

KINETICS OF 1-BUTANOL, DI-(1-BUTYL) ETHER AND 1-BUTENE REACTIONS ON ALUMINAS PARTIALLY DEACTIVATED BY SODIUM

František KRAMPERA* and Ludvík BERÁNEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

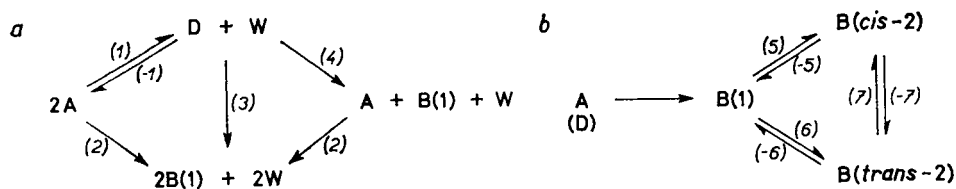
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Dedicated to late Academician Eduard Hála.

The initial rates of six reactions taking place in 1-butanol dehydration at 260°C in vapour phase were measured on alumina samples differing in sodium content. The reactants were 1-butanol, di-(1-butyl) ether and 1-butene, resp. The parameters of the best fitting rate equations for each reaction were evaluated. The reaction rates as well as the rate constants and adsorption coefficients of the individual reactions show different sensitivity to catalyst acidity. Therefore, the selectivity of product formation can be influenced by sodium content of the catalyst. The selectivities (with the exception of 1-butene isomerization) strongly depend also on the partial pressure of the starting reactants. Thus, these two factors can be used to control the selectivity for preparative purposes. The results of this paper clearly demonstrate the nonseparability of the deactivation kinetics in 1-butanol dehydration on sodium poisoned aluminas.

In the preceding paper¹ we have investigated the system of reactions occurring when 1-butanol is catalytically transformed in vapour phase on alumina: the ether and olefin forming dehydrations of 1-butanol, olefin forming dehydration and disproportionation of di-(1-butyl) ether, and isomerization of 1-butene to *cis*- and *trans*-2-butene. The validity of the following complex reaction network has been verified (Schemes 1a and 1b):



SCHEME 1

* Present address: Research Institute for Organic Syntheses, 532 18 Pardubice-Rybitví.

We have found the best fitting kinetic equations for initial rates of the reactions (1) to (6) of the Schemes 1a and 1b and evaluated the parameters of the equations. We also have expressed the reversible inhibiting effect of water on the rate of these reactions.

The general reaction network of alcohol dehydration can serve as a suitable model for studying the problems of selectivity and selective catalyst poisoning. The poisoning by metal ions, above all by alkali metal ions²⁻¹⁷, or by organic nitrogen base^{2,6,14,15,18-21} is most frequently used for this purpose. As a rule, the olefin formation is more suppressed than the ether formation by catalyst poisoning, and, as far as olefins susceptible to isomerization are formed, the isomerization is more strongly inhibited by poisons than the dehydration. The effects of the above mentioned poisons on the ether transformations have been much less investigated.

In the present paper we have studied the effect of addition of sodium ions to alumina on the kinetics of the six reactions of the 1-butanol dehydration network. We have followed the changes of the parameters of rate equations in dependence on the amount of the poison added. This enabled us to express the effect of successive catalyst deactivation on the selectivity of formation of individual products and to get information regarding the sensitivity of various reactions to catalyst acidity. This may be of importance in practical preparation of alumina as a carrier or a catalyst; during its production a certain amount of sodium can get into the product influencing thus strongly its final properties.

One of the aims of this paper was also to contribute to the discussion on the separability or non-separability of the kinetics in mathematical modelling of catalyst deactivation²²⁻²⁵. Contrary to earlier views²⁶⁻³³ assuming that in modelling the deactivation kinetics the effect of actual reaction conditions (concentration, temperature) can be separated from the past history of the catalyst (the deactivation itself), the opinion is now widely accepted^{13,21,34-39} that these two effects cannot be separated in mathematical description of the reaction kinetics on catalyst with decreasing activity. The problem is more general but it has been studied also in connection with the alcohol (methanol and ethanol) dehydration on alumina deactivated by sodium ions¹³ or on aluminosilicate poisoned by 1-butylamine²¹.

EXPERIMENTAL

Chemicals: 1-Butanol, di-(1-butyl) ether, 1-butene and nitrogen were of the same origin and were purified in the same way as described in the paper¹. Sodium hydroxide was analytical grade (Lachema, Brno).

