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Influence of Catalyst Preparation on the Kinetics of β-Phenyl-ethyl Alcohol Decomposition Over Zinc Oxide

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The decomposition of β-phenyl-ethyl alcohol to give styrene and β-phenyl aldehyde has been kinetically investigated on two different zinc oxide catalysts. The investigations have been performed in the temperature range of 300°–360°C. The different activities of the two catalysts and their aging provide information on the reaction mechanism, which is consistent with the physical and chemical characteristics of the catalysts, such as surface areas and oxygen chemisorption.

INTRODUCTION

The reactions of dehydration and dehydrogenation of alcohols on metallic oxides have been the object of extensive investigations (*1–3*). Such reactions, in fact, offer a model for the study of a system of two parallel reactions. Two problems that arise in the analysis of these processes are the participation of one or two different active sites for two parallel reactions, and the influence of the preparation of catalyst on its activity.

The selectivity of the catalysts is a very important, but still unsolved, problem, although many attempts have been made in correlating such a factor with the electronic properties of the solid (*4*). It has been also suggested (*5*) that the metal ions preferentially exposed in the surface are active sites for dehydrogenation, while the dehydration reaction should be essentially ascribed to the acid-base properties of the solid catalyst (*6*).

In the present paper, the results of an investigation on the dehydrogenation and dehydration of a primary alcohol on zinc oxide are reported with the aim of deepening our understanding of these points. Ethanol decomposition has often been studied in this context on other oxides. However, since ethanol gives essentially dehydrogenation on ZnO our research was performed on β-phenyl-ethyl alcohol, on which the competition between the two parallel reactions can be better observed.

EXPERIMENTAL METHODS

Materials. β-Phenyl-ethyl alcohol was a Schuchard product (purity 99%, refractive index $D_{25}^{25} = 1.01 - 1.02$). Nitrogen was taken from a commercial cylinder, purity 99.999%. Zinc chloride was a C. Erba RP-ACS product; sodium hydroxide was a C. Erba R.P. Product.

Catalyst preparation. The zinc oxide catalyst was prepared by the following procedure, suggested by Teichner and coworkers (*7*). A solution of sodium hydroxide $2\,N$ has been added to a solution of zinc chloride. The precipitated zinc hydroxide, after washing, has been treated with a concentrated solution of ammonia and then reprecipitated by evaporating ammonia under vacuum. The zinc hydroxide so obtained was divided into two parts, which were separately dehydrated by means of two different treatments. In both cases, the thermal treatment was performed in a tubular furnace at 400°C in nitrogen. In the

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former case the total pressure in the furnace was 10^{-4} mm Hg for 10 hr (this catalyst will be indicated by A). In the latter case, the total pressure in the furnace was 10^{-2} mm Hg for 14 hr (this catalyst will be indicated by B).

Catalyst A. The surface area, determined by the B.E.T. method, was 37.8 m^2/g. An analysis of oxygen adsorption was performed by means of a "CAHN RH" microbalance. A sample of catalyst on a pan of the balance was flushed with nitrogen for 12 hr. Afterwards, the temperature was increased to 400°C always in the nitrogen stream. After cooling, the stream of nitrogen was stopped and the sample weighed. The sample was then heated at 400°C in an oxygen stream for 4 hr, that is, until the attainment of stationary conditions. After cooling, the sample was weighed in an oxygen atmosphere. Blank runs revealed that different gas densities did not affect the results. The results obtained are summarized in Table 1.

Catalyst B. The surface area was 8.7 m^2/g. The results of thermal gravimetric analysis are given in Table 2. It can be observed that catalyst B does not adsorb oxygen. IR, DTA, and X-ray analysis did not reveal significant differences between the two samples. Since the diffractograms of A samples were weaker than those of B samples, it follows that the former catalyst has lower crystallinity. This finding is consistent with the higher surface area of catalyst A.

TABLE 2

THERMOGRAVIMETRIC ANALYSIS DATA OF CATALYST B[a]

Run no.	*a*	*b*	*c*
1	16.357	16.090	16.082
2	43.656	42.948	42.952
3	15.472	15.438	15.434

[a] For meanings of abbreviations, see footnote *a* to Table 1.

Apparatus. The runs were performed in a glass tubular reactor. A simplified drawing of the equipment is illustrated in Fig. 1. The feeds consisted of mixtures of nitrogen and β-phenyl-ethyl alcohol obtained by evaporation of alcohol.

