

KINETICS AND ADSORPTION ON ACID CATALYSTS. VI.*

THE KINETICS OF VAPOUR-PHASE REACTIONS
ON ION EXCHANGER CATALYSTS CONTAINING ACTIVE GROUPS
OF DIFFERENT ACIDITY

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A kinetic study was made of the reesterification of ethyl acetate by methanol at 120°C and the dehydration of tert-butanol at 95°C in gaseous phase on macroreticular ion exchanger catalysts of styrene-divinylbenzene type containing different combinations of the acidic groups $-\text{SO}_3\text{H}$, $-\text{PO}(\text{OH})_2$, or $-\text{P}(\text{OH})_2$. Also studied was the kinetics on the pure components of these catalysts which were subjected to the same mechanical treatment as was employed in preparing the mixtures. It was verified that the kinetics of the reaction on the catalysts containing different active groups can be expressed by the summation of rate expressions for the pure components. From the obtained dependence of kinetic constants on acid strength of the ion exchangers used, the distribution of catalytic activity has been calculated for the surface of a catalyst which would possess continuous distribution of the acid strength of active sites on the surface. The results of this work rendered it possible to estimate the possibility of approximating the kinetics on non-uniform surfaces by means of rate equations not considering the non-equivalency of active centers.

In the kinetics of heterogeneous catalytic reactions a question which still remains to be solved is whether in deriving the rate equations the non-equivalency of active centers of the catalysts should be taken into account or not. In the earlier papers of this series^{1,2} we demonstrated for a catalyst containing equivalent active centers (a sulphonated macroreticular ion exchanger) that the use of Langmuir-Hinshelwood kinetics is justified and that the so called kinetic adsorption coefficients may have physical meaning. In a later study³ we analysed the equations of Langmuir-Hinshelwood type, varying the strength and number of acidic active groups of ion exchanger catalysts. In contrast to these, intentionally simple catalysts, in most of the catalysts so far employed in practice the catalytically active centers cannot be identified and hence one cannot decide whether they are or are not equivalent. On attempting to obtain data on whether the catalyst possess several types of active centers as well as to estimate the contribution of each to overall kinetics, some authors used indirect methods⁴⁻⁶. Thus, for example, Yoneda⁶ has found by using mathematical method of "regional analysis" that of several regions of acidic centers of nickel sulphate, which were determined by titration with amine, only the two are catalytically active in oligomerisation of propylene and in depolymerisation of paraacetaldehyde; at the same

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time, the difference in their activity, particularly in oligomerisation of propylene, was insignificant. Kolboe⁴ concluded on the intervention of several types of active centers from the better agreement of experimental kinetic curves with the curves calculated according to the equations assuming participation of two types of active centers than with those derived under the assumption of the centers of one type. In another work⁵ the author made an attempt to describe thermal desorption curves of isopropanol on zinc oxide and the kinetics of its dehydrogenation under the assumption that the adsorption and catalytic reaction proceed on five kinds of active sites. He achieved a rather good agreement between the calculation and the experiment. Its significance cannot be however overvalued because of a great number of the constants having been simultaneously determined by regression analysis.

The aim of this work was to prepare a catalyst which would contain active centers of several kinds, the kinetic characteristics of which could be determined separately and directly beforehand. On this catalyst it would be then possible to verify by kinetic study of a suitable reaction whether the contributions of individual kinds of active sites to the over-all catalytic activity are additive, and at what difference in their activity the contribution of some of them could be neglected and therefore the surface of such a catalyst could be regarded as uniform from the point of view of catalytic activity. From previous studies^{1,3} we had at disposal kinetic data on reesterification of organic esters by alcohols and on dehydration of tert-butanol in gaseous phase on macroreticular styrene-divinylbenzene copolymers containing one of the following groups, $-\text{SO}_3\text{H}$, $-\text{PO}(\text{OH})_2$, and $-\text{P}(\text{OH})_2$, which differ in acid strength⁷. In this work, by pressing very fine powder of these ion exchangers, we prepared the catalysts containing always the two of these groups and that in different relative proportion, and studied on them reesterification of ethyl acetate and dehydration of tert-butanol.

EXPERIMENTAL

Starting compounds were the same as in previous studies^{1,3}. The catalysts were prepared from ion exchangers containing $-\text{SO}_3\text{H}$, $-\text{PO}(\text{OH})_2$ or $-\text{P}(\text{OH})_2$ groups, whose provenience, preparation and properties were also described earlier^{1,3,8}. The ion exchangers were powdered (particle size around $40\ \mu$), mixed in appropriate ratio and pressed to pellets, using the pressure of around 200 atm. The pellets were then ground to the particles of the size 0.16–0.32 mm which were used in kinetic experiments. The composition of the prepared catalysts is recorded in Table I.

