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Kinetics of Dehydrogenation of Isopropyl Alcohol Over a Zinc Oxide Catalyst

II. Prediction of Reaction Rates

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Measurements have been made of the adsorption function and dehydrogenation rates of isopropyl alcohol on two specially selected samples of zinc oxide having widely differing morphological properties.

The measurements were carried out to test a previously proposed hypothesis that surface heterogeneity of catalyst surfaces (due to the existence of several crystal faces) should be explicitly taken into account, and that this heterogeneity may constitute a major cause for seemingly abnormal behavior of catalysts.

Adsorption entropy and enthalpies, as well as entropy of activation and activation energies have previously been determined for a zinc oxide catalyst made from zinc carbonate. These results were used in conjunction with the morphological factors of the two new samples to predict the adsorptive and catalytic properties of these samples, with satisfactory results, thus affirming the proposition.

A beginning identification of the properties of the individual crystal faces is obtained as a corollary.

NOMENCLATURE

a_i	Adsorption equilibrium constant for isopropyl alcohol over active center C_i
C_i	Active center type i
E_i	Activation energy over C_i
ΔH_i	Adsorption enthalpy over C_i
k_i	Rate constant over C_i
k_{i0}	Pre-exponential factor of rate constant over C_i
p_A	Partial pressure of isopropyl alcohol
r	Rate
R	Gas constant
s	Standard deviation estimate
ΔS	Adsorption entropy on catalyst (does not depend upon a particular set of sites)
ΔS_i	Adsorption entropy over C_i
$\Delta S^{\neq}$	Entropy of activation (does not depend upon a particular set of sites)
T	Absolute temperature
W	Adsorbed quantity
W_{0i}	Adsorbed quantity at saturation over C_i
κ	Natural logarithm of the pre-exponential factor for the rate constant
κ_i	Natural logarithm of the pre-exponential factor for the rate constant over C_i

INTRODUCTION

In a series of previously published articles the author has investigated the effect of explicitly introducing the notion that the various crystal faces necessarily present on a catalyst surface may, and probably do, exhibit different adsorptive and catalytic properties (*1–5*). The larger part of the work has been devoted to a study of the isopropyl alcohol/zinc oxide system (*2–4*). It was shown that a good mathematical description of the adsorption func-

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tion of isopropyl alcohol on zinc oxide was obtained when the analysis was based on a model assuming Langmuir adsorption on a heterogeneous surface (*2*, *3*). Likewise, it was shown that the adsorption parameters thus determined (entropies and enthalpies of adsorption) were fully consistent with measured dehydrogenation rates of isopropyl alcohol on the same catalyst (*4*). The rate measurements led to estimates for activation energies and frequency factors (essentially equivalent to entropies of activation).

So far, the measurements referred to above have been carried out on zinc oxide from only one source of preparation. According to the model used for interpreting the experimental results one may, however, expect that the fundamental physical parameters, i.e., entropies of adsorption, enthalpies of adsorption, entropies of activation, and activation energies should be the same for other types of zinc oxide, provided they are of comparable purity and are comparably aged. In that case only the relative importance of the various crystal faces should differ, and possible differences in adsorptive and catalytic properties between samples of zinc oxide from different sources should be explainable on that basis alone. Consequently, using the data already published it should be possible to obtain a good description of the adsorption function of a different sample of zinc oxide by only allowing the W_{0i} in Eq. (1) to vary.

$$W = \sum_{i=1}^{N} \frac{W_{0i}a_i p_A}{1 + a_i p_A} \qquad (1)$$

When the W_{0i} have been determined it should be possible to predict quantitatively the kinetics of isopropyl alcohol dehydrogenation (i.e., the reaction rate at any temperature or isopropyl alcohol partial pressure) without recourse to any further experimental information.

The purpose of the work reported here is to investigate to what extent the model referred to above survives such a test. Specimens of zinc oxide, having a satisfactory purity (the influence of impurities is so far not known) and a clearly differing morphology are not easily available, but the author has obtained two such samples from the New Jersey Zinc Co.

