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Kinetics of Dehydrogenation of Isopropyl Alcohol over a Zinc Oxide Catalyst

Consistency with the Adsorption Function of Isopropyl Alcohol on Zinc Oxide

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The rate of dehydrogenation of isopropyl alcohol over a zinc oxide catalyst has been measured at 158–195°C, at an isopropyl alcohol pressure range of 0.03–100 torr.

The rate measurements have been tested for consistency with a previously determined adsorption function of isopropyl alcohol on zinc oxide. The adsorption function assumes Langmuir adsorption on a heterogeneous surface with five sets of adsorbing sites.

The corresponding kinetic equation could be well fitted to the experimental rates using a suitable set of rate constants and activation energies, but using the previously determined adsorption function directly. In the experimental range which covered a factor of more than 3000 in isopropyl alcohol pressure and a factor in reaction rates of 170 the mean deviation between observed and calculated rates was less than 6%. The results are therefore an indication that a previously proposed model, assuming that a heterogeneously catalyzed reaction may take place on more than one set of active centers on the catalyst, is correct.

INTRODUCTION

The two preceding papers (*1*, *2*) present a mathematical description of the adsorption function for isopropyl alcohol on a zinc oxide catalyst.

It was found that on fresh (nonaged) samples of zinc oxide made by heating zinc carbonate to 350°C in air for 24 hr the adsorption function could be described by the following equation

$$W = \sum_{i=1}^{5} \frac{W_{0i} a_i p_A}{1 + a_i p_A} \qquad (1)$$

with $a_i = \exp(\Delta S_i/R - \Delta H_i/RT)$

Equation (1) corresponds to the assumption that the adsorption is a Langmuir adsorption on a heterogeneous surface where there are five distinct sets of adsorption sites. The values of the 15 parameters of Eq. (1) have been determined (*2*). They are given in Table 1 of the preceding paper (*2*).

On the basis of a recently advanced theory that there may be more than one set of active centers on a catalyst (*3*), it was found to be of much interest to see if the adsorption function of isopropyl alcohol on zinc oxide is consistent with rate data for the dehydrogenation reaction of the alcohol on the catalyst. The system isopropyl alcohol/zinc oxide was chosen because previous work (*4*) had shown that rate measurements in this system could not be fitted to the kinetic equations of Hougen and Watson (*5*).

At this point it may be mentioned that Schrage and Burwell (*6*) have recently given evidence that isotopic exchange between cyclopentane and deuterium on palladium-on-alumina catalysts takes place on more than one set of catalytically active centers.

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 center C_i
ΔH_i	Adsorption enthalpy over center C_i
k_i	Rate constant over C_i
k_{i0}	Pre-exponential factor of rate constant over center C_i
p_A	Partial pressure of isopropyl alcohol
r	Rate
r_η	Rate at conversion η
$r_{\eta=0}$	Rate at zero conversion
R	General gas constant
s	Standard deviation estimate
ΔS_i	Adsorption entropy over center C_i
T	Absolute temperature
W	Adsorbed quantity
W_{0i}	Adsorbed quantity at saturation over center C_i
η	Conversion of isopropyl alcohol to acetone
κ_i	Natural logarithm of the pre-exponential factor for the rate constant over C_i

EXPERIMENTAL

Apparatus. A flow system of essentially the same construction as previously described was employed (*1*). The following important features were not mentioned previously: The apparatus was equipped with an additional inlet for carrier gas between the saturator and the reactor. Both branches were equipped with a needle valve and flow meter, so that the flow in each branch could be varied at will, thus allowing a wide range of isopropyl alcohol partial pressures in the reactor. The whole apparatus (from the saturator on) was heated to 70° to 80°C so that condensation of isopropyl alcohol at high partial pressures was avoided.

Materials. The catalyst was not aged ZnO (from $ZnCO_3$) previously described (*1*). Isopropyl alcohol and carrier gas were also as previously described (*1*).

Procedure. The reaction rates were found by multiplying the acetone concentrations in the effluent gas from the reactor by the flow rate through the sampling device. This flow rate was not measured directly, but was calculated from the measured carrier gas flows, correcting for effects from pressure, isopropyl alcohol concentration, and temperature. All measurements were carried out at a total pressure in the reactor between 1.0 and 1.2 kP/cm^2. The pressure drop from inside the reactor to the outside took place mainly in the sintered glass disc which supported the catalyst.