Kinetic measurements were carried out in a glass flow reactor heated by circulating silicone oil bath. In the case of dehydration of tert-butanol the reactor was connected directly with gas chromatograph *via* six-way valve with sample loop, in the reesterification of ethyl acetate the products were first condensed in the trap cooled by dry ice and then analysed separately. The apparatus and procedure used in kinetic measurements, along with analytical methods were described in detail in previous papers^{1,3}.

RESULTS

The kinetics of dehydration of tert-butanol was studied at 95°C on catalysts PO–P 50, PO–P 10, and S–PO 50. On preparing these mixed catalysts by pressing, the tex-

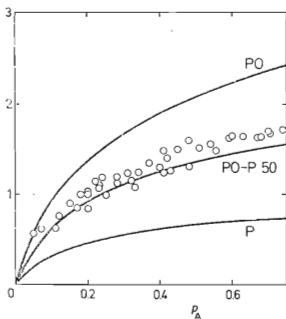
ture and catalytic properties of some of them were found to undergo changes due to this mechanical treatment⁹. For this reason not only the mixed catalysts, but also the pure components S, PO, and P, were converted to the form of pressed particles, using the same treatment in both cases. With all these catalysts the kinetic was measured in the same way as in a previous work³ and was interpreted by rate equation (1), which turned out to be the best one for all primary ion exchangers. The constants of Eq. (1) for pressed ion exchangers S, PO, and P are presented in Table II, along with the analogous data for primary ion exchangers reported previously³.

$$r = kK_A p_A / [1 + 2\sqrt{(K_A p_A)}]^3 \quad (1)$$

Fig. 1 illustrates how experimental dependence of the reaction rates of dehydration of tert-butanol, obtained for the PO-P 50 mixed catalyst, on the partial pressure of the alcohol agrees with the curve calculated under the assumption of the additivity of the contributions of both components, using Eq. (1) and the values of the constants for pure pressed components PO and P from Table II. For comparison purposes the curves for pure pressed components PO and P are also presented in this figure. It is seen that experimental points are close to the curve calculated for the mixed catalysts, the majority of them lie however slightly above the curve. Although, as was shown in our previous work⁹, in contrast to catalyst PO-P 10, much better agreement with the assumption of the additivity of the effect of mechanical treatment on the textural properties of individual components has been achieved with the catalyst just discussed, a certain deviation from this assumption is obviously the reason of small shift of the experimental from the calculated data.

FIG. 1
Dependence of Initial Reaction Rate of Dehydration of tert-Butanol on Its Initial Partial Pressure

Curve PO-P 50 was calculated by means of linear combination of the equations of type (1) for mixed catalyst, using the values of the constant from Table II (right-hand side). Points are experimental values for the same catalyst. The curves PO and P correspond to the data for pure pressed components.



Further catalyst studied, S-PO 50, consists of components whose catalytic activity for the reaction under study differs by more than two orders of magnitude (Table II). As it can readily be calculated, the contribution of the less active component PO to the reaction rate, irrespective of whether we consider the primary or the pressed component, amounts to less than 1 per cent. This value is lower than the reproducibility of the method of kinetic analysis, and we did not find in fact the contribution of ion exchanger PO when carrying out kinetic measurements with this catalyst.

For a study of the kinetics of reesterification we have chosen an ethyl acetate(A)-methanol(B) system at 120°C and catalysts S-P 50 and S-P 10. The procedure employed was the same as in our previous work¹ from which we took also the results

TABLE I
Components of Catalysts Used (wt. %)

Denotation	S ^a	PO ^b	P ^c
S-P 50	50	—	50
S-P 10	10	—	90
S-PO 50	50	50	—
PO-P 50	—	50	50
PO-P 10	—	10	90

^a Ion exchanger S contained 2.4 mequiv./g — SO₃H groups; ^b ion exchanger PO 3.9 mequiv./g — PO(OH)₂ groups; ^c ion exchanger P 4.0 mequiv./g — P(OH)₂ groups.