Catalysts: Pure aluminium hydroxide (Pural SB, Condea Chemie GmbH, F.R.G.) was kneaded at room temperature for 1 h with distilled water or sodium hydroxide solutions of different concentration to form a paste which was then extruded at 3.5 MPa. For further treatment of the extrudates see preceding paper¹. Five alumina catalysts differing in the sodium

content (0.0, 0.09, 0.17, 0.31, 0.50 wt. %) were prepared in this way. Textural characteristics of these catalysts did not reveal any trend in dependence on the sodium content and varied rather randomly in the following ranges: BET surface between 198 and 250 m² g⁻¹, pore volume between 0.48 and 0.61 ml g⁻¹, most frequent pore radius between 3.4 and 4.0 nm. The surface acidity was measured by the indicator method according to Benesi^{40,41} with the use of Dimethyl Yellow, benzeneazodiphenylamine and anthraquinone (all analytical grade, Lachema Brno). Total acidity and acid strength distribution of the catalysts are given in Table I.

The apparatus and procedure, gas chromatographic analysis of the reaction products and the procedure of initial reaction rate determinations were described in the preceding paper¹. The length of the periods necessary to achieve steady catalyst activities became shorter with increasing sodium content; with the catalyst containing 0.5 wt. % sodium, the steady activity was achieved during 3 hours.

RESULTS AND DISCUSSION

Kinetics of Single Reactions

In the same way as for pure alumina in the preceding paper¹ the initial rates of the reactions (1) to (6) (Schemes 1a and 1b) were measured in this paper at 260°C on four alumina catalysts poisoned with various amounts of sodium ions. The transformations of 1-butanol, di-(1-butyl) ether and 1-butene were investigated separately in the low conversion region. The last of these reactions was studied only on aluminas containing 0.09 and 0.17 wt. % Na; on more deactivated aluminas the isomerization of 1-butene was too slow to be reliably measured. The isomerization of 2-butenes was not investigated. The dependencies of initial rates r^0 of the reactions (1) to (4) on the initial partial pressure of the starting reactant are shown in Figs 1 and 2.

TABLE I
Surface acidity of the aluminas

Na content c_{Na} , wt. %	Acid strength distribution ^a , mmol g ⁻¹				Total acidity, $\sum A_i$	
	A_1	A_2	A_3	A_4	mmol g ⁻¹	$\mu\text{mol m}^{-2}$
0.00	0.050	0.075	0	0.075	0.20	1.0
0.09	0.025	0.125	0.075	0	0.225	0.90
0.17	0.025	0.10	0.025	0	0.15	0.68
0.31	0	0.10	0.025	0	0.125	0.63
0.50	0	0.05	0.025	0	0.075	0.35

^a A_1 – A_4 represent the acidities in the acid strength regions defined by the following values of the Hammett acidity function H_0 : A_1 : $3.3 \geq H_0 \geq 1.5$; A_2 : $1.5 \geq H_0 \geq -5.6$; A_3 : $-5.6 \geq H_0 \geq -8.2$; A_4 : $H_0 \leq -8.2$; A_1 determined with accuracy $\pm 15\%$.

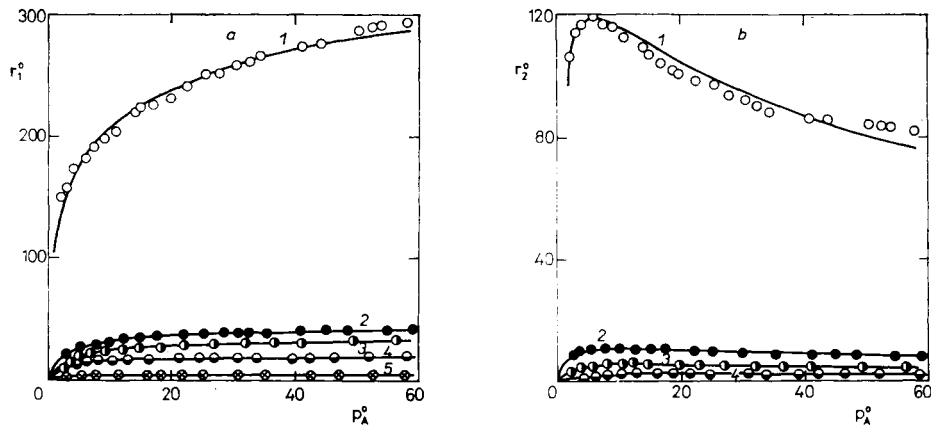


FIG. 1

Dependencies of initial rates of 1-butanol transformations r_j^0 ($\text{mol h}^{-1} \text{kg}^{-1}$) on its initial partial pressure p_A^0 (kPa) catalyzed by aluminas with different sodium content (wt. % Na): 1 0.0, 2 0.09, 3 0.17, 4 0.31, 5 0.50. The points are experimental values, the curves were calculated with the use of the rate equations and parameter values shown in Table III. *a* ether formation (r_1^0), *b* olefin formation (r_2^0)