Most of the isopropyl alcohol partial pressures were measured directly in the tail gas, but at the highest partial pressures saturation effects in the detector of the gas chromatograph occurred. A relation is, however, easily established between the isopropyl alcohol partial pressure in the sampling valve, and the partial pressure in the gas leaving the saturator, or in the reactor, so the isopropyl alcohol pressures were known within a few percent in all experiments. In order to minimize possible time effects as far as possible the measurements were carried out in partly random order at each temperature.

RESULTS AND DISCUSSION

The reaction rates which have been obtained are given in Table 1 together with the isopropyl alcohol partial pressures and conversions. It is seen that the majority of the rates have been obtained at very low conversions. Separate experiments have shown that in the temperature and pressure range where these measurements have been carried out, the following relation is approximately fulfilled at conversions up to a few percent

$$\frac{r_{\eta=0}}{r_\eta} = 1 + 0.005\eta p_A \qquad (2)$$

where η is in percent and p_A in torr.

It is obvious from Eq. (2) that when it applies, all the rates given in Table 1 are essentially independent of conversion. The assumption is therefore made in the following that the measured rates represent true differential rate data (probably not strictly correct for the rates at the two highest conversions).

The adsorption function previously reported (*1*, *2*) was measured on a nonaged catalyst sample, consequently the rate measurements reported here have been obtained from nonaged catalyst samples too.

TABLE 1
ISOPROPYL ALCOHOL PARTIAL PRESSURES, CONVERSIONS, AND DEHYDROGENATION RATES

p_A (torr)	% Conversion	Rate (nanomole/sec m²)
	158°C	
105.9	0.004	0.1562
105.9	0.003	0.1381
4.824	0.037	0.6300
2.235	0.10	0.7424
1.165	0.24	0.9143
2.259	0.13	0.6890
0.706	0.52	0.8660
0.229	1.14	0.9780
	178°C	
62.94	0.072	1.249
31.77	0.089	1.907
20.71	0.11	2.355
11.88	0.20	2.934
7.012	0.35	3.331
3.765	0.59	4.047
3.035	0.64	4.996
2.153	0.88	5.709
0.346	5.0	6.328
0.134	10.2	6.864
0.065	16.4	6.138
0.036	21.1	4.822
15.53	0.15	2.704
10.18	0.15	2.952
6.118	0.15	3.685
3.229	0.30	4.555
1.076	0.27	6.466
0.771	0.40	6.892
0.624	0.67	7.292
0.371	1.05	6.860
2.153	0.19	5.412
	195°C	
2.188	0.78	22.01
3.035	0.62	18.79
20.82	0.31	10.87
1.118	1.03	25.68
0.682	1.78	26.26
0.371	3.18	25.44
0.271	4.30	24.74
8.824	0.71	13.12
9.882	0.67	13.00
11.82	0.63	12.92
14.65	0.55	11.56
117.6	0.14	4.920

The rate measurements obtained are shown in Fig. 1. From this figure it is clear that only rate expressions of the type

$$r = \frac{k_1 a_1 p_A}{(1 + a_1 p_A)^n} \qquad (3)$$

with $n \geqq 2$ can be consistent with the measurements. If the adsorption function [Eq. (1)] is to be consistent with the rate measurements reported here it must be possible to fit the following equation to the data:

$$r = \sum_{i=1}^{15} \frac{W_{0i} k_i a_i p_A}{(1 + a_i p_A)^n}$$

where

$$k_i = \exp[\kappa_i - (E_i/RT)] = k_{i0} \exp(-E_i/RT) \qquad (4)$$

and

$$a_i = \exp(\Delta S_i/R - \Delta H_i/RT)$$

where κ_i and E_i are unknown parameters and W_{0i}, ΔS_i, and ΔH_i are the previously determined adsorption parameters (*2*) given in Table 1 of the preceding paper (*2*).

Equation (4) has been fitted to the data by the standard least-squares technique, making the sum of squared percentage deviations become a minimum [see ref. (*3*)] for three values of n, viz. $n = 2$, 3, and 4. A digital computer was used to carry out the computations. Due to the fact that the adsorption constants were given (thus fixed) there was littlec oupling between the parameters and the iterative procedure necessary to find the parameter set leading to the smallest possible sum of squared residuals converged rapidly. The parameter estimates and standard deviation estimates of the rate measurements for $n = 2$, 3, and 4 are given in Table 2. Calculated and observed values are shown in Figs. 1, 2, and 3. It is seen that Eq. (4) can be fitted to the experimental points with fair accuracy with n having any of the values 2, 3, and 4. It is, however, doubtful that $n = 2$ is really consistent with the measurements. The standard deviation estimate for the experimental points is higher than the corresponding estimate when $n = 4$, although the significance is weak. It is also apparent from Fig. 1 that Eq. (4) with $n = 2$ cannot be fitted to the experimental points at the two lowest isopropyl alcohol pressures,

