$$K_2\theta_E\theta_H = \theta_x p_H{}^a, \qquad (8)$$

where K_2 is an equilibrium constant and p_H is the hydrogen partial pressure. The rate of hydrogenolysis is simply the rate of step 3, and is given by the expression:

$$r = k_3\theta_x. \qquad (9)$$

Combining Eqs. 7, 8, and 9, we obtain the rate equation:

$$r = k_1p_E/(1 + bp_H{}^a), \qquad (10)$$

where $b = k'_1/k_3K_2$. This analysis differs from a previously published one (*1*), since step 3 of the reaction sequence does not involve hydrogen as a reactant. Since the parameter b is temperature dependent, the dependence of the rate on hydrogen pressure is a function of temperature. If b decreases with increasing temperature, as found for cobalt (*1*, *11*), the rate equation at a sufficiently high temperature becomes simply, $r = k_1p_E$. This corresponds to the situation in which the chemisorption of ethane is completely irreversible. Under such conditions, step 2 of the reaction sequence may also become irreversible, so that the overall reaction may be considered simply as a sequence of irreversible steps. On the other hand, at a sufficiently low temperature, the term $bp_H{}^a$ in Eq. 10 becomes large compared to unity, and the rate equation becomes:

$$r = k_1p_E/bp_H{}^a = k_3K_1K_2p_E/p_H{}^a, \qquad (11)$$

where K_1 is the equilibrium constant of step 1 of the reaction sequence. Equation 11 corresponds to adsorption equilibrium being established between C_2H_6 and adsorbed C_2H_x, and is equivalent to Eq. 6 for $n = 1$. The equilibrium constant K in Eqs. 4–6 is equal to the product of K_1 and K_2.

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Some Remarks on the Activation Energy Variation in the Methanol Decomposition on Zinc Oxide

The kinetics of the methanol decomposition on zinc oxide has been investigated early by Dohse (*1*), who remarked on the Arrhenius plot a variation in the activation energy. That has been attributed to the consecutive steps:

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

with activation energies of ~20 and ~40 kcal mole^{-1}, respectively; the step (I) has been assumed as rate-limiting at higher and the step (II) at lower temperatures.

Wicke and Brotz (*2*) interpreted the lowering of the apparent activation energy as a transition from the chemical to the strong-pore diffusion regime within the catalyst. Diffusion effects within ZnO pellets in the methanol decomposition have been cited by Weisz and Prater (*3*) and a relation between the effective diffusion coefficient and the conversion rate has been established by Alder (*4*). Fuderer-Luetić and Sviben (*5*) attributed the variation in activation energy, revealed on undoped and doped ZnO, to either a change in semiconductivity of the catalyst or a change in the controlling step of the overall reaction. According to Wencke and Heise (*6*), the Arrhenius plot for $ZnO–Cr_2O_3$ mixed oxides shows a break, which has been attributed to the diffusion of CH_2O formed into the catalyst bed.

From the above literature it results that some discrepancies on the interpretations, often not well supported, of the breaks on the Arrhenius plot still exist. In the present note, runs have been carried out in order to look for the occurrence of inter- and intraparticle diffusion resistances, which might contribute to the variation in activation energy.

The zinc oxide powder has been obtained by calcining for 14 hr in a current of nitrogen the zinc oxalate (zinc nitrate and ammonium oxalate molar solutions). Six types of zinc oxide have been employed. ZnO(I), ZnO(II), ZnO(III), and ZnO(IV), reported in a previous paper (*7*), have been prepared by sintering the zinc oxide powder at 300°C for 3 hr under various compacting pressures ranging from 235 to 4000 kg/cm^2:

ZnO(I) —pelleted at 235 kg/cm^2;
ZnO(II) —pelleted at a pressure the exact value of which could not be measured 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 effect of the compacting pressure upon surface area, pore volume and crystallography of these catalysts has been reported elsewhere (*7*). ZnO(V) and ZnO(VI) have been prepared in the form of cylindrical pellets 3 and 5 mm, respectively, in both diameter and length by compacting the powder at room temperature under a pressure of 2100 kg/cm^2. The pellets, so obtained, have been successively calcined at 300°C for 3 hr. Particles of smaller sizes have been obtained by crushing the primary pellets.

The reaction has been followed in the flow system previously described (*7*), with helium as carrier gas; analysis of the gas stream has been accomplished on a chromatography. The methanol conversion was kept low, generally less than 10% (*8, 9*). The rate constant K has been computed from the zeroth-order equation (*8–10*):

$$C_0X = K\tau,$$

where

C_0 = methanol concentration in the stream entering the catalyst bed (mole/meter^3);
X = methanol conversion;
K = rate constant (mole/hour × grams catalyst);
τ = spatial time defined as ratio between the catalyst weight (in grams) and the volumetric rate of gas stream (meter^3/hour).

The straight lines which fit the data previously obtained in the lower temperature range (*7*) with ZnO(I), (II), (III), and (IV) are reported on the Arrhenius plots of Fig. 1. As no effect of the catalyst weight and particle size was revealed, it was deduced that the reaction step on the catalytic centers controls the process rate in the lower temperature range investigated, and the differences in the activation energy with the compacting pressure were attributed to either energetically different lattice defects generated on compacting or differences in the extent of reduction in H_2 as influenced by compacting.