EXPERIMENTAL METHODS

Apparatus. The apparatus was essentially the same as that previously described (*2*, *4*). Some rate measurements reported below were carried out on zinc oxide made from zinc carbonate, i.e., the sample previously investigated (*2*, *4*). These measurements were made to extend the range of experimental conditions beyond that previously reported. They were carried out in an apparatus basically similar to the one previously described, although different in detail. Because of the ancillary nature of these measurements a detailed description is hardly warranted.

Materials. The catalysts (A and B) were obtained from the New Jersey Zinc Co. They were not aged prior to the experiments. According to the manufacturer they had been prepared by the French process (air oxidation of metallic zinc vapor). The main impurities of A and B were found by emission spectrography to be essentially the same: SiO_2, 0.01–0.05%; Fe_2O_3, 0.005%; CuO, MgO, and PbO less than 0.001%. SiO_2 was thus by far the most important impurity.

Sample A was found by electron microscopy and scanning electron microscopy to contain a large proportion of needle-like and sheet-like crystals, typically forming fourlings. The morphology of zinc oxide of this type has been investigated in detail by Cowley, Rees and Spink (*6*). A typical (although idealized) crystal of zinc oxide of this type is shown in Fig. 1. Cowley, Rees and Spink showed that the crystal planes are of the $(10\bar{1}0)$ type, sheets and spines being related by twinning on $(1\ 1\ \bar{2}\ 2)$ planes (*6*). The specific surface area was found to be 5.3 m²/g by the BET method.

Sample B is a nodular type with no special plane predominating. Surface area 5.3 m²/g.

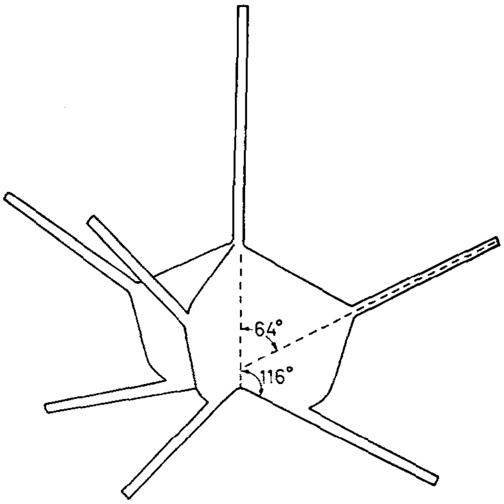

FIG. 1. Idealized "typical" crystal of zinc oxide sample A, showing three sheets and seven spines, related by (1 1 $\bar{2}$ 2) twinning. Reproduced after drawing by Cowley, Rees and Spink (*6*), by permission, and with acknowledgment to the Institute of Physics. Electron microscopy and scanning electron microscopy showed the zinc oxide crystals from sample A to be similar to this drawing.

Isopropyl alcohol and carrier gas were as previously described (*4*).

Procedure. This was essentially as previously described, but the desorption curves can now be followed to higher temperatures where a considerable conversion of isopropyl alcohol to acetone and/or propylene may take place; see Appendix for a discussion.

RESULTS AND DISCUSSION

a. Refinements of Earlier Results

Before the main task can be tackled we shall need to discuss in some detail the previously published results.

By fitting an equation derived from Eq. (1) to data obtained from temperature programmed desorption experiments it was found that physically reasonable values were obtained for W_{0i}, ΔS_i and ΔH_i when five different sets of adsorbing sets were assumed, i.e., $N = 5$. The fitted equation was rather close to the experimental results. The computations were carried out so that W_{0i}, ΔS_i, and ΔH_i could take any value, but it was stressed that one should expect the adsorption entropies to be rather similar, and it was taken as indicating soundness of the approach that the ΔS_i estimates did turn out to be rather similar. When discussing the estimates for ΔS_i and ΔH_i which had been obtained, it was pointed out that the individual ΔS_i and ΔH_i would have rather wide confidence intervals, because the effect of varying ΔS_i can be largely compensated by varying the corresponding ΔH_i and *vice versa* (*3*).

Because the goal of the work reported here is to predict desorption curves for zinc oxide samples having a morphology different from the previously investigated type without allowing other parameters than W_{0i} (the morphology dependent parameters) of Eq. (1) to vary, it is important that the estimates for ΔS_i and ΔH_i should be as correct as possible. The next goal then is to predict without any adjustable parameters the dehydrogenation rate of isopropyl alcohol on the new zinc oxide samples. The correctness of this prediction will also depend upon good estimates for ΔS_i and ΔH_i.