TABLE 2

ESTIMATED VALUES OF PRE-EXPONENTIAL FACTORS (NATURAL LOGARITHM) AND ACTIVATION ENERGIES OF EQ. (4) FOR $n = 2$, 3, AND 4, AND RATE CONSTANTS AT 178°C

	$n = 2$			$n = 3$			$n = 4$		
i	κ_i	E_i (cal/mole)	k_i^a	κ_i	E_i (cal/mole)	k_i^a	κ_i	E_i (cal/mole)	k_i^a
1	33.319	30000^b	0.854	36.180	32000^b	1.608	36.742	32000^b	2.433
2	Does not contribute			37.382	31820	6.535	36.616	30480	13.91
3	30.850	26610	3.185	29.208	24510	6.421	32.307	26760	11.48
4	33.979	28270	11.42	39.651	32260	38.68	40.977	32970	65.83
5	40.080	33780	10.90	39.006	32430	16.78	40.814	33870	21.18
	Estimated standard deviation from this model, $s = 11.0\%$			Estimated standard deviation from this model, $s = 9.06\%$			Estimated standard deviation from this model, $s = 8.85\%$		
	Mean deviation between calculated and observed values, 7.27%			Mean deviation between calculated and observed values, 6.34%			Mean deviation between calculated and observed values, 5.95%		

[a] Rate constant at 178°C.

[b] Not estimated from the least-squares procedure because the lack of experimental points at high pressure makes this impossible. The value was chosen to be similar to the other activation energies.

where the calculated rates are much smaller than the observed ones (which should perhaps be even higher at zero conversion).

The values of n, $n = 3$, or $n = 4$ in Eq. (4) are seen to lead to calculated rate curves which are fully consistent with the rate points, and it must be considered very satisfactory that $n = 4$ leads to a mean percentage deviation between observed and calculated rates of only 5.95% when it is taken into account that the rates vary by a factor of 170 and the isopropyl alcohol pressures vary by a factor of more than 3000. It is also a satisfactory result that, when $n = 3$ or $n = 4$ in Eq. (4), all adsorption sites are found to contribute to the dehydrogenation rate, as is seen from the rate constants at 178°C which are given in Table 2.

It would have been desirable to extend

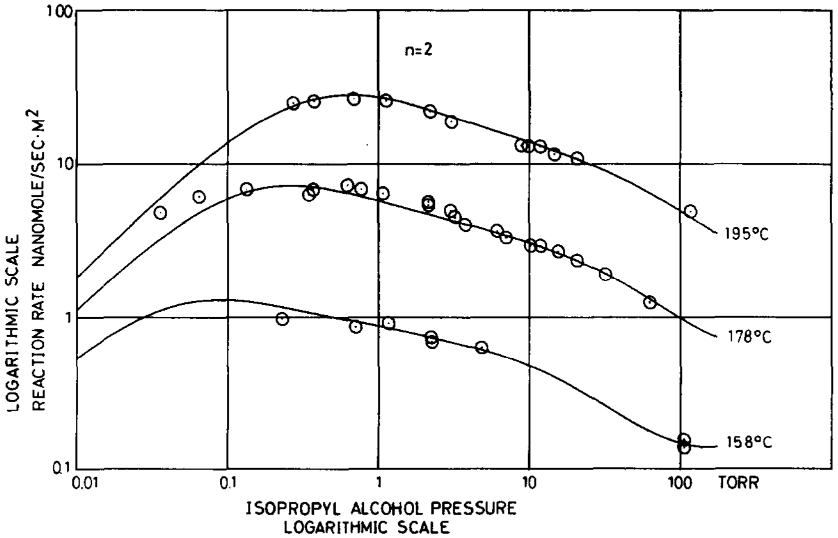

FIG. 1. Observed and calculated rates at 158°, 178°, and 195°C. The calculated rates have been obtained from Eq. (4) with $n = 2$, using the parameter values given in Table 1 of ref. (*2*) and Table 2 of this paper.

