THE EFFECT OF NONUNIFORMITY OF ACID SITES ON KINETICS OF DEHYDRATION OF TERT-BUTANOL ON A SiO_2-MgO-Al_2O_3 CATALYST*

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Kinetics of gas phase dehydration of tert-butanol has been studied at 95—150°C on SiO_2-MgO--Al_2O_3 catalysts unpoisoned and poisoned to a different degree by alkali metal ions. Contributions of 6 fractions of sites of different acid strength to overall kinetics have been determined and the kinetics on these fractions has been separately evaluated. The dependence of the rate constant on Hammett H_0 acidity function obeys the Brønsted relation, the activation energy increases with decreasing acid strength. Heats of adsorption and entropy changes of adsorption correspond to chemisorption on the most acidic sites and to physical adsorption on the other fractions of sites. The reaction proceeds from 90 per cent on the most acidic sites within 1·5 H_0 unit, which correspond to less than 5% of the total number of sites. The contribution of the other, predominant part of the sites is negligible and the effect of the nonuniformity of catalyst surface can be neglected in deriving rate equations.

Kinetics of heterogeneous catalytic reactions is frequently described by the equations of Langmuir–Hinshelwood type, the active sites of a given catalyst being regarded as equivalent. These equations have been questioned especially in that the presumed equivalency of sites on catalyst surface is not fulfilled[1]. On the other hand, however, the equations of Langmuir–Hinshelwood type fit mostly well kinetic data. In several previous works we have analysed the validity of Langmuir–Hinshelwood equations for the reactions catalysed by organic ion exchangers, *i.e.* the catalysts with defined and equivalent active sites[2–4]. For dehydration of tert-butanol and reesterification of ethyl acetate by methanol on ion exchangers we have determined the effect of nonuniformity of active sites on the kinetics of reactions taking place on the catalysts containing at the same time several types of acidic groups ($—SO_3H$, $—PO(OH)_2$, and $P(OH)_2$) and also on hypothetical catalyst which possesses a continual distribution of active sites according to their acid strength[4,5]. It has been shown that particularly dehydration of tert-butanol proceeds practically only on a very narrow fraction of the most acidic sites and that the nonuniformity of active sites can be neglected in deriving kinetic description of the reactions.

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Discussion about the effect of the nonuniformity of active sites of the real inorganic catalysts, both metals and oxides, has been so far unsubstantiated, since there have been no studies which would determine experimentally the character of nonuniformity (distribution of the activity of sites) and its effect upon the kinetics of catalytic reaction. In the present work we have made an attempt to study the kinetics of dehydration of tert-butanol in gas phase on fractions of the surface of a MgO–SiO_2–Al_2O_3 catalyst differing in acid strength which were deliminated by gradual poisoning of the catalyst by alkali metal ions. The aim of the study was to ascertain whether and how the kinetics of the reaction (the form of rate equation) changes with acid strength and how the latter factor reflects in the constants of rate equations or the parameters of Arrhenius and van't Hoff relations. The results obtained by such a study could also demonstrate how significant is the contribution of individual fractions differing in acid strength of sites to the total activity, and whether it is possible to neglect their nonuniformity in the kinetic description of reaction.

EXPERIMENTAL

Chemicals

Catalysts were prepared by using the following compounds: sodium silicate, pure; magnesium acetate, pure; aluminium nitrate nonahydrate, pure; 25% aqueous ammonia; lithium hydroxide, for analysis; potassium carbonate, for analysis; all were supplied by Lachema, Brno.

Distribution of sites according to their acid strength was determined with the aid of the following substances: n-butylamine, pure (Koch-Light Ltd.), toluene, for analysis (Lachema, Brno) dried by sodium, Methyl Red and Dimethyl Yellow (both Lachema, Brno), benzeneazodiphenylamine (BDH). Dicinnamalacetone was prepared by condensation of acetone with cinnamyl aldehyde in sodium hydroxide solution according to ref.[6].

Kinetic measurements were made using the following chemicals: tert-butanol (Reanal, Budapest) was dried by distillation through a column filled with sodium, b.p. 83°C, m.p. 25°C, nitrogen for lamps (Technoplyn, Ostrava) was dried by passing over Linde 5A molecular sieve which was activated at 400°C.