TABLE II
The Values of Constants of Kinetic Equation (*I*) for Dehydration of Tert-butanol at 95°C, the Relative Acid Strengths and Surface Area of the Catalysts Used

Catalyst	<i>A/A</i> ₀	Primary ion exchanger ³		After mechanical treatment		
		<i>k</i>	<i>k</i> _A	<i>k</i>	<i>K</i> _A	surface m ² /g
S	1	46 080	0.12	46 080	0.12	70
PO	0.023	186	0.31	832	0.24	33
P	0.0031	25.6	1.00	23.5	0.34	87

^a Parameter *A* is the value of the adsorption coefficient of dimethyl ether as a weak base, determined by measuring its irreversible adsorption on the ion exchanger used⁷.

for the pure catalyst S, *i.e.* kinetic equation (2) and the values of constants $k = 2625 \text{ mol h}^{-1} \text{ kg}^{-1}$, $K_A = 1.35 \text{ at}^{-1}$, and $K_B = 0.34 \text{ at}^{-1}$. For catalyst P and the same equation (2) we found in this work $k = 43.2 \text{ mol h}^{-1} \text{ kg}^{-1}$, $K_A = 2.3 \text{ at}^{-1}$, and $K_B = 10.3 \text{ at}^{-1}$. The effect of pressing was not considered here, due to its lesser importance⁹ for ion exchanger P and the negligible effect for ion exchanger S. As follows from these data for the pure components, similarly to the dehydration of tert-butanol³, the values of adsorption coefficients, in particular of the alcohol, increase with decreasing acid strength of the catalyst.

$$r = kK_A K_B p_A p_B / [1 + K_A p_A + \sqrt{(K_B p_B)}]^3. \quad (2)$$

With mixed catalysts S-P 50 and S-P 10, we measured the values of initial reaction rates of the reesterification at different partial pressures of the alcohol and of the ester and compared them with the values calculated by means of linear combination of the equations of type (2), using the corresponding values for the pure components. The results are graphically represented in Fig. 2. Apart from usual dispersion, the data are in good agreement.

DISCUSSION

In the kinetics of heterogeneous catalytic reactions, in most cases the non-equivalency of active centers is not taken into account. One of the approaches not neglecting the non-uniformity of the surface assumes the presence of several types of active sites and sums up the respective reaction rates^{5,10}. On the basis of our experimental data we will show what practical difference exists between these two approaches.

In the case of dehydration of tert-butanol on a catalyst containing several types of active centers, the reaction rate should be given by the summation (3) of Langmuir-Hinshelwood expressions (1)

$$r = \sum_{i=1}^n s_i k_i K_{A,i} p_A / [1 + 2 \sqrt{(K_{A,i} p_A)}]^3. \quad (3)$$

The relation (3) is valid in case that no interactions between individual types of active sites or no other complicating phenomena occur, and that the mechanism does not differ on the sites of different type. We have found that with the mixed ion exchanger catalysts used such complications do not arise (except for a certain effect of pressing on the texture of some ion exchangers, which could be largely eliminated). The results shown in Figs 1 and 2 demonstrate that on acid catalysts with different sorts of active centers the summation of rate equations for the pure components can be successfully applied.

In Fig. 3 the curve 1 represents the dependence $r = f(p_A)$ for $n = 2$ and the values of the constants from Table II. If we attempt to describe this dependence by simple equation (1), by non-linear regression we get the constants listed in Table III. The

TABLE III
The Values of Constants of Kinetic Equation (1) for Approximative Expression of Composite Rate Function (3)

Method of calculation	k	K_A	Curve in Fig. 3
According to Eq. (3)	83.2 ^a 23.5 ^b	0.24 ^a 0.34 ^b	1
Linear regression to curve 1 (Fig. 3)	52.86	0.266	2
Mean values of the constants for components PO and P	53.35	0.29	3
According to approximative expressions (4) and (5)	52.4	0.266	4

^a For component PO; ^b for component P.

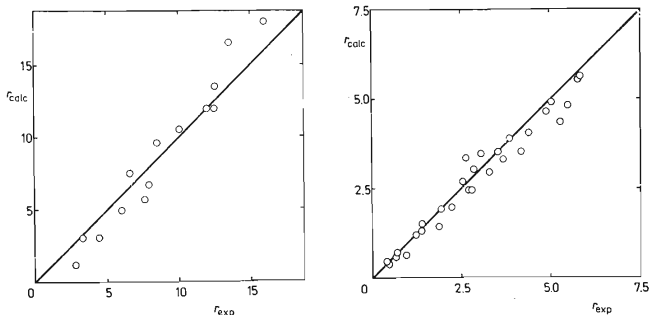


FIG. 2

Relationship between Experimental Initial Reaction Rates of Reesterification of Ethyl Acetate by Methanol and the Values Calculated by Means of Linear Combination of the Equations of Type (2) for Pure Components S and P

^a For catalyst S-P 50, ^b for catalyst S-P 10.

curve 2 calculated by using these constants is practically identical with the curve 1 calculated by means of expression (3) for the two kinds of active centers, which contains four constants. The values of the rate constant and adsorption coefficient obtained from simple equation (1) lie between the values for components PO and P (Table III), but they do not represent the mean values. The curve 3 calculated by means of the mean values differs somewhat from the curve 1.