Analysis. A gas chromatographic analysis was performed on the reactant (β-phenylethyl alcohol) and products (styrene, water, and phenylacetaldehyde) by means of a Fractovap B/F (Carlo Erba). The chromatographic columns (diameter 5 mm, length 2 m) contained Chromosorb W 60-80 mesh plus 9% di-2-ethyl-esil-sebacate, 1% polypropylene glycol and were operated at 125°C using hydrogen (0.5 atm) as carrier gas. Samples consisted of 3 cc of gas mixtures.

RESULTS

Kinetics of decomposition were studied at 300, 320, 340, and 360°C. Some examples are given in Fig. 2a–d where the conversions of alcohol to styrene and aldehyde are given as a function of the time factor τ (g

TABLE 1

THERMOGRAVIMETRIC ANALYSIS DATA OF CATALYST A[a]

Run no.	*a*	*b*	*c*	*d*	*e*	*f*
1	91.807	90.377	90.453	1.11×10^{-3}	4.75×10^{-6}	4.27×10^{-3}
2	48.745	47.972	48.013	0.59×10^{-3}	2.56×10^{-6}	4.34×10^{-3}
3	43.394	42.918	42.956	0.53×10^{-3}	2.37×10^{-6}	4.50×10^{-3}
					Mean value	4.4×10^{-3}

[a] *a* = initial sample weight (mg); *b* = weight after heating in nitrogen stream; *c* = weight after heating in oxygen stream; *d* = mole number of ZnO = c/M_{ZnO} (M_{ZnO} molecular weight of ZnO); *e* = number of adsorbed oxygen atoms = $(c - b)/M_0$ (atomic weight of O); *f* = number of adsorbed atoms per moles ZnO = *e*/*d*. The differences between *a* and *b* give the weight lost due to humidity.

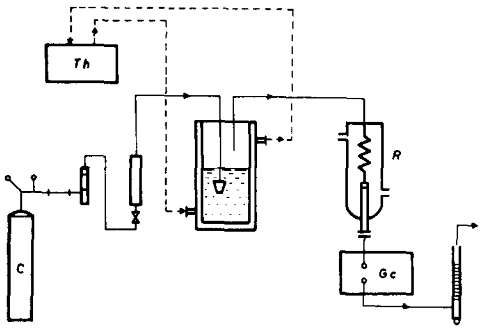


FIG. 1. Scheme of the apparatus. C, nitrogen cylinder; Th, thermostatic controller of evaporator; R, reactor; and Gc, gas chromatograph.

of catalyst/g of alcohol/hr). Also kinetic runs with different a = (nitrogen/alcohol) ratios in the feed were performed in order to obtain a different partial pressure of reactants in the range of 10–150 mm Hg.

In order to analyze the stability of the catalysts and their behavior, a set of experiments, whose details will be given below, was performed.

Catalyst deactivation and behavior. First, it was verified that in the range of temperature, partial pressures, and flow rates used, the reactants and products were stable.

In order to verify the behavior of the catalyst, some runs were made at 300°C for a time up to 110 hr.

The results obtained for catalyst B are summarized in Table 3. It emerges that while the conversion of aldehyde (x_c) is not significantly affected by the working time of the catalyst, the conversion to styrene decreases with time. Such a result can be understood by assuming that dehydration and dehydrogenation reactions occur on different active sites, since only the former reaction is deactivated.

In order to verify whether the deactivation is due to thermal aging of catalyst or to a selective poisoning, all the kinetic runs performed at different temperatures were duplicated after 8 hr at 300°C. Despite the values of the working temperatures in the first 8 hr, the same conversions were obtained for all the performed runs at the same contact time. In other words, the conversion at the lower temperatures (300°C) were unaffected by previous treatments of the catalyst at higher temperatures. This fact reveals that the deactivation in the dehydration reaction cannot be attributed to the thermal aging.

TABLE 3

SELECTIVITY VARIATION WITH TIME, AT DIFFERENT CONTACT TIMES[a]

Time (hr)	τ(g cat hr/ g alcohol)	(x_b/x_c)	x_c (%)
2	5.17	4.24	5.66
	7.07	3.01	7.24
	9.04	3.24	6.27
	11.27	3.48	7.24
10	5.11	1.6	3.89
	7.88	1.65	5.26
	8.96	2.48	5.11
	13.50	1.87	7.47
110	4.89	0.516	3.93
	7.09	0.711	4.68
	9.27	0.730	6.42
	13.16	0.735	6.92

[a] x_c = conversion to aldehyde; x_b = conversion to styrene. Aging performed at 300°C at a contact time of 10(g cat hr/g alcohol).