The main contribution to the adsorption entropy is the loss of translational entropy (which is 38.1 cal mole^{-1} K^{-1} at 25°C and 1 atm). This contribution is independent of the properties of the site. The loss of rotational and vibrational degrees of freedom may not be strictly equal on all sites, but on account of the overwhelming importance of the translational contribution it seems fair to assume that the ΔS_i may well be within ± 1 cal mole^{-1} K^{-1}. If so, the differences between the various ΔS_i are much smaller than the uncertainties of the estimates, and they may thus all be put equal. The general subject of entropies of adsorption has been discussed by Kemball (*7*).

The computations necessary to obtain estimates for ΔS and ΔH_i under the assumption outlined above were carried out. The main reason for repeating the parameter evaluations with a constant adsorption entropy ΔS on all sites was that, because of the strong coupling between the estimates for adsorption entropy and adsorption enthalpy, considerably more precise enthalpy estimates are likely to be obtained. They are then a more trustworthy basis for extrapolations. A further, general, advantage of such a parameter reduction (in the present case from 15 to 11), is that because of this parameter reduction the strong couplings between corresponding pairs of ΔS_i and ΔH_i are removed (because all $\Delta S_i = \Delta S$), thereby cutting computation time drastically.

In the theoretical treatment given previously, the high temperature portion of the desorption curve (where a considerable conversion to products may take place) was not satisfactorily treated (*3*). Actually, this portion of the desorption curve really presents no difficulty. A complete treatment is given in the Appendix.

The parameters for the adsorption function of isopropyl alcohol on zinc oxide (made from zinc carbonate) which result after incorporation of the improvements mentioned above are given in Table 1. These values are considered more reliable than the values given previously (*3*).

In the preceding article (*4*), where measured dehydrogenation rates were tested for consistency with the adsorption function, and where activation energies and frequency factors (entropies of activation) were determined, it was pointed out that the measurements should ideally have been carried to a higher reactant pressure than had been possible, and that such an increase would improve the precision of the estimates. Furthermore, it was pointed out that the frequency factors on different sets of sites should probably be essentially equal. The fact that the computations did give similar values was considered an asset for the treatment, but no restriction was imposed on the frequency factors. In the present situation where a more severe test on the model is envisaged, it was found highly desirable to extend the range of isopropyl alcohol pressures used during the rate measurements, and repeat the parameter evaluation for this wider range, while also imposing the restriction that all activation entropies are made equal. This means only that it is believed that differences between activation entropies are smaller than the experimental uncertainty. Much space could be devoted to the discussion of this point, but the author considers it more useful to use this simplified model without further discussion until experimental results of such a high precision that the model can be shown untenable are eventually obtained.

TABLE 1

ADSORPTION PARAMETERS CORRESPONDING TO PARAMETERS GIVEN IN TABLE 1 [REF. (*3*)] WHEN IMPOSING THE RESTRICTION THAT ALL ΔS_i ARE EQUAL

	W_{0i} (mg/g catalyst)	ΔS (cal/mole degree) (pressure unit Torr)	ΔH_i (cal/mole)
1	5.136	−48.0	−15 480
2	1.869	−48.0	−17 900
3	1.111	−48.0	−19 520
4	0.6445	−48.0	−21 300
5	2.500	−48.0	−23 500

The additional experimental dehydrogenation rates beyond those previously published (*4*) are given in Table 2. The total isopropyl alcohol pressure range then extends from 0.03 to 700 Torr.

In the preceding paper (*4*) it was found that the dehydrogenation reaction of isopropyl alcohol was well described by the following equation

$$r = \sum_{i=1}^{5} \frac{W_{0i} k_i a_i p_A}{(1 + a_i p_A)^n}, \qquad (2)$$

but no unequivocal choice of the value to be assigned to n (number of sites taking part in the rate determining step) could be made. It could be 2, 3, or 4, although $n = 3$ gave the best fit. The extended range of isopropyl alcohol pressures now available, in conjunction with the imposed restrictions $\Delta S_i = \Delta S$ and $\kappa_i = \kappa$ (i.e., $\Delta S_i\ddagger = \Delta S\ddagger$), lead to a satisfactory fit only for $n = 3$.

