diffractometer. The measurements were calibrated using the (111) reflection of silicon for the (100), (002), and (101) diffractions and the (531) reflection of silicon for the (213) diffraction.

Apparatus. The kinetics of the methanol decomposition was followed in a flow system with helium as a carrier gas. A schematic representation of the system is given in Fig. 1. The flow rate of helium was measured accurately by a soap flow meter (B) placed after a rotameter (A). The pressure was recorded on a manometer. The gas was passed through a drying tower (C) filled with $CaCl_2$, then through a tower (D) the upper part of which is filled with NaOH pellets and the lower with clean steel wool. This part is cooled with a carbon dioxide–ethyl alcohol freezing mixture. The saturator consists of two parts. The first part is an evaporator (E) equipped with a Mariote vessel (F) and kept at constant temperature by a thermostatic bath. The second part is a condenser (G) kept at a slightly lower temperature in order to ensure the complete saturation of the gas with alcohol vapor. The reactor (H) consists of a 9 mm i.d. Pyrex glass tube 30 cm long. The catalyst in the reactor is supported by glass pellets and wool; its tem-

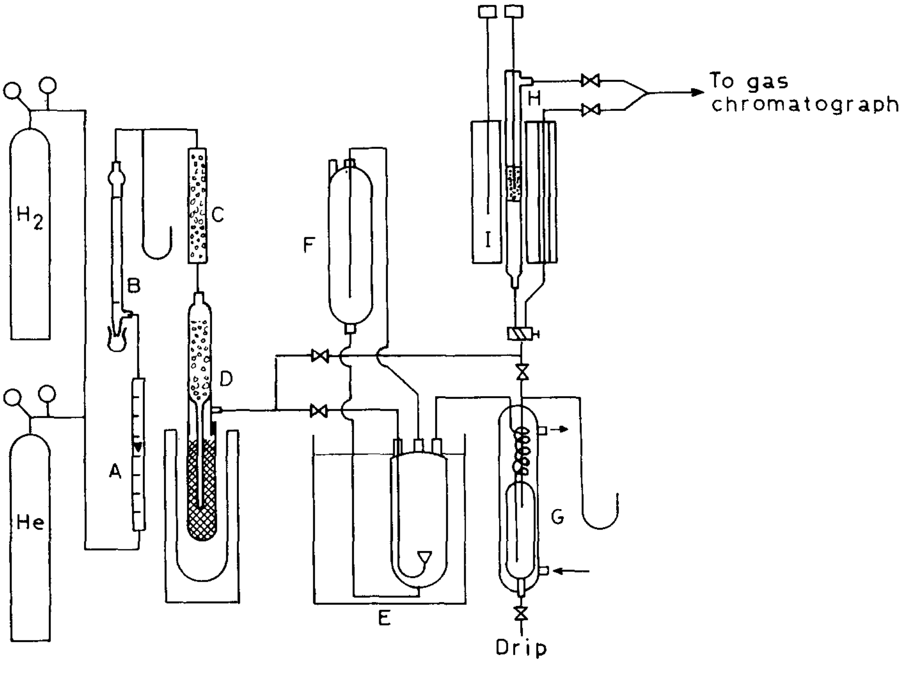

FIG. 1. Diagram of the experimental equipment.

perature is measured by a thermocouple. The reactor is enclosed in a bronze jacket (I) electrically heated, the temperature of which is maintained constant by a thermoregulator within an accuracy of ±0.1°C.

Analytical procedure. The gas streams, both from the saturator and from the reactor, were analyzed on a gas chromatograph (Carlo Erba mod GV apparatus equipped with thermal conductivity detector) where H_2, CO, CO_2, and CH_3OH could be determined (*10*).

Materials used. The methanol was a Carlo Erba product with a water content less than 0.05%. The helium was a pure grade product, with purity superior to 99.99%. The zinc nitrate and ammonium oxalate were RP Carlo Erba products.

RESULTS AND DISCUSSION

The Catalyst Structure

The dependence of the surface area and the pore volume on the compacting pressure is reported in Table 1. While the surface area may be considered practically unaffected by the compacting pressure, major changes in the pore volume occur.