Measurements of Surface Acidity Distribution

The measurements were made by the method of discontinual titration by n-butylamine with the use of a series of acid-base indicators in aprotic medium, which was proposed by Benesi[7]. The method was little modified for our purpose. The indicators used were the following: Methyl Red (pK 5·0), Dimethyl Yellow (pK 3·3), benzeneazodiphenylamine (pK 1·5), and dicinnamalacetone (pK −3·0). The known amount of the catalyst (0·01—1 g) was placed into a series of Elenmayer flasks provided with a grinded stopper and then 0·025M solution of n-butylamine in toluene has been introduced. The ratio of n-butylamine to the catalyst and thus also the degree of neutralization of acid sites changed from one flask to another. After stirring the mixture, 1 drop of 0·5% solution of the indicator in toluene was added to each flask and the suspension was stirred shortly again. The approximate point of equivalence was determined after 20 hours (minimal time) according to the amount of n-butylamine corresponding to the two successive titration mixtures between which discolouration of the catalyst suspension took place. Based on the results obtained, further mixtures of the catalyst with n-butylamine were prepared such that the region around the point of equivalence was gradually narrowed down. The final value of the point of equivalence was determined with an accuracy of ±0·01 mequiv/g. Some findings concerning the application of this method were reported elsewhere[8,9].

Preparation of the Catalyst

Sodium silicate (3000 g) was dissolved in 18 l of distilled water. The solution was decationized by pouring onto the columns filled with Wofatit KPS cation exchanger (Chemische Werke, Biterfeld, GDR). The eluted sol (pH 5·0—5·5) turned gellous in several hours. Then, a mixture of solutions of magnesium acetate (655 g of $(CH_3COO)_2Mg.4\ H_2O$ in 1850 ml of distilled water) and aluminium nitrate (9·8 g of $Al(NO_3)_3.9\ H_2O$ in 20 ml of distilled water) was added into the gel under intense stirring. After stirring for 1 h, the reaction mixture (pH 6·5) was made alkaline (pH 10) by the addition of 500 ml of 3M aqueous ammonia solution and stirring was continued for another 2 h. Then the mixture was set aside for 3 days, the gel was filtered off with suction and dried on air at 100—130°C. The dry gel was desintegrated to particles whose diameter was smaller than 0·63 mm. As the catalysts so prepared did not possess sufficient amount of strongly acidic sites, the content of aluminium was increased by reimpregnation of the catalysts with aluminium nitrate (19·3 g of $Al(NO_3)_3.9\ H_2O$ in 1 l of water) followed by separation by filtration with suction, washing with water and treatment with 500 ml of 3M aqueous ammonia. After drying at 110°C, the catalyst was calcinated at 535 ± 10°C for 6 h. In order that the degree of dehydration of the surface be similar to conditions of the catalytic reaction (dehydration of tert-butanol), the calcinated catalyst was rehydrated and dried on air 64 h at 130°C. The content of aluminium and magnesium determined analytically[10] was 0·75% wt. and 10·82% wt., respectively. The surface area determined by BET method using adsorption of benzene was 440 m^2/g, the prevailing radius of pores was 2·6 nm. Particles used had 0·08—0·315 mm size.

Poisoning of Acid Sites by Alkali Metal Ions

An aqueous solution of lithium carbonate ($1 . 10^{-2}$ or $2 . 10^{-2}$ mol/l) was poured onto the appropriate amount of the catalyst. The higher degree of poisoning was achieved with the use of lithium hydroxide ($1 . 10^{-1}$ mol/l) and the highest one by using potassium carbonate ($1 . 10^{-1}$ mol/l). Suspension of the catalyst in alkali solution was shaken, after 24 h the catalyst was removed by filtration with suction, washed with distilled water on sintered glass filter and dried in air overnight at 130°C. The degree of poisoning of active sites depended upon pH of the alkaline solution used (pH 11—13) and upon the volume of the solution per weight unit of the catalyst (it varied in the 10—100 ml/g range). Changes in acidity distribution caused by poisoning were followed by the indicator method described above, the amount of captured alkali was determined by atomic absorption spectrometry. Neither specific surfaces nor pore distribution of the catalysts were substantially affected by poisoning.