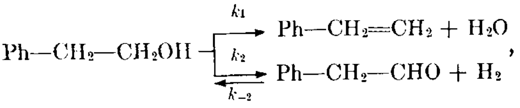
INFLUENCE OF INTERNAL DIFFUSION

It has been verified that the diffusion process of reactant inside the catalysts did not affect the rate of the overall process. For a mean catalyst particle, we obtained the following data: internal porosity, $\theta \simeq 0.8$; pore radii: catalyst A = 3.7×10^{-6} cm; catalyst B = 1.6×10^{-5} cm; mean particle diameter = 10^{-3} cm, determined by optical microscopy.

The value of the diffusion coefficient of alcohol in nitrogen was D = 1.2 cm^2/sec at 360°C. By taking a tortuosity factor equal to 2 and simulating the kinetic data with a first order law, a value of Thiele modulus equal to 10^{-2} was obtained at the highest temperature. This very small value, essentially due to the very small sizes of particles, ensures a negligible influence of internal diffusion even if some of the assumptions employed in the calculations (e.g., the value of the tortuosity factor and the assumption of a first order rate law) are questionable.

HYPOTHESES FOR REACTION MECHANISMS AND KINETIC ANALYSIS

The following scheme of two parallel reactions is operative for the system under examination:



$$\mathrm{Ph{-}CH_2{-}CH_2OH}\begin{cases}\xrightarrow{k_1}\mathrm{Ph{-}CH_2{=}CH_2 + H_2O}\\ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\mathrm{Ph{-}CH_2{-}CHO + H_2}\end{cases},$$

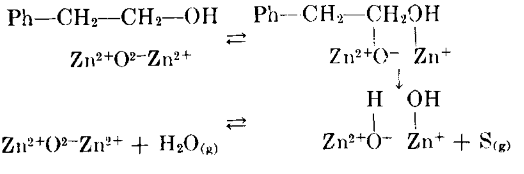
where Ph is the phenyl group.

In the following discussion we shall use Ac for alcohol, S for styrene and Ad for aldehyde. For the dehydrogenation, the reverse reaction must also be taken into account. Since experimental data were not available, the equilibrium constants at different temperatures were determined by an analysis of conversion at high contact time when the dehydrogenation reaction is at equilibrium. The obtained equilibrium constants fit the following expression of standard reaction free energy change:

$$\Delta C^0 = 32.0 - (3.9 \times 10^{-2})T \quad \text{kcal/mole.}$$

In order to avoid any influence of catalyst deactivation on kinetic analysis, the kinetic runs were performed for a time not longer than 4 hr and some measurements were duplicated. After every run it was always verified that the aging of the catalyst was negligible and did not affect the kinetic results.

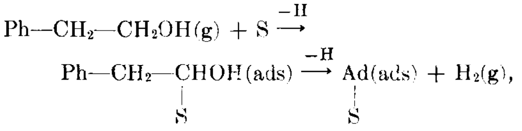
The dehydration reaction can be described through a heterolytic breaking of a C–OH bond on ZnO center pairs that act as acid–base systems:



$$\underset{\mathrm{Zn^{2+}O^{2-}Zn^{2+}}}{\mathrm{Ph{-}CH_2{-}CH_2{-}OH}} \rightleftharpoons \underset{\mathrm{Zn^{2+}O^{-}\ Zn^{+}}}{\mathrm{Ph{-}CH_2{-}CH_2OH}} \downarrow \underset{\mathrm{Zn^{2+}O^{-}\ Zn^{+}}}{\mathrm{H\ \ OH}} + \mathrm{S_{(g)}} \rightleftharpoons \mathrm{Zn^{2+}O^{2-}Zn^{2+}} + \mathrm{H_2O_{(g)}}$$

In the given description the chemisorption of the alcohol involves the participation of surface coordinatively unsaturated ions and the driving force of the process is the resulting reduction of charge separation between the anion and cation of the active site.