TABLE 1
SURFACE AREA AND PORE VOLUME OF ZINC OXIDES PELLETED AT VARIOUS PRESSURES

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)
ZnO(I)	10	0.37
ZnO(II)	10.3	0.14
ZnO(III)	9.3	0.09
ZnO(IV)	9.6	—

The crystallography of the differently compressed zinc oxides is given in Table 2. Plainly, it shows that the compacting pressure does not have a measurable effect on the lattice distances. Nevertheless, the compacting pressure has an influence on crystallinity, as is shown by the broadening of the diffraction peaks observed on the powder patterns of Fig. 2. At the present stage, no attempt has been made to measure quantitatively this broadening. However, this effect may be qualitatively visualized recording the (213) diffraction utilizing the $CuK\alpha_1$ and $CuK\alpha_2$ doublet of radiations. Figure 2, where the separation of the $K\alpha_1$ and $K\alpha_2$ radiations is observed, emphasizes that with the increase of the compacting pressure a marked broadening of the diffraction peaks occurs. The effect is visualized by the decreasing separation of the two radiations. For comparison, the (531) diffraction of silicon, carried out under the same conditions, is reported.

The behavior may be clearly attributed to a decrease of crystallinity with increasing the compacting pressure. Because the change in the surface area is not noticeable and consequently it may be supposed that disintegration of the particle has not occurred, the change in crystallinity may be essentially ascribed to lattice defects induced on sintering.

The Catalyst Activity

Tests performed in the absence of catalyst at 385°C and high contact times did not show measurable decomposition of methanol. The extent of reaction has been evaluated on the reactant concentration

TABLE 2
INTERPLANAR DISTANCES OF ZINC OXIDES PELLETED AT VARIOUS PRESSURES

	Interplanar distance d_{hkl} (Å)					
Diffraction	ZnO unsintered	ZnO (I)	ZnO (II)	ZnO (III)	ZnO (IV)	ZnO ASTM 5-0664
(100)	2.820	2.820	—	—	2.818	2.816
(002)	2.608	2.608	—	—	2.606	2.602
(101)	2.480	2.480	—	—	2.478	2.476
(213)	0.9068	0.9068	0.9068	0.9068	0.9069	0.9069

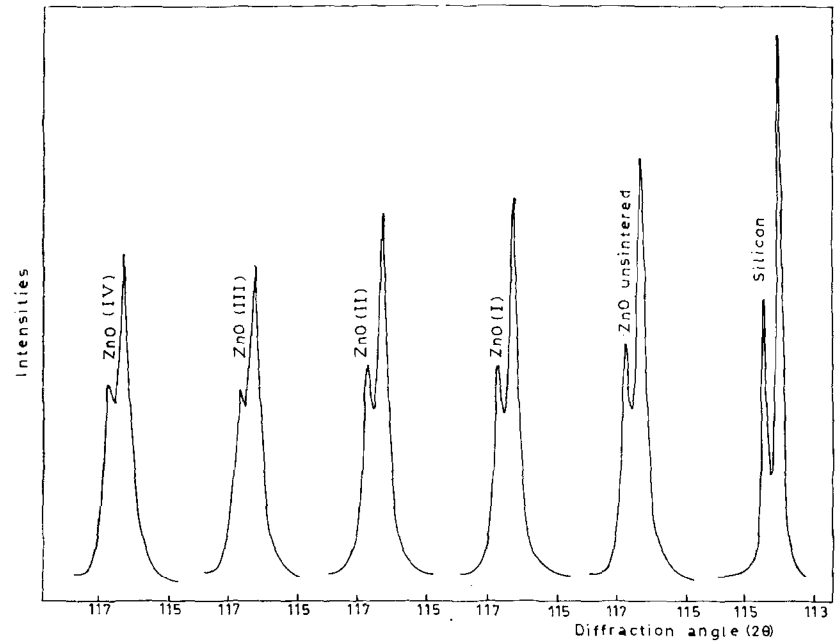

FIG. 2. X-Ray powder diffraction patterns.

decrease at the outlet of the reactor. Most of runs have been carried out with methanol concentrations of 4 to 5 mol/m^3. The methanol conversion was kept low, generally less than 10% (*10*). Preliminary runs, reported elsewhere (*11*), showed that the reaction rate may be fairly well considered independent of the methanol concentration, i.e., of zeroth-order, in agreement with that reported by Dohse (*3*), Hütting and Feher (*12*), Baccaredda (*13*), Shekter and Moshkoskiĭ (*14*), Menold (*15*), Frackiewicz (*16*), and Dandy (*17*). Therefore, the kinetic data have been computed from the equation:

$$C_0X = K\tau$$

where

C_0 = methanol concentration in the stream entering the catalyst bed (mole/m^3)