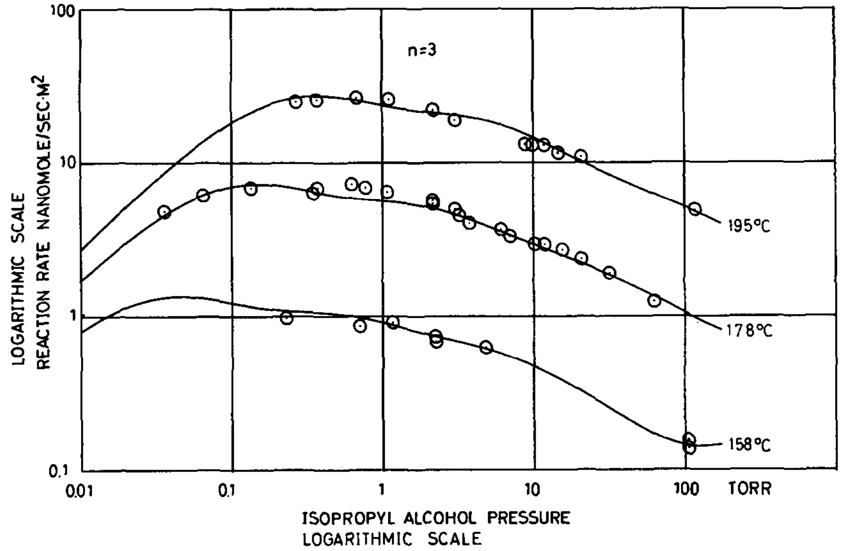

FIG. 2. Observed and calculated rates at 158°, 178°, and 195°C. The calculated rates have been obtained from Eq. (4) with $n = 3$, using the parameter values given in Tables 1 [ref. (*2*)] and 2.

the pressure range by another factor of 10 to 100 upwards, as this increase of isopropyl alcohol pressure is necessary in order to get full information about the weakest adsorbing site. A pressure apparatus making this possible is under construction. Also the temperature range could profitably have been extended upwards, but this was not possible when working with a nonaged catalyst, because fresh catalyst samples exhibit a rapid decline in activity at higher temperatures (*7*).

It was pointed out above that the mean percentage deviation between observed and calculated values was 5.95% ($s = 8.85\%$). The true standard deviation of the rate measurements at constant catalyst activity is not accurately known (it will depend upon the

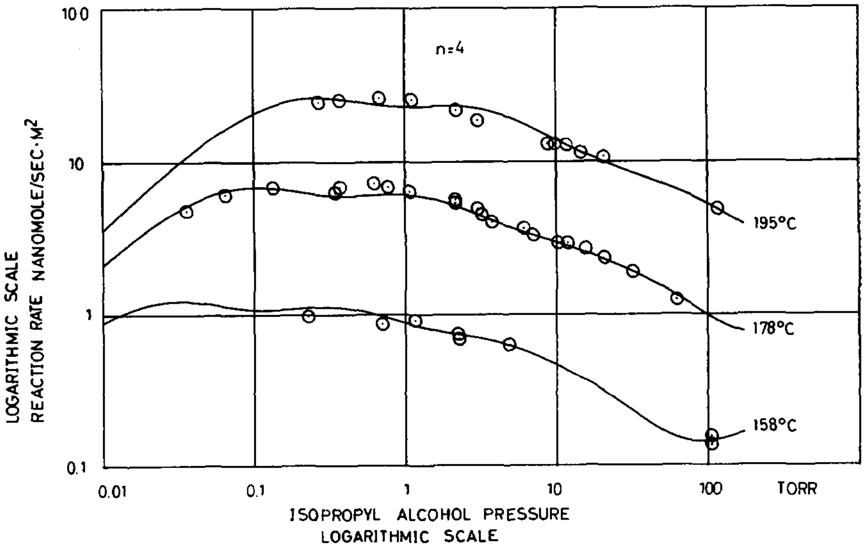

FIG. 3. Observed and calculated rates at 158°, 178°, and 195°C. The calculated rates have been obtained from Eq. (4) with $n = 4$, using the parameter values given in Tables 1 [ref. (*2*)] and 2.

particular conditions necessary to obtain a given rate) but it is believed to be somewhat less than 3%, except when measuring rates at 158°C at low isopropyl alcohol pressures, when 5% standard deviation is probably a better estimate. In the present case the overall standard deviation will be higher, however, because there was undoubtedly some activity decrease of the catalyst due to aging taking place when the measurements were carried out. It is believed that this catalyst aging will increase the standard deviation to about 6–7%. The standard deviation estimate ($s = 8.85\%$) from the fitting of Eq. (4) is still higher than the expected standard deviation of the rate measurements. But all errors in the adsorption parameters in Table 1 of ref. (*1*) (which have not been varied) will increase the standard deviation estimate from Eq. (4) of the experimental rates above the true least-squares minimum. The two standard deviation estimates, $s = 6\text{–}7\%$, and $s = 8.85\%$, can therefore be considered to be in full agreement.