As to the mechanism of the dehydrogenation reaction, it can be described as follows:



$$\mathrm{Ph{-}CH_2{-}CH_2OH(g)} + \mathrm{S} \xrightarrow{-\mathrm{H}} \underset{\mathrm{S}}{\mathrm{Ph{-}CH_2{-}CHOH(ads)}} \xrightarrow{-\mathrm{H}} \underset{\mathrm{S}}{\mathrm{Ad(ads)}} + \mathrm{H_2(g)},$$

where S = surface.

The first stage of the reaction implies the breaking of a C–H bond. This process may take place heterolytically or homolytically. In the former case the participation of ZnO pair sites that act as acid–base systems is still involved, while the latter case prevails when the electronic redox properties of the catalyst play an important role in the dehydrogenation reaction.

In order to describe the kinetics of the reaction, two models have been taken into consideration for the dehydration reaction. Both were obtained by applying the Langmuir–Hinshelwood surface rate limiting scheme assuming that on adsorption the reacting molecule interacts with a single site or a double site, respectively.

From a physical point of view in the first model, the assumption is included that the acidic and basic centers are located at the surface of the catalyst in such a way that each center does not "communicate" with more than one center of the other type (*8*). In other words, each center is constituted by an acid–base system that behaves as a single center, on which the reaction of the alcohol takes place. Such centers may consist of zinc ions in the trigonal holes in a close packed layer of oxide ions as already suggested for the interpretation of chemisorption of hydrogen and water on ZnO (*9*).

In the second model, each acid and basic site behaves as a single site. A straightforward treatment leads to the following rate equations:

$$r_1 = \frac{k_1(b_{1,\mathrm{Ac}}P_{\mathrm{Ac}})^n}{1 + (b_{1,\mathrm{Ac}}P_{\mathrm{Ac}})^n + b_{\mathrm{H_2O}}P_{\mathrm{H_2O}}},$$

with $n = 1$ for a single site and $n = 0.5$ for the second model

$$r_2 = \frac{k_2 b_{2,\mathrm{Ac}}P_{\mathrm{Ac}} - k_{-2}b_{\mathrm{Ad}}P_{\mathrm{Ad}}P_{\mathrm{H_2}}}{1 + b_{2,\mathrm{Ac}}P_{\mathrm{Ac}} + b_{\mathrm{Ad}}P_{\mathrm{Ad}}},$$

where k_i are the kinetic constants and b_i the adsorption equilibrium constants.

Due to the acid-base character of the ZnO surface, more importance has been attributed to the adsorption of polar species in order to take into account the influence of the adsorption of different species on reaction rates. Since it is reasonable to assume the existence of a strong chemisorption of reactants, according to Balandin (*10*), it is possible to neglect unity in the denominator of the preceding equations. This gives:

$$r_1 = k_1 \frac{P_{\mathrm{Ac}}{}^n}{P_{\mathrm{Ac}}{}^n + Z_{\mathrm{H_2O}} P_{\mathrm{H_2O}}}$$

$$r_2 = k_2 \frac{P_{\mathrm{Ac}} - P_{\mathrm{Ad}} P_{\mathrm{H_2}} / K_{\mathrm{eq}}}{P_{\mathrm{Ac}} + Z_{\mathrm{Ad}} P_{\mathrm{Ad}}},$$

where $Z_i = b_i/b_{\mathrm{Ac}}{}^n$ is the relative adsorption coefficient of species i with respect to Ac. It is advisable to express the partial pressure of different species as follows:

$$\frac{dx_s}{d\tau} = k_1 \frac{(1 - x_s - x_{\mathrm{Ad}})^n}{(1 - x_s - x_{\mathrm{Ad}})^n + Z_{\mathrm{H_2O}} x_{\mathrm{H_2O}} P^{1-n} (1 + a + x_s + x_{\mathrm{Ad}})^{n-1}}$$

$$\frac{dx_{\mathrm{Ad}}}{d\tau} = k_2 \frac{(1 - x_s - x_{\mathrm{Ad}}) - x_{\mathrm{Ad}}{}^2 P / K_{\mathrm{eq}} (1 + a + x_s + x_{\mathrm{Ad}})}{(1 - x_s - x_{\mathrm{Ad}}) + Z_{\mathrm{Ad}} x_{\mathrm{Ad}}},$$

where x_i is the molar fraction of different compound referred to organic substances ($x_{\mathrm{Ac}} + x_s + x_{\mathrm{Ad}} = 1$); a is the (nitrogen/alcohol) ratio in the feed; and $Z_{\mathrm{H_2O}} = b_{\mathrm{H_2O}}/b_{\mathrm{Ac}}{}^n$.