The resulting estimates for the parameters which were to be obtained from rate measurements (frequency factor and activation energies over each set of sites) are given in Table 3. The value of the pre-

TABLE 2

Dehydrogenation Rates at Isopropyl Alcohol Pressures Beyond Previously Reported Values (*4*)

Isopropyl alcohol pressure (Torr)	Reaction rate (nmole/sec m²)	Temp (°C)
227.9	0.1369	158
42.48	0.2032	158
84.53	0.1549	158
479.8	0.1021	158
238.1	0.1193	158
713.4	0.0833	158
269.2	0.8128	178
588.8	0.7990	178

exponential factor which was obtained, $k_0 = 1.77 \times 10^{16}$ mole sec^{-1} m^{-2} = 0.55×10^{14} molecules site^{-1} sec^{-1}, is equivalent to an entropy of activation $\Delta S\ddagger \approx 1.5$ cal mole^{-1} degree^{-1}. For a dissociation reaction with a fairly "loose" entropy of activation such a small positive entropy of activation is just the result to be expected (*8*).

The concordance between measured rates and calculated rates [using Eq. (2) and the parameters given in Tables 1 and 3] is borne out by Fig. 2.

TABLE 3

Estimates for Pre-exponential Factor (Natural Logarithm) and Activation Energies of Eq. (2) with $n = 3$[a]

i	κ[b]	E_i (cal/mole)
1	37.42	33 610
2	37.42	32 470
3	37.42	31 170
4	37.42	30 190
5	37.42	31 160

[a] Standard deviation estimate from this model, $s = 8.9\%$. Mean deviation between calculated and observed values, 6.8%.

[b] $\kappa = \ln k_0$, i.e., $k_0 = 1.77 \times 10^{16}$.

It may be remarked *en passant* that the restrictions put on some of the parameters and the extended range of experimental points for the dehydrogenation rate have led to considerably faster converging computations for the parameter evaluations, and better parameter estimates. The total number of parameters is also significantly reduced, particularly for the kinetic equations where a total of six parameters remain (covering three orders of magni-

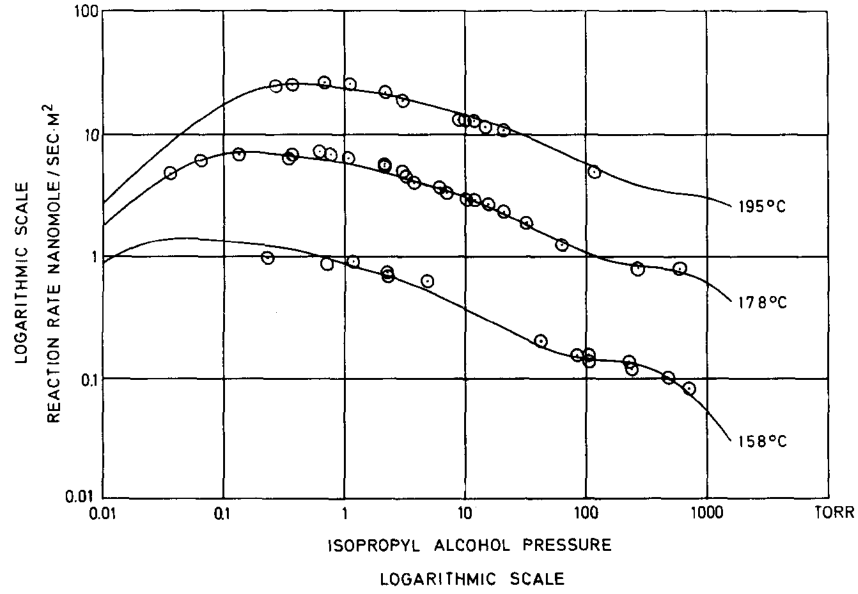

Fig. 2. Observed and calculated rates of dehydrogenation of isopropyl alcohol over zinc oxide made from zinc carbonate. The calculated rates have been obtained from Eq. (2), with $n = 3$, using the parameters given in Tables 1 and 3.