Kinetic Measurements and Treatment of Data

The apparatus and procedure were similar as those used in previous works[2,4]. A glass flow reactor provided with a jacket thermostatted by running glycerine was fed at a constant rate by vapours of tert-butanol diluted with nitrogen; the partial pressure of tert-butanol was varied from 0·025 to 0·95 atm. The weighted amount of the catalyst placed into the reactor amounted to 0·005 to 0·6 g, exceptionally 2—4 g (in dependence upon the activity of a given catalyst). Temperature (95—150°C) was measured by thermocouple which was placed into a small glass tube located in the catalyst bed, the temperature was maintained constant with an accuracy of ±0·5°C. The reactor was connected *via* six-way valve and feeding loop directly to a gas chromatograph. After steady state has been established, the reaction products were analysed at least four times. Conversion (the ratio of the partial pressure of isobutylene to the sum of partial pressures of isobutylene and tert-butanol in the analysed reaction mixture) was calculated as the mean value of the analyses made. The analyses were carried out on a gas chromatograph which was equipped with a flame-ionisation detector and an integrator; the column was 1 m long and was filled with 15% wt. poly(ethylene glycol) 100 on Chromosorb W (Carlo Erba, 60—80 mesh); the oven temperature was 107°C and nitrogen was used as the carrier gas.

With the use of the unpoisoned (most active) catalyst, such conditions have been found under which neither internal nor external diffusion plays a role. Kinetic analysis was made by the method of initial reaction rates. For each temperature and catalyst 24—70 values of conversion at varying partial pressures of the alcohol were determined. It was verified that up to conversions $x = 0{\cdot}03$ the initial reaction rate can be calculated from the relation $r \approx x/(W/F)$. Reaction rates were determined with an accuracy of ±5 rel.%.

Since in the case of some catalysts, especially those most active, their activity somewhat decreased with time of their performance, the catalyst sample was always replaced after ten conversion measurements by the fresh one. A decrease in the activity of the catalyst during its performance was taken into account such that the first determination was repeated at the end of the series of measurements and the conversions found between these two measurements were corrected by using the assumption that the catalyst activity decreases linearly between the first and last determinations of conversion. For conversions measured at higher temperatures (135 and 150°C) the allowance has been made also for the value corresponding to noncatalytic thermal reaction. Its contribution did not exceed 15% of the total conversion determined. Contributions of the noncatalytic reaction were found by carrying out the reaction under analogous conditions in the absence of catalyst, in a reactor filled only with glass balls.

Treatment of initial reaction rate data for dehydration of tert-butanol in dependence upon initial partial pressures of the alcohol was performed by two-parameter nonlinear regression on a computer, using the sum of squared deviations of the experimental from calculated reaction rates as the minimised function.

RESULTS

For the purpose of this study it was necessary to develop a catalyst which would have a continual spectrum of active sites in a broad interval of acid strength. The results of this investigation have been reported separately[11]. We have finally suceeded in finding the suitable catalyst on the basis of magnesium silicate with the added small amount of aluminium oxide. The distribution of acid strength for this catalyst (expressed by means of Hammett H_0 function) is given in the first row of Table I. This catalyst has smaller number (<20% of the total) of the most acidic sites ($H_0 \leqq -3{\cdot}0$) and the relative amount of the other sites then increases on going from the more acidic to less acidic sites (with the exception of the region $5{\cdot}0 \geqq H_0 \geqq 3{\cdot}3$, which, however, was only slightly catalytically active). This nonuniform distribution with small proportion of the most active sites and with increasing number of the less active sites was suitable for the purpose of the intended kinetic study.

TABLE I

Acid Strength Distribution for the Catalysts Used

The region of the most active sites in a given catalyst is framed up. ΔN_i is the number of sites in the most acidic region which was deliminated by gradual poisoning, *i.e.* the number of sites in fraction f_i.