The comparison of the two models has been performed through a non-linear regression analysis by minimizing the following objective function:

$$\Phi(k_1, k_2, Z_{\mathrm{H_2O}}, z_{\mathrm{Ad}}) = \sum_i \left(\left| \frac{x_{c,i} - x_{e,i}}{x_{e,i}} \right| + \left| \frac{x_{c,i} - x_{e,i}}{x_{c,i}} \right| \right),$$

where the sum is overall the experimental data and $x_{c,i}$ are the calculated values of conversion, and $x_{e,i}$ the experimental ones.

The $x_{c,i}$ were evaluated by numerical integration of equations (*1, 2*). Such calculations gave percentage errors for a set of 35 runs distributed over a temperature range between 300 and 360°C and an alcohol partial pressure range between 10 and 150 mm Hg as follows: for $n = 1$, errors of 7 and 5% for catalysts A and B, respectively; and for $n = 0.5$, errors of 10 and 5% for A and B, respectively.

The obtained final values of the parameters are shown in Table 4 for $n = 1$.

In Fig. 2a–d, some comparisons between calculated and experimental conversions of alcohol versus time are illustrated for the model with $n = 1$.

Arrhenius plots for the rate constants, $k = A \exp(-E^{\ddagger}/RT)$, are given in Figs. 3 and 4. The kinetic parameters for the two reactions are summarized in Table 5.

Finally, in Figs. 5 and 6, the plots of the logarithms of the relative adsorption coefficients versus reciprocal temperature are reported.

DISCUSSION

The small difference between the errors of the two models actually hinders the possibility of making a selection between them. This fact seems to confirm the well-known difficulty of distinguishing a reaction mechanism only on the basis of kinetic data.

In any case, the difficulty does not affect

TABLE 4

REACTION RATE CONSTANTS AND RELATIVE ADSORPTION COEFFICIENTS

Temp (°C)	$k_1 10^3$(moles/m² hr)		$k_2 10^3$(moles/m² hr)		$Z_{\mathrm{H_2O}}$		Z_{Ad}	
Catalyst	A	B	A	B	A	B	A	B
300	7.9	4.6	2.6	1.8	13.5	0.21	19	5.0
320	10.6	9.2	4.5	3.7	3.8	0.54	16	4.0
340	15.3	29	8.5	9.2	1.0	1.17	9.6	2.7
360	21.1	91	14.5	23	0.27	2.66	8.7	2.24

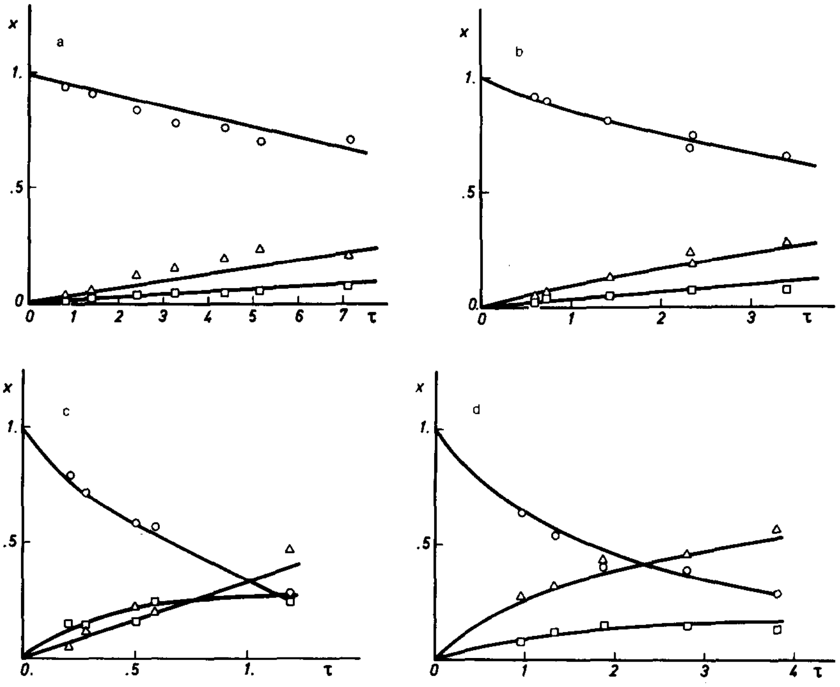


FIG. 2. Molar fraction composition of products versus contact time τ = g catalyst hr/g alcohol. (○) Alcohol, (△) styrene, (□) aldehyde. (a) catalyst B, T = 300°C; (b) catalyst B, T = 320°C; (c) catalyst A, T = 340°C; (d) catalyst A, T = 320°C.

the following discussion essentially based on the behavior of the two catalysts and their relative reactivities.