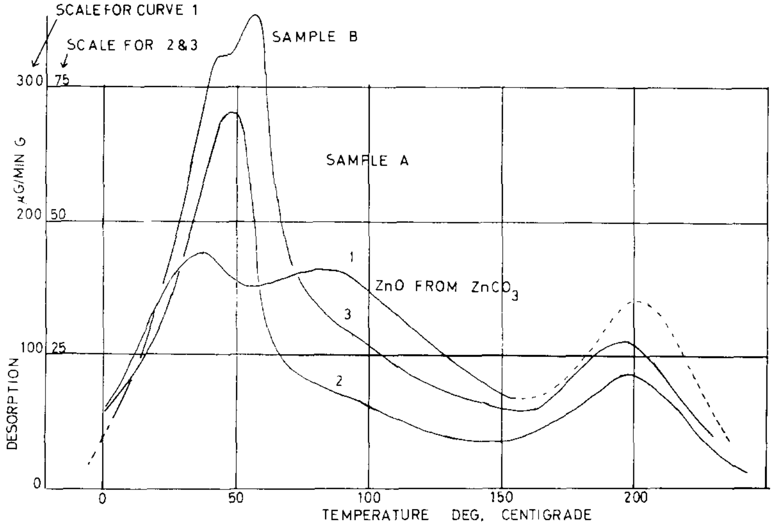

FIG. 3. Thermodesorption curves of three different samples of zinc oxide: (1) made from zinc carbonate; (2) of the acicular type, here called sample A; (3) the nodular type, here called sample B. The curves have been obtained by the previously described technique (*2*). Predesorption times and temperatures are similar for all three oxide types; $-15°C$ and 40 min. The ordinate scales have been chosen so that the visual heights of the curves are in fair accord with actual isopropyl alcohol pressures during the experiment. (But the peak isopropyl alcohol pressure over sample A was 30% higher than the peak pressure over sample B, so, as is explained in the text, the shift of the first peak towards higher temperatures when going from ZnO made from $ZnCO_3$ to sample B, and then to sample A is in accord with this increasing isopropyl alcohol pressure.)

tude of rates, and four orders of magnitude of reactant pressures).

It may also be remarked at this point that the more refined treatment given here was completed well before the additional zinc oxide samples were obtained.

b. Predictions on New Catalysts

The results obtained on the new, morphologically different zinc oxide samples are reported below.

Adsorption function. Thermodesorption curves of samples A and B were obtained by the previously described technique (*2*). The results are shown in Fig. 3 together with the previously published desorption curve for a sample of zinc oxide made from zinc carbonate. Samples A and B are also markedly different from each other. It is clear from Eq. (A1) in the Appendix that the temperature where maximum desorption from a given site takes place increases with the isopropyl alcohol pressure (the product of pressure and adsorption constant stays essentially constant), which again depends upon the precise experimental conditions. The displacements of the lowest lying peaks of the three curves are consistent with this observation.

The experimental results shown in Fig. 3 were treated according to the theory previously outlined (*3*), while allowing for the fact that the desorption experiment may be carried on to temperatures where most of the isopropyl alcohol is converted to products with no detrimental effect to the analysis, as shown in the Appendix. The adsorption entropy and the adsorption enthalpies were assigned the values obtained for zinc oxide made from zinc carbonate (Table 1).† Thus, essentially only

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† Apart from a free range of approximately 100 cal/mole for the adsorption enthalpies to take care of uncertainties of the temperature measurements (due to the dynamic conditions under which the experiments are carried out). The uncertainty of the temperature measurements were estimated to about 2°C. For a desorption peak at 300 K with an adsorption enthalpy 15 000 cal/mole an error of 2°C is easily seen to lead to an error of 100 cal/mole for the adsorption enthalpy.