It can be hence said that the kinetics of a reaction on a catalyst containing more kinds of active centers (in our case their activity and acid strength differed by about one order of magnitude) can very well be described even by simple expression of Langmuir-Hinshelwood type. This approximation will be obviously valid only within limited region of pressures (in our case the pressure region used was from 0.1 to 0.9 atm). The constants of the simple equation can be approximately determined beforehand from the constants for individual kinds of active centers: by developing the individual expressions in Eq. (3) into series, summing up the terms with the same power of partial pressure and by comparing the first two members of the series with the first members of the expression (1) developed into series in the same way. One obtains relations (4) and (5).

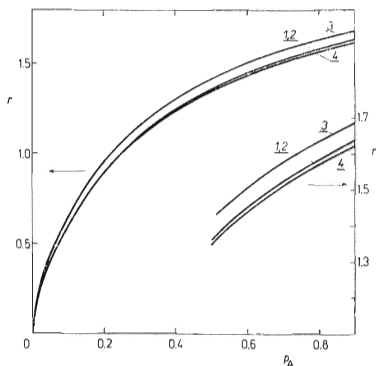


FIG. 3

Calculated Dependences of Initial Reaction Rate of Dehydration of Tert-butanol on Its Initial Partial Pressure on Catalyst PO-P 50

Curve 1 was calculated according to relation (3), curves 2–4 according to simple equation (1); the values of the constants are listed in Table III.

$$k = \frac{(s_1 k_1 K_{A,1} + s_2 k_2 K_{A,2})^3}{(s_1 k_1 K_{A,1}^{3/2} + s_2 k_2 K_{A,2}^{3/2})^2} \quad (4)$$

$$K_A = \left(\frac{s_1 k_1 K_{A,1}^{3/2} + s_2 k_2 K_{A,2}^{3/2}}{s_1 k_1 K_{A,1} + s_2 k_2 K_{A,2}} \right)^2 \quad (5)$$

The curve 4 in Fig. 3 was calculated using the values of k and K_A obtained by this procedure (Table III). As it is seen it agrees better with the curve 1 than the curve 3 which was obtained on the basis of mean values.

On the example when the activity of individual kinds of active sites differs more than in the preceding case (*e.g.* for ion exchangers S and PO by more than two orders of magnitude), we will show how great is the contribution of the less active component. In Fig. 4 are shown the courses of the $r-p_A$ dependence. The curve for catalyst S-PO 50 (related for comparison to the weighted amount of the pure component S, similarly as the other curves in Fig. 4) cannot be distinguished at all from the curve for pure S (the deviations are about 0.3%). If the ratio of the components

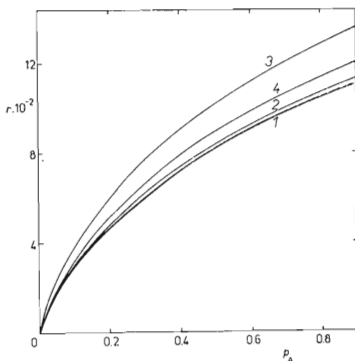


FIG. 4

Calculated Dependences of Initial Reaction Rates of Dehydration of Tert-butanol (Related to the Weighted Amount of Pure Component S) on Its Initial Partial Pressure

Calculations were performed by means of an equation of type (3), using experimental values of the constants for the pure substances from Table II (right-hand side). 1 Catalyst S, 2 catalyst S-PO 10, 3 catalyst containing 1 wt.% of component S and 99 wt.% of component PO, 4 catalyst containing 1 wt.% of components S, 9 wt.% of component PO and 90 wt.% of component P.

is 1 : 9 in favour of the less active component PO (curve 2)) the course of the $r-p_A$ plot does not practically differ from curve 1. Only when the distribution of the acidic components is extreme (1 : 99 ratio) the contribution of the less active sites cannot be neglected (curve 3). We made further an attempt to simulate the course of the $r-p_A$ dependence for the three-component catalyst S-PO-P. If the distribution of these types of active sites were linear (all components present in equal amounts) the course of the $r-p_A$ dependence would not be different from curve 1, since the contribution of component PO, and more so of component P, is negligible with regard to the highly active component S. Only if one assumes the distribution of sites to be roughly logarithmic (catalyst S-PO-P in the ratio of 1 : 9 : 90), one would obtain the rate values represented by the curve 4, which, nevertheless, differ from the values of the curve 1 for the catalyst with equivalent active sites by only 10 per cent.