Besides, our work has shown that the two parallel reactions take place on different active sites. The slow selective nonthermal aging of the dehydrating active sites could be attributed to a local formation of styrene polymers or to an irreversible chemisorption of water that could give rise to an irreversible modification of the dehydrating active sites.

In the dehydrogenation reaction, the activation energies for catalysts A and B do not differ greatly. Another important point arising from a comparison of the rates referred to unit surface of catalyst A is that catalyst A appears to be slightly more active in dehydrogenation than catalyst B. Actually, A is oxygen deficient with respect to B, and this fact suggests the presence of

TABLE 5

ACTIVATION ENERGIES (kcal mole^{-1})

Catalyst	Dehydration $E_1^‡$	Dehydrogenation $E_2^‡$
A	12.35	20.60
B	35.60	27.40

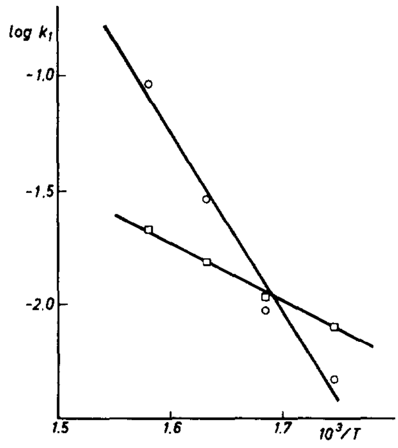


FIG. 3. Arrhenius plot of kinetic constant k_1. (□) Catalyst A; (○) catalyst B.

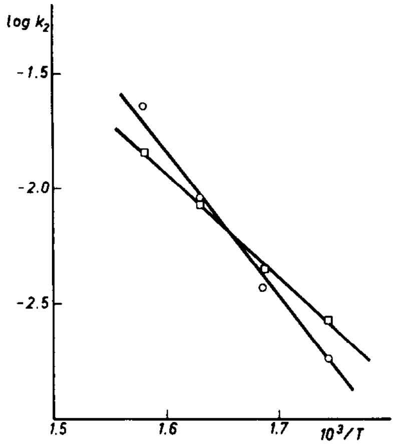


FIG. 4. Arrhenius plot of kinetic constant k_2. (□) Catalyst A; (○) catalyst B.

interstitial reduced zinc according to the reaction (*11*):

$$Zn^{2+}O^{2-} \rightleftarrows (\tfrac{1}{2})n\, O_{2(g)} + (Zn_{1-n}{}^{2+} n\, Zn_i{}^{+})(O_{1-n}{}^{2-}) \rightleftarrows (\tfrac{1}{2})n\, O_{2(g)} + ne^- + (Zn_{1-n}{}^{2+} n\, Zn_i{}^{+})(O_{1-n}{}^{2+}).$$

It follows that the presence of interstitial reduced or metallic zinc could favor the occurrence of dehydrogenation reaction through a homolytic breaking of the C–H bond. This fact seems to confirm the intervention in dehydrogenation of a mechanism in which the C–H hydrogen forms a hydride-like bond with a surface ion or metal atom. In other words, the dehydrogenation reaction is favored by the quasi-metallic properties of the catalyst (*12*).

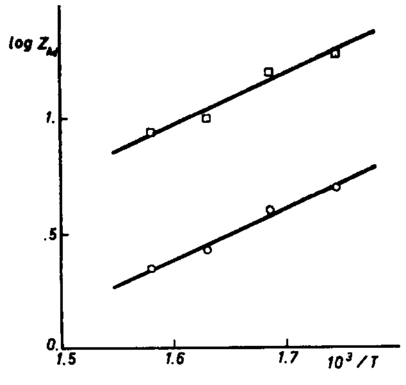


FIG. 5. Logarithm of relative adsorption constant Z_{Ad} versus $10^3/T$. □, catalyst A; ○, catalyst B.