TABLE 4

THE PARAMETERS OF EQ. (1) [MORE PRECISELY EQ. (A1)] FOR THE THREE DIFFERENT SAMPLES OF ZINC OXIDE INVESTIGATED HERE[a]

from $ZnCO_3$		Sample A		Sample B		
W_{0i}	%	W_{0i}	%	W_{0i}	%	ΔH_i (cal/mole)
5.136	45.6	1.272	75.1	0.956	55.2	15 600 ± 100
1.869	16.6	0.047	2.8	0.230	13.3	17 800 ± 150
1.111	9.9	0.126	7.5	0.159	9.2	19 500 ± 150
0.645	5.7	0.058	3.4	0.097	5.6	21 350 ± 50
2.500	22.2	0.190	11.2	0.291	16.8	23 500 ± 100

[a] $\Delta S = -48.0$ cal/mole degree.

the W_{0i} of Eq. (1) were allowed to vary. The estimates obtained for W_{0i} (and the mean values for the adsorption enthalpies) are given in Table 4. Desorption curves calculated from Eq. (A1) of the Appendix using the parameters of Table 4 and the adsorption entropy of Table 1 are shown in Fig. 4A and 4B.

It is a pleasing fact that the desorption curves and the W_{0i} estimates derived from

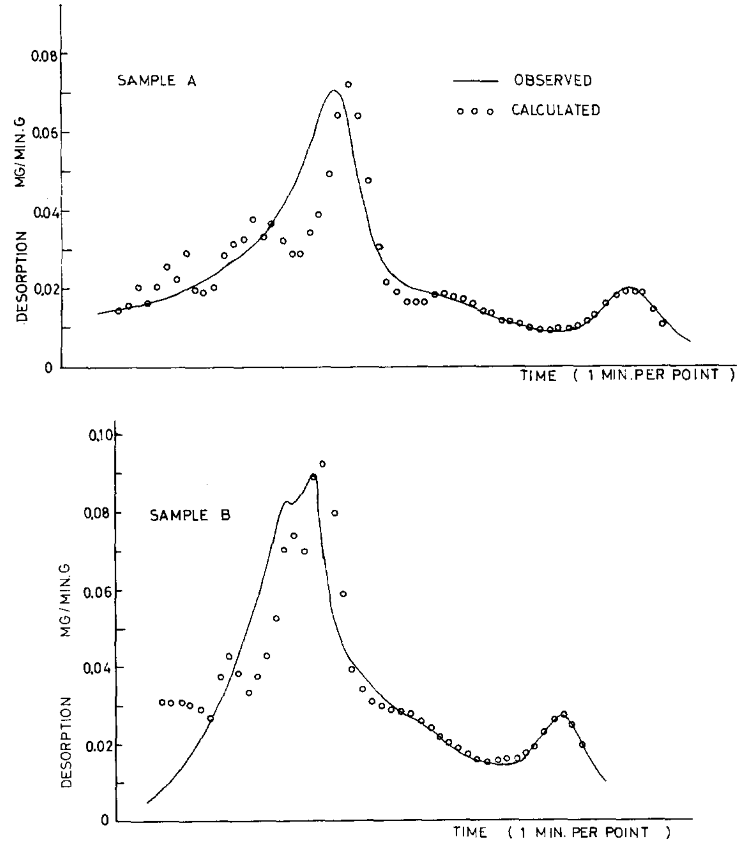

FIG. 4A and B. Comparison between observed and calculated thermodesorption curves of zinc oxide, samples A and B. The calculated points were obtained using Eq. (A1) of the Appendix. The discrepancy between observed and calculated desorption curve around the highest peak is discussed in the text.

them are fully consistent with the visual morphological result of Fig. 1. The zinc oxide of the acicular type, sample A, exhibits an essentially homogeneous surface. Sample B, which is of a nodular type, also appears from the desorption measurements to have a far less homogeneous surface. In spite of the pronounced difference between the three desorption curves the fundamental physical parameters, i.e., adsorption entropy and enthalpies, are the same.