The effect of inequality of active sites on the kinetics of acid-catalysed dehydration of tert-butanol is therefore weak. In our previous paper³ we have shown what distribution of reaction rate of dehydration of tert-butanol would likely be on the catalyst which would possess continuous linear distribution of the centers within the range of the acid strength of functional groups of the ion exchangers employed

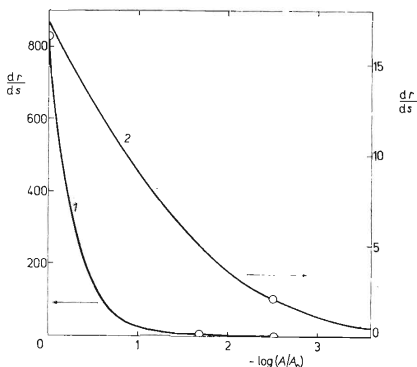


FIG. 5

Distribution of Reaction Rate on Surface Acid of Catalyst with Continuous Linear Distribution of Centers According to Acid Strength

Curve 1 was calculated³ for dehydration of tert-butanol at 95°C, $p_A = 0.5$; curve 2 represents reesterification of ethyl acetate by methanol at 120°C, $p_A = 0.25$, $p_B = 0.25$; points are experimental values.

(from $-\text{SO}_3\text{H}$ to $-\text{P}(\text{OH})_2$). In Fig. 5 is the so obtained dependence represented by curve 1. Kinetic results of the reesterification of ethyl acetate by methanol on catalysts S and P, presented in this work, enabled us to make an approximate estimation of the distribution of reaction rate of this reaction on the same model of linearly nonuniform surface. The calculation was performed in the same way as in the earlier treatment of kinetic data on dehydration of tert-butanol³ and it was assumed, similarly that also the rate constants and adsorption coefficients of the reesterification are linearly dependent (in logarithmic coordinates) on relative acid strength of active centers. The calculation yielded the curve 2 shown in Fig. 5. From its course it follows that the distribution of the reaction rate of the reesterification with regard to different acid centers is more even than in the dehydration of tert-butanol. The region of acid strength, $\log(A/A_0)$, from 0 to -1 , which in the dehydration of tert-butanol represents over 90 per cent of the catalyst activity, contributes in the reesterification to the over-all activity only by somewhat more than by one half. If we express the contributions of centers within the region of $\log(A/A_0)$ from 0 to -4 , which significantly contribute to over-all reaction rate, we obtain the following percentual proportions: for the region of $\log(A/A_0)$ from 0 to -1 it is 59.6%; from -1 to -2 it is 27.5%; from -2 to -3 it is 10.0%, and from -3 to -4 it is 2.9%.

Contrarily to hypothetical distributions reported in literature (*e.g.*¹¹) with postulated values of the coefficients of linear relations, the distributions in Fig. 5 are based on the values obtained experimentally, even though in the case of the reesterification only the data for two ion exchangers of different acid strengths were available. While in the dehydration of tert-butanol the over-all activity was practically determined by the most acidic centers within the region of one order of magnitude of acid strength, and the catalytically active surface could then be assumed to be approximately uniform, the centers which participate in the reesterification lie within a broader acidity region, this being apparently associated with the character of the adsorption of reactants and with the detailed mechanism of the reaction. In this case the catalytically active surface cannot be regarded as uniform. However, similarly to the dehydration of tert-butanol, also here it can be demonstrated by calculation that the kinetics of reesterification (which is more complicated, since we deal here with bimolecular reaction) on this nonuniform surface can be well approximated by simple equations of Langmuir-Hinshelwood type (for the partial pressures of from 0.025 to 0.9 atm the deviations are about 1–2%, exceptionally over 3 per cent).

LIST OF SYMBOLS

- A acid strength, expressed by means of the adsorption coefficient of dimethyl ether as a weak base chemisorbed on ion exchangers⁷ (at^{-1})
 k rate constant ($\text{mol h}^{-1} \text{kg}^{-1}$)
 K_A, K_B adsorption coefficients of reactants (at^{-1})
 n number of different types of active sites

p_A, p_B	initial partial pressures of reactants (at)
r	initial reaction rate ($\text{mol h}^{-1} \text{kg}^{-1}$)
s	relative representation of a given kind of active sites

Indices

$i, 1, 2$	denote corresponding type of active sites
0	denotes values corresponding to the most acidic active sites
calc	calculated values
exp	experimental values

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