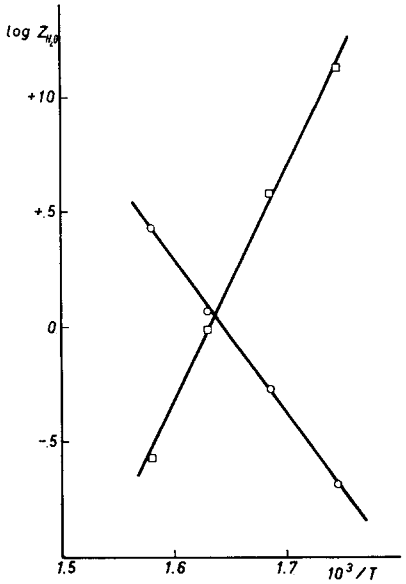


FIG. 6. Logarithm of relative adsorption constant Z_{H_2O} versus $10^3/T$. □, catalyst A; ○, catalyst B.

The relative adsorption coefficients are related to the chemisorption heats Q of Ad and Ac by means of the following relation:

$$Z_{Ad} = \frac{b_{Ad}}{b_{Ac}} = \frac{b_{Ad}{}^0 \epsilon^{Q_{Ad}/RT}}{b_{Ac}{}^0 \epsilon^{Q_{Ac}/RT}} = \frac{b_{Ad}{}^0}{b_{Ac}{}^0}\, e^{(Q_{Ad}-Q_{Ac})/RT}.$$

The slope of the plots in Fig. 5 represents the difference between the adsorption heats of alcohol and aldehyde. As the two lines are parallel, the difference is the same on the two catalysts, while the difference in pre-exponential factors indicates a different freedom of adsorbed species on the two catalysts.

In the dehydration reaction a significant difference both in activation energies and relative adsorption coefficients has been found in the two catalysts. Particularly, the dependence on temperature of Z_{H_2O} has different slopes on the two catalysts.

In this case we have:

$$Z_{H_2O} = \frac{b_{H_2O}}{b_{Ac}{}^n} = \frac{b_{H_2O}{}^0}{b_{Ac}{}^{on}}\, e^{(Q_{H_2O}-Q_{Ac}{}^n)/RT}.$$

On the basis of the behavior of the lines in Fig. 6 and of the value given in Table 5 the following scheme can be derived:

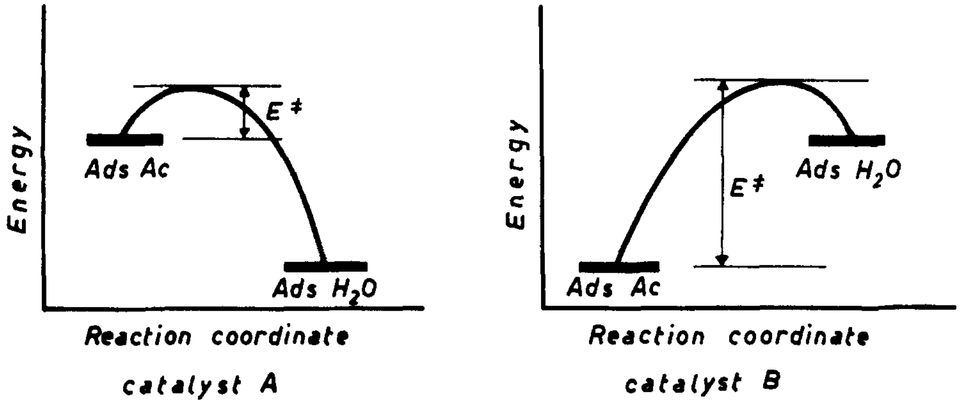


FIG. 7. Reaction paths for dehydration reaction with catalyst A and B, respectively.

Catalyst	$Q_{H_2O} - Q_{Ac}{}^{\circ}$	$E_i^\ddagger$
A	>0	Low
B	<0	High

In catalyst A, the heat of chemisorption of water is higher than the heat of chemisorption of alcohol and the contrary for catalyst B.

Such a finding suggests the surface reaction path given in Fig. 7. The behavior of the curves justifies the experimental relative values of activation energies for the two catalysts. In fact, as pointed out by Hammond (*13*), in high exothermic steps it will be expected that the transition states will resemble reactants closely, while in endothermic steps the products will provide the best models for the transition states.

From the previous discussion, it appears that the different activities of the two catalysts for the dehydration reaction can be attributed to surface heterogeneity as far as it affects the relative values of the chemisorption heats of alcohol and water.

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