The order of catalyst	Acid strength distribution, mequiv/g $5{\cdot}0 \geqq H_0 \geqq 3{\cdot}3$	$3{\cdot}3 \geqq H_0 \geqq 1{\cdot}5$	$1{\cdot}5 \geqq H_0 \geqq -3{\cdot}0$	$H_0 \leqq -3{\cdot}0$	Fractions of sites f_i deliminated by gradual poisoning	ΔN_i mequiv/g
0	0·11	0·16	0·14	$\boxed{0{\cdot}09}$		
					f_1	0·02
1	0·14	0·10	0·20	$\boxed{0{\cdot}07}$		
					f_2	0·04
2	0·12	0·10	0·26	$\boxed{0{\cdot}03}$		
					f_3	0·03
3	0·11	0·14	$\boxed{0{\cdot}29}$	0		
					f_4	0·16
4	0	0·12	$\boxed{0{\cdot}13}$	0		
					f_5	0·13
5	0	$\boxed{0{\cdot}20}$	0	0	f_6	0·20

The aim of this work was to determine the kinetics of a model reaction on several fractions of catalyst surface which differ one from another by their acid strength. However, since the kinetics on individual fractions cannot be measured directly, the original catalyst was gradually poisoned to a different degree by alkali metal ion (lithium or potassium). As this ion occupied always the most acidic portion of sites and caused equivalent decrease in the catalytic activity, the difference of the experimental kinetic dependences $r = f(p_A)$ between two successively poisoned catalysts has yielded kinetic data corresponding to the just poisoned sites. A total of 6 fractions of sites has been delimitated by this way (denoted as $f_1 - f_6$ in Table I). The gradual poisoning of the catalyst led not only to a decrease in the amount of the most acidic sites but also in some cases to certain shifts in the distribution of weaker acidic sites. However, as followed from kinetic measurements, catalytically important is always only the most acidic portion of the sites and changes in the distribution in the region of weaker acidic sites cannot be important practically.

Kinetics of dehydration of tert-butanol was measured at three temperatures (except the last, least active catalyst) in a region of 95 to 150°C. Experimental data on initial reaction rates were treated by nonlinear regression with the use of 9 equations of Langmuir–Hinshelwood type[12], and of a power-type equation. The data found for the least active catalyst (corresponding to the fraction of sites denoted as f_6 in Table I) were smoothed by the equation with the lowest residual sum of squared deviations and the so smoothed values of reaction rates were substracted from the values of experimental reaction rates for the preceding, less poisoned catalyst. These differences corresponded to reaction rates on the fractions of sites poisoned in the last step (denoted as f_5 in Table I). Data for the other, gradually less poisoned catalysts were treated successively in a similar way up to the original catalyst. This procedure yielded reaction rate data in dependence upon the partial pressure of the alcohol at different temperatures for all the fractions of sites of varying acid strength, which are denoted as $f_1 - f_6$ in Table I. These separated rate data for individual fractions of sites were treated by nonlinear regression according to the same rate equations as were the original nonseparated data. As the best for all the sets of data (different fractions of sites, different temperatures) have turned out to be the following three equations (*1*)–(*3*).

$$r = k\,K_A p_A/[1 + 2(K_A p_A)^{0,5}]^3\,, \tag{1}$$

$$r = k\,K_A p_A/[1 + 2(K_A p_A)^{0,5}]^4\,, \tag{2}$$

$$r = 8k\,K_A p_A/[1 + (1 + 8K_A p_A)^{0,5}]^3\,. \tag{3}$$

The results obtained can be disscused on several different levels. The immediate, but the least general information, is provided by direct experimental data (*e.g.* by the dependence of the reaction rate upon the degree of poisoning of the catalysts, Fig. 1). The more general information, less reliable, however, is obtained from the constants of rate equations (rate constant and adsorption coefficient) determined by primary calculation from the experimental data obtained at one temperature. On including temperature as another variable, one obtains yet the more general information (activation energy, heats and entropies of adsorption). Its reliability is, however, yet lesser, and – as will be seen later – it allows only qualitative discussion.