X = methanol conversion

K = rate constant (mole/hr g cat)

τ = spatial time, defined as ratio between the catalyst weight (in g) and the volumetric rate of gas stream (m^3/hr)

The rate constant is reported in Fig. 3 on the Arrhenius plot for the four types of zinc oxides with various pellet sizes (the temperature range has been explored with both increasing and decreasing temperature without revealing any evidence of catalyst deactivation during the runs). The K values have been obtained on different catalyst weights. Because no effect of the catalyst weight and particle size results, in the temperature range investigated the reaction step on the catalytic centers controls the process rate and the activation energies are dependent on the compacting pressure (Table 3). A maximum value of the activation energy is given by the catalyst sintered at 1975 kg/cm^2.

While Ogino and Nakajima (*2*) attributed the change in activation energy to the variation in lattice distance, this explanation is unsatisfactory for the present case, where the lattice distances may be considered fairly well unchanged. Rather, the compression of the catalyst powder, on generating lattice defects as shown by the crystallinity behavior, may be supposed to form new types of active centers of different activation energy. Because the zinc oxide gives rise to a nonstoichiometric solid (*18*), the lattice defects may be related to the oxygen content, which, accord-

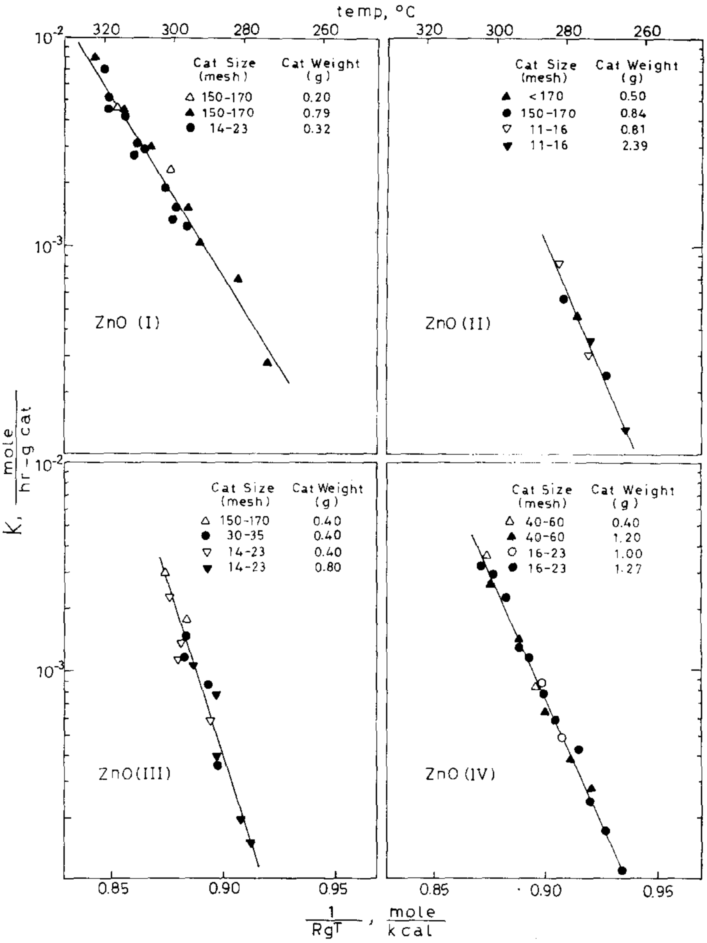

FIG. 3. Arrhenius plots for zinc oxides pelleted at various pressures.

ing to Ogino and Nakajima (*2*), is dependent on the compacting pressure. Otherwise, the change in activation energy may be attributed to differences in the extent of reduction in H_2 as influenced by compacting, by which the differently compressed zinc oxides, after hydrogen treatment, are differently oxygen deficient.

TABLE 3

ACTIVATION ENERGIES GIVEN BY ZINC OXIDES PELLETED AT VARIOUS PRESSURES

Catalyst	Activation energy (kcal $mole^{-1}$)
ZnO(I)	41
ZnO(II)	59
ZnO(III)	77
ZnO(IV)	55

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