The data obtained in the upper temperature range, given in Fig. 1, show that for the four types of catalyst a variation in the activation energy with increasing temperature results, according to the previously

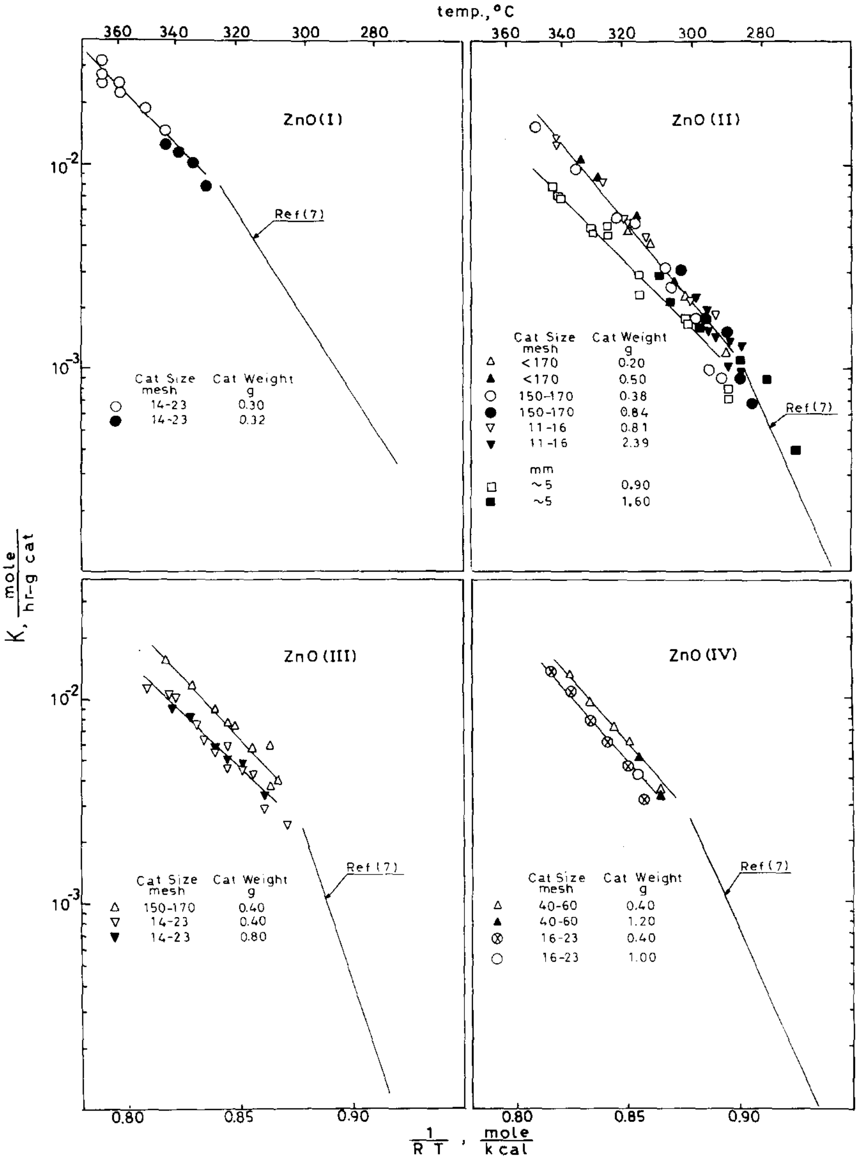

FIG. 1. Arrhenius plots for zinc oxides pelleted at various pressures.

cited authors (*1–6*). Whereas the runs carried out with different catalyst weights can rule out diffusional effects outside the catalyst particle, in the upper temperature range an effect on the rate constant may be played by the pellet size and, consequently, diffusional resistances within the catalyst must be taken into account too. Undoubtedly, from the results obtained on the ZnO(II) particles smaller than 5 mm, the rate constant appears independent of the catalyst size and in this case the variation in the activation energy cannot be attributed to diffusion effects, but rather to such phenomena as a change in the catalyst semiconductivity or in the controlling step of the overall reaction, according to Fuderer-Luetić and Sviben (*5*). The pellets of about 5 mm in size in the upper temperature range give both a lower rate constant and activation energy, revealing the occurrence of diffusional phenomena.

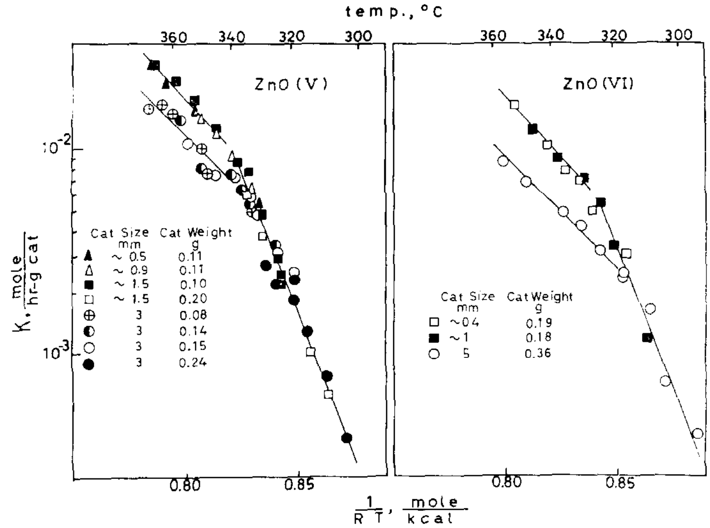

FIG. 2. Arrhenius plots for zinc oxides pelleted at 2100 kg/cm^2.

Likewise, diffusive effects can be noted on ZnO(III) and ZnO(IV) in the upper temperature range.

ZnO(V) and ZnO(VI) show a similar behavior on the Arrhenius plots of Fig. 2. ZnO(VI) is more active than ZnO(V), but both catalysts, pelleted at the same pressure, have the same activation energy in the lower temperature range.

Therefore, it can be concluded that the variation in the activation energy, which occurs in the methanol decomposition on zinc oxide with increasing the reaction temperature, is caused by a change either in the catalyst properties or in the reaction mechanism. Diffusive effects may occur too, contributing to the lowering of the activation energy when the particle size is high enough.

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