It has earlier been stated that the experimental results obtained for thermodesorption of isopropyl alcohol from zinc oxide made from zinc carbonate did not allow definite conclusions regarding the adequacy of an adsorption model assuming Langmuir adsorption on a heterogeneous surface, although it was pointed out that in principle the neglect of any interaction between adsorbate molecules necessarily is an approximation (3). Figure 4A and B suggests that the model can hardly be fully adequate. Additional, so far unpublished, experiments strongly indicate that the model is somewhat oversimplified. Apparently the introduction of a fairly weak attraction between adsorbed molecules should be introduced (*9*); this is in accord with theoretical and experimental results for other systems (*10, 11*). Introducing these refinements here would only obscure the main points and no results or conclusions would be essentially changed, so the whole analysis in this paper is based on an unmodified Langmuir adsorption model for heterogeneous surfaces.**

Kinetic equation. According to the point of view developed here, all the physical quantities needed to predict the reaction rate of isopropyl alcohol dehydrogenation at any temperature or isopropyl alcohol pressure on any of the two catalysts A or B are now available. The rate is given by Eq. (3), which is obtained from Eq. (2) by putting $n = 3$, in accordance with the results mentioned above.

$$r = \sum_{i=1}^{r} \frac{W_{0i}k_i a_i p_A}{(1 + a_i p_A)^3} \tag{3}$$

with

$$k_i = \exp(\kappa - E_i/RT) = k_0 \exp(-E_i/RT),$$
$$a_i = \exp(\Delta S/R - \Delta H_i/RT),$$

κ, E_i, ΔS, and ΔH_i are assigned the values determined for zinc oxide made from zinc carbonate. They are given in Tables 1 and 3.

Reaction rates over the two catalysts A and B have been predicted according to Eq. (3) and compared with the observed values at various isopropyl alcohol pressures. It was not considered of interest to cover any wide range of temperatures, because the mere fact that the rate level is of the correct order of magnitude indicates that the activation energy is essentially correct. [Rate measurements which were carried out at other temperatures (not shown) agree with this conclusion.] The results are shown in Fig. 5A and B. The predicted reaction rates are evidently not in full quantitative agreement with the observed values: the predicted values should have been about twice as high for sample A (the sample exhibiting a large portion of planes of the $(1\,0\,\bar{1}\,0)$ type), and the predicted values for sample B should have been about 20% lower, provided there are no systematic errors in the rate measurements. Taking into account that part of the difference may be due to experimental inaccuracy, and that the model upon which the predictions are based is rather simple (the only refinement beyond the simplest possible adsorption isotherm being that the existence of more than one crystal face is explicitly taken into account) the author considers the agreement satisfactory. It should also be

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** The discrepancy referred to above does not result because the adsorption enthalpies are not the best possible. This has been shown by extended computations. As was pointed out previously (*3*), the computed results are obtained by subtracting fairly large numbers so that small errors in each of the terms may give rise to substantial errors in the result. The fact that the analysis is really carried out for the derivative of the adsorption function also makes the analysis show any lack of agreement rather exaggeratedly.

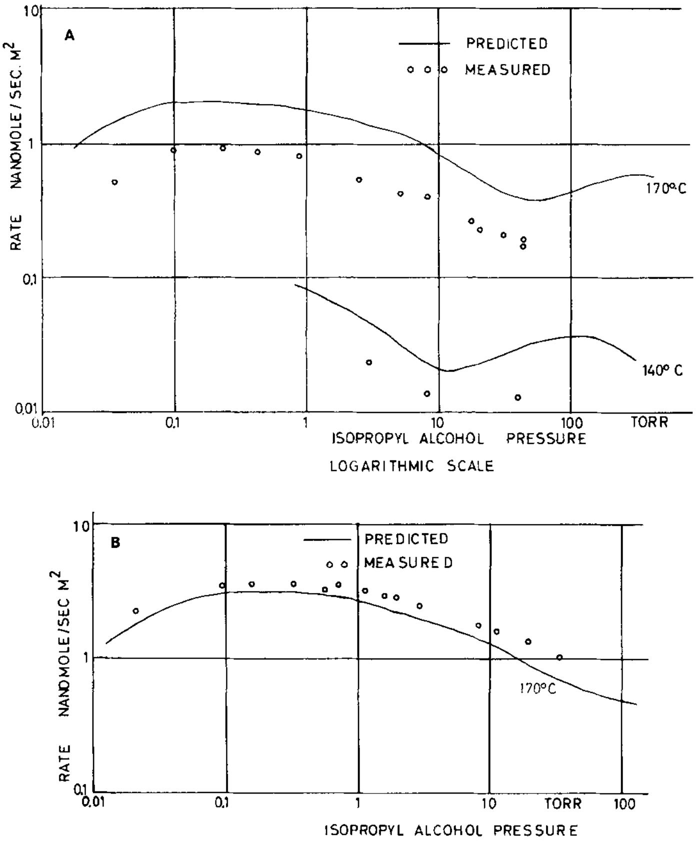

FIG. 5A and B. Predicted and observed dehydrogenation rates of isopropyl alcohol over zinc oxide, samples A and B. Predictions were based on adsorption entropy, adsorption enthalpies, activation entropy and activation energies determined on another type of zinc oxide, viz., one made by heating zinc carbonate to 350°C in air, and were calculated using Eq. (2).