The obtained parameters of kinetic equations can be correlated with the acid strength of individual fractions of sites. It is of course necessary to express the range of acid strength of a given fraction by one value. For this purpose we have assumed a linear distribution of sites according to their acid strength within the fraction and used the arithmetic mean values of H_0. For the fraction f_6 such H_0 value is 2·4. Fractions f_4 and f_5 form roughly the same parts in the interval delimitated by the two neighbouring indicators (benzeneazodiphenylamine, pK + 1·5, and dicinnamalacetone, p*K* − 3·0), *i.e.* H_0 is 1·5 to −0·75 for the fraction f_5 (the mean value c. 0·4) and −0·75 to −3·0 for the fraction f_4 (the mean value −1·9). The reliable value of the acid strength cannot be ascribed directly to fractions $f_1 - f_3$ ($H_0 \leqq -3·0$)

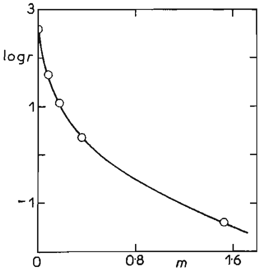

FIG. 1

Dependence of Logarithm of Initial Reaction Rate (mol h^{-1} kg^{-1}) of Dehydration of Tert-Butanol at 120°C and $p_A = 0·4$ atm on the Amount of Lithium *m* (mequiv/g) Captured on Catalyst

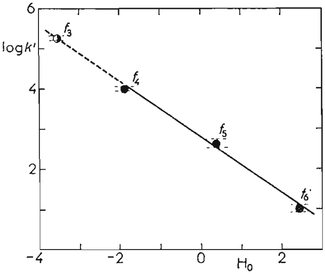

FIG. 2

Dependence of Logarithm of Rate Constant *k'* (mol $equiv^{-1}$ h^{-1}) of Dehydration of Tert-Butanol at 150°C (Eq. (*2*)) on the Mean Acid Strength of Fractions $f_4 - f_6$ of Sites (●) Based upon H_0 Values Determined by Means of Indicators

◑ Extrapolated point for fraction f_3. The error in determination of *k'* is indicated by broken horizontal lines around points.

since this could not be differentiated from one another, because of the lack of suitable indicators for this region. The mean value of the acid strength of fractions $f_4 - f_6$ was thus correlated with the values of the logarithms of rate constants which were obtained from Eq. (*2*) for temperature 150°C and which were related to the unit amount of sites in the fractions. A good linear dependence has been found (Fig. 2) which corresponds to Brønsted relation used in homogeneous acid-base catalysis. Similarly good linear correlation has been obtained also on using Eqs (*1*) and (*3*). In Fig. 2 is shown also the value of log k' for the fraction f_3 such that it lies on the straight line extrapolated from the found linear dependence for fractions $f_4 - f_6$. Providing that such an extrapolation is correct, the acid strength which would correspond to the fraction f_3 will be approximately H_0 $-3{\cdot}6$. The support for the approximate correctness of this extrapolated H_0 value is provided by the fact that when used for correlation with other experimental values of k' than are those on the basis of which it was obtained by extrapolation (*i.e.* for the temperature 120°C), it gives again a good linear dependence (Fig. 3) with the values for f_4 and f_5 (based upon reliable H_0 values). From this dependence in Fig. 3 we have attempted to estimate the corresponding values of H_0 for fractions f_2 and f_1 by extrapolation, using the corresponding values of log k' (H_0 for fraction f_2 is approx. $-4{\cdot}0$ and for fraction f_1 it is approx. $-5{\cdot}7$).

In Fig. 4 is graphically represented the dependence of adsorption coefficients of tert-butanol K_A found for 120°C according to Eq. (*2*) upon the above mentioned directly or indirectly determined values of the acidity function H_0. As the values of adsorption coefficients were obtained with lesser accuracy than rate constants, this dependence can be discussed only semiquantitatively. Nevertheless, it is evident that in the region of strongly acidic sites there exists correlation between adsorption coefficients and acid strength. An increase in K_A values with decreasing acid strength is analogous to that found by us for dehydration of tert-butanol catalysed by ion

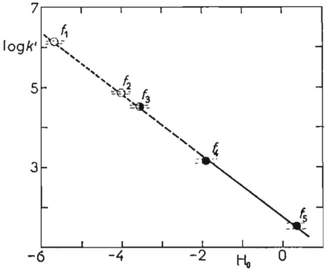

FIG. 3

Dependence of Logarithm of Rate Constant k' (mol equiv^{-1} h^{-1}) of Dehydration of Tert-Butanol at 120°C (Eq. (*2*)) on the Mean Acid Strength of Fractions of Sites

● Points based upon the H_0 value determined by means of indicators, ◑ the point corresponding to the H_0 value obtained by independent extrapolation at 150°C (Fig. 2) for the fraction f_3; ○ extrapolated points for fractions f_1 and f_2.

exchangers of varying acid strength[4]. In the region of less acidic sites the values of adsorption coefficients are practically independent of the acid strength. Similar dependences were obtained also with K_A values determined by using Eqs (*1*) and (*3*) as well as with the values found for temperatures other than 120°C.