If the experimental rates are expressed as molecules transformed per second and gram catalyst, and the values of W_{0i} are expressed as sites per gram catalyst, the k_i's and thus also the k_{i0}'s are seen from Eq. (4) to have the dimension molecules site $^{-1}$ sec^{-1}. So far the following units have been used: r, nanomole sec^{-1} m^{-2}; W_{0i}, mg isopropyl alcohol adsorbed per gram catalyst. The rate r is expressed as desired after multiplying by $N \times S \times 10^{-9}$ where N is Avogadro's number and S is the surface area of the catalyst, which is 52 m^2/g (*1*). W_{0i} is converted to sites g^{-1} by multiplying by 1.0×10^{-19} (i.e., molecules isopropyl alcohol per mg). The conversion factor for expressing k_i (and k_{i0}) in units molecules site^{-1} sec^{-1} is thus $N \times S \times 10^{-9} \times 10^{-19} = 3.13 \times 10^{-3}$. The values of the k_{i0}'s have been calculated in these units and they were found to be of the order of magnitude 10^{14} molecules/site sec. [The mean value (geometric) of the five sites was found to be 0.5×10^{14} molecules site^{-1} sec^{-1} when $n = 4$.] This is the same order of magnitude as the vibrational frequencies of hydrogen atoms in molecules, which are known from infrared spectroscopy to be closely centered around 1.0×10^{14} sec^{-1}. When an agreement between the adsorption function of a system and the reaction rates in the same system is sought for, it is implicitly assumed that the catalytic reaction is not confined to a very few active centers on the catalyst. Rather it is assumed that over large areas of the catalyst an adsorbing site is also a catalytically active site. The agreement found here between the pre-exponential factor (frequency factor) and the vibrational frequencies of hydrogen atoms is therefore highly satisfactory.

CONCLUSION

It is apparent from the preceding discussion that a model assuming that the dehydrogenation reaction of isopropyl alcohol on zinc oxide is taking place simultaneously on several (five) sets of active centers is in complete agreement with the experimental results. The reaction is described mathematically by Eq. (4) with $n = 3$ or 4 ($n = 2$ cannot be rigorously excluded but seems unlikely). According to the model the rate-determining step is a surface reaction, and in the rate-determining step an adsorbed isopropyl alcohol molecule reacts simultaneously with two or three neighboring free active centers (*5*). Detailed reaction mechanisms in agreement with such a model can be proposed, but at the present state of knowledge this is hardly warranted.

It is of interest to compare the results obtained here with results previously obtained for the dehydrogenation reaction of *sec*-butyl alcohol over a brass catalyst (*3, 8*). The brass catalyst had been oxidized in air at 430°C and was then reduced in hydrogen at the same temperature. It is thus inferred that the brass was covered by zinc oxide (possibly mixed with copper oxide) and copper. The presence of zinc oxide makes a similarity with a pure zinc oxide catalyst likely. It is therefore to be expected that the reaction mechanism of dehydrogenation of *sec*-butyl alcohol over a brass catalyst will be similar to the reaction mechanism of dehydrogenation of isopropyl alcohol over a zinc oxide catalyst. This expectation is in fact in agreement with the results obtained so far. The results on dehydrogenation of *sec*-butyl alcohol were consistent with a model assuming the same mechanisms as proposed above (*3*). Also in that case no clear choice between mechanisms assuming simultaneous reaction between an adsorbed alcohol molecule and two or three free active centers could be made. But a model assuming reaction between an adsorbed alcohol molecule and one free active center was on the whole not satisfactory. When the dehydrogenation of *sec*-butyl alcohol was investigated a model assuming only two sets of active centers was satisfactory, whereas the analysis carried out here is based on the assumption that there are five sets of active centers. This difference does not imply that there is a discrepancy between the two investigations, however. The results concerning dehydrogenation of *sec*-butyl alcohol were obtained on a different catalyst which had been given a different pretreatment, so the adsorption function may be rather different. The measurements were also carried out over a much smaller pressure range at considerably higher pressures. No detailed correspondence can therefore be expected.

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