borne in mind that possible errors associated with W_{0i} may be of importance. This uncertainty will especially be important for the smaller W_{0i}, where the percentage error may be rather large.

It would have been of interest to carry the rate measurements to higher pressures than have been done here (as was done for the measurements on zinc oxide from zinc carbonate). At the time the measurements on samples A and B were made, however, the necessary apparatus no longer existed. Furthermore, because of the much smaller specific surface area of these samples and the small amounts of catalyst available it was unlikely that sufficiently precise measurements to be of any value could be obtained. No attempt was therefore made to obtain measurements in that range. Even if the predicted rates are not in full concordance with the observed rates, it should be stressed that the shapes of the rate vs isopropyl alcohol pressure curves are excellently predicted. As a matter of fact, the concordance is so good that part of it may be fortuitous.

CONCLUSION

The results reported here lend a strong support to the hypothesis that surface heterogeneity due to the presence of several crystal faces may be an important factor which should not be neglected in catalysis research. A consequence of the results reported is that a first step towards identification of the properties of the various crystal faces in the system zinc oxide/isopropyl alcohol can be made. From the investigations carried out by Cowley, Rees and Spink (*6*) it is clear that the predominant surface planes of sample A are of the $(1\ 0\ \bar{1}\ 0)$ type. The adsorption and catalytic properties of this plane can therefore be considered to be known in broad lines. Later identification of other planes will undoubtedly be possible. The basic idea behind this series of papers is that because a catalyst surface has a surface with several different crystal faces it will in many cases be necessary to take this surface heterogeneity into account, and in principle it should always be done. It should be pointed out, however, that this does not necessarily mean that a single surface plane will behave as a homogeneous surface for adsorption. Adsorbate interaction may be of some importance, but more important, preliminary experiments have shown that partially reduced (aged) zinc oxide binds isopropyl alcohol much more strongly than oxidized samples. The effect is reversible. This means that at intermediate stages of reduction a crystallographically homogeneous surface plane may behave as two different planes for adsorption (*9*).

ACKNOWLEDGMENT

The author expresses his gratitude to the New Jersey Zinc Co. for the gift of the two special samples of zinc oxide used for investigation in this article.

APPENDIX

The mathematical apparatus used for establishing the adsorption function and determining the values of the parameters involved was given in Ref. (*3*). It was, however, stated there that the high temperature ends of the thermodesorption curves were uncertain and that the contribution from the strongest binding set of sites was underestimated because it did not really give off significant quantities of isopropyl alcohol until a large portion of the alcohol reacted to products (acetone or propylene). This reaction does not really constitute a serious difficulty, however, as long as one can rest assured that the overwhelming part of the alcohol has been present on the surface as unreacted alcohol, as has been shown to be the case for ZnO. Because Eq. (7) of Ref. (*3*) was based on a general mass balance equation it can be generalized to read

$$v \cdot F \cdot (p_A + p_1 + p_2) = -\sum_{i=1}^{N} \frac{W_{0i}\exp(\Delta S/R - \Delta H_i/RT)}{(1 + p_A \exp(\Delta S/R - \Delta H_i/RT))^2} \times \left(\frac{dp_A}{dt} + p_A \frac{\Delta H_i}{RT^2}\frac{dT}{dt}\right) \quad \text{(A1)}$$

where p_A is the alcohol partial pressure, p_1 may be the acetone partial pressure and p_2 may be the propylene partial pressure, (p_1 and p_2 might as well stand for the equivalent partial pressures of hydrogen and water). The other symbols are the same as previously defined. The extension to any number of reaction products is obvious.

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