A more general information can be provided by the parameters of temperature dependences of kinetic constants. These parameters are, however, ladden with rather great error. From Fig. 5 it can be – at least qualitatively – concluded that the activation energy of the dehydration of tert-butanol (the average error in determination is c. ±30%) on the fractions of sites f_2 ($H_0 \approx -4{\cdot}0$) to f_5 ($H_0 \approx +0{\cdot}4$) increases with decreasing acid strength, which agrees with the mechanism of an acid catalysed reaction[13]. The value of activation energy for the most acidic sites (fraction f_1, $H_0 \doteq -5{\cdot}7$) is beyond this dependence, which could be due to the greater error

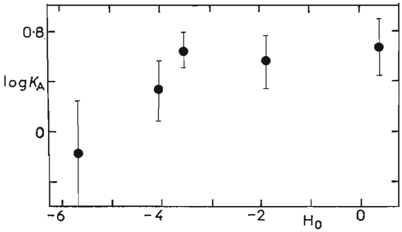

FIG. 4

Dependence of Logarithm of Adsorption Coefficient K_A (atm^{-1}) of Tert-Butanol at 120°C (Eq. (*2*)) upon the Mean Acid Strength of Fractions of Sites Expressed by H_0 Acidity Function

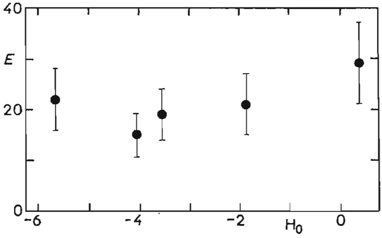

FIG. 5

Dependence of Activation Energy E (kcal/mol) of Dehydration of Tert-Butanol upon the Mean Acid Strength, H_0, of Fractions of Sites of the measurement on the unpoisoned, much more active catalyst or likely also by a partial intercorrelation of rate and adsorption constants in their evaluation from the data for some temperatures.

Heats of adsorption of the alcohol were determined with an average error of approx. ±50% (Table II). Despite of this, they correspond to the heat of chemisorption (25 kcal/mol) for the most acidic sites, while they acquire values corresponding rather to physical adsorption (5 – 6 kcal/mol) for the region of less acidic sites (fractions $f_2 - f_4$). In this region there is no distinct dependence of the heats of adsorption upon the acid strength of sites. The heat of adsorption for the fraction f_5 is close to zero. Calculated entropies of adsorption of the alcohol (Table II) satisfy the criteria formulated by Boudart[14] (except the value for the fraction f_5).

DISCUSSION

We do not discuss intentionally the results obtained in terms of reaction mechanism. We wished only to appreciate phenomenologically how the values of kinetic parameters would change when the acid strength of active sites is varied. Nevertheless, from these results it follows that the found parameters of kinetic relations have certain physical meaning. In the case of activation energies this meaning is supported by an increase in activation energy with decreasing acid strength, in the case of rate constant by its correlation according to Brønsted relation. The validity of this relation was confirmed also for dehydration of cyclohexanol on the same series of catalysts. Logarithms of rate constants of this reaction correlate linearly with the

TABLE II

Standard Heats of Adsorption ΔH^0_{ads} (kcal/mol) and Standard Entropy[a] ΔS^0_{ads} (cal/mol grad) of Adsorption of tert-Butanol on Fractions of Sites of Varying Acid Strength

Fractions of sites	ΔH^0_{ads}	ΔS^0_{ads}
f_1	-25 ± 12	-62 ± 30[b]
f_2	-6 ± 2	-11 ± 6
f_3	-5 ± 3	-7 ± 6
f_4	-6 ± 3	-8 ± 6
f_5	$0 \pm 0{\cdot}5$	$+3 \pm 2$

[a] Standard state; the ideal gas of a pressure of 760 Torr and the surface covered from one half by adsorbate.[b] Standard entropy of gaseous tert-butanol[15] at 400 K and 760 Torr is 86·96 cal/mol grad.

logarithms of the rate constants of the dehydration of tert. butanol with the slope 1·04 (Fig. 6). Heat of adsorption, taken as the measure of the strength of adsorption bond, is greatest on the most acidic sites (this is followed also by the greatest entropy of adsorption, Table II). Heats of adsorption in the less acidic region are substantially smaller and are no more dependent upon acid strength. In agreement with this are also small entropies of adsorption on these less acidic fractions of sites, which indicates the presence of little ordered formation, presumably physically adsorbed mobile layer. It seems likely that on the least acidic sites the adsorption coefficients have no more any physical meaning ($\Delta H^0_{\mathrm{ads}}$ for the fraction f_5 was found to be close to zero and $\Delta S^0_{\mathrm{ads}}$ to be positive). It cannot be excluded, however, that in this case the mechanism of the reaction turns to noncatalytic one. This is indicated also by an increase in the values of activation energy with decreasing acid strength, these values approaching those observed usually for noncatalytic reactions.

The results of this work render it possible to ascertain to what extent the individual fractions of catalyst surface of different acid strength contribute to the total reaction rate. While the hitherto discussions[1] could only postulate the type of nonuniformity

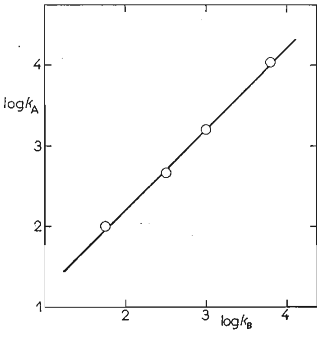

FIG. 6

Correlation of Logarithms of Rate Constants k (mol h^{-1} kg^{-1}) of Dehydration of Tert-Butanol (A, 120°C) with Dehydration of Cyclohexanol (B, 200°C) on Unpoisoned and Three Gradually Poisoned Catalysts

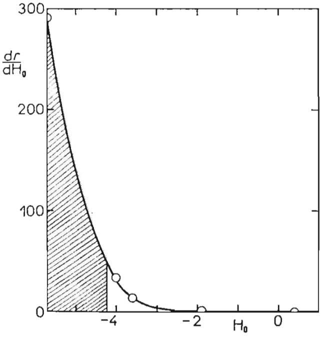

FIG. 7

Distribution of Reaction Rate r (mol h^{-1} . . kg^{-1}) of Dehydration of Tert-Butanol at 120°C and $p_A = 0{\cdot}4$ atm with Respect to the Acid Strength H_0 of Active Sites

Cross-hatched area corresponds to the reaction rate belonging to the interval of one and half unit of H_0 of the most acidic sites.

and have offered only hypothesis concerning its effect upon kinetics, in the present work we can support discussion by direct experimental data. We have found that the dehydration of tert-butanol is effected from 90% on the most acidic sites from the interval of one and half H_0 unit (this is represented by cross-hatched area in Fig. 7). These sites constitute only 5% of the total amount of acid sites of the Al_2O_3–MgO–SiO_2 catalyst (Table I). Therefore, only relatively narrow fraction of sites is catalytically important, whereas the contribution of the prevailing part of the other sites is negligible. The effect of the nonuniformity of acid surface can be thus neglected in deriving kinetic model for the real inorganic catalyst and it is possible to use the equations of Langmuir–Hinshelwood type.

LIST OF SYMBOLS

E	activation energy
F	feeding rate of tert-butanol
F/W	space velocity of tert-butanol
ΔH^0_{ads}	standard heat of adsorption of tert-butanol
H_0	Hammett acidity function
k	rate constant
k'	rate constant related to the equivalent of acid sites
K_A	adsorption coefficient of tert-butanol
m	amount of lithium captured on catalyst
p_A	initial partial pressure of tert-butanol
r	initial reaction rate of dehydration of tert-butanol
ΔS^0_{ads}	standard entropy of adsorption
W	amount of catalyst
x	degree of conversion

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