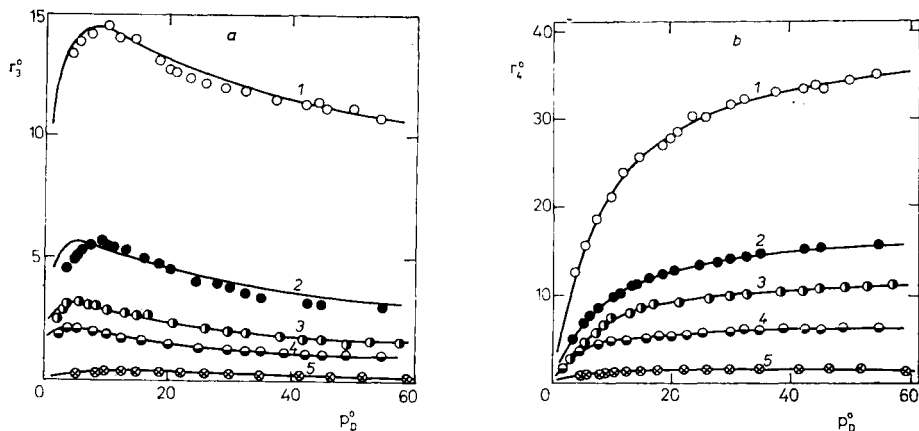


FIG. 2

Dependencies of initial rates of di-(1-butyl) ether transformations r_j^0 ($\text{mol h}^{-1} \text{kg}^{-1}$) on its initial partial pressure p_B^0 (kPa) catalyzed by aluminas with different sodium content. Denotation of the curves see Fig. 1. The points are experimental values, the curves were calculated with the use of the rate equations and parameter values shown in Table III. *a* olefin formation (reaction (3)), *b* disproportionation (reaction (4))

The r^0 dependencies of the formation of cis- and trans-2-butenes (reactions (5) and (6)) on the initial partial pressure of 1-butene were almost linear.

Figs 1 and 2 show the ether reactions (3) and (4) to be less sensitive to the content of sodium in alumina than the alcohol reactions (1) and (2). That means they are less dependent on the catalyst acidity (see also Table II summarizing the relative catalyst activities for the investigated reactions measured at $p^0 = 50$ kPa). It is worth mentioning that we found here (similarly as with pure alumina¹) a certain analogy between reactions (1) and (4) on one side and reactions (2) and (3) on the other side; in the latter case the reaction isotherms pass through a maximum whereas in the former case they have an asymptotic form. Table II also reveals that the ether formation from the alcohol (reaction (1)) is less sensitive to catalyst poisoning by sodium ions than the olefin formation (2) (see also^{12,16}), and the disproportionation of the ether (4) is less sensitive than the decomposition to the olefin (3). In other words, we again find a similarity between the reactions (1) and (4) on one side and the reactions (2) and (3) on the other side. This observation might be connected with the fact that we are dealing with two pairs of chemically related reactions: in the elimination reactions (2) and (3), all C—O bonds are split and only olefin and water are formed, whereas in the case of the substitution reactions (1) and (4) at least one C—O bond is retained since ether or alcohol are formed. Therefore, the similarity of the kinetics and of the sensitivity to catalyst acidity might indicate also a similarity of the mechanism within each pair of the reactions mentioned.

A non-linear decrease of the initial rates of all reactions investigated with increasing sodium content in alumina can be seen from Table II; even a very slight Na

TABLE II

Relative activities of the catalysts r_{rel} in 1-butanol dehydration network in dependence on the sodium content c_{Na}

Na content c_{Na} , wt. %	Relative activities r_{rel}^a (%) in the reaction ^b						
	(1)	(2)	(3)	(4)	(1) + (2)	(3) + (4)	(5) + (6)
0.00	100	100	100	100	100	100	100
0.09	14.80	10.07	26.56	45.03	13.74	40.63	9.26
0.17	11.57	5.48	14.72	32.10	10.19	22.64	1.11
0.31	6.73	2.48	9.06	18.47	5.84	16.22	—
0.50	1.45	0.61	1.39	4.82	1.25	4.00	—

^a Relative activities r_{rel} were calculated from the r_j^0 values at the initial partial pressure of the starting reactant $p_i^0 = 50$ kPa and are related to the r_j^0 values of pure alumina; ^b denotation of the reactions see Schemes 1a and 1b.

content causes a remarkable loss of catalytic activity. The activity decrease is the most important with 1-butene isomerization and the sensitivity of the other reactions to catalyst poisoning diminishes in the following order: reaction (2) > reaction (1) > reaction (3) > reaction (4).

All the measured kinetic data $r_j^0 - p_i^0$ were treated, similarly as in the preceding paper¹, by the nonlinear regression with the use of a set of Langmuir-Hinshelwood and power-law type rate equations. For each catalyst and reaction the parameters of the best fitting equations were evaluated and the order of suitability of the equations determined. Although the order of suitability for a given reaction slightly varied in the series of the catalysts investigated, the differences were not statistically significant and for each reaction at least one rate equation could be found that satisfactorily described its kinetics on all the catalysts. These equations and their parameter values are given in Table III.

It follows from Table III that the values of rate constants k_j for all the reactions investigated decrease with increasing sodium deactivation of the catalyst; this could be expected with these acid catalyzed reactions. The decrease is, like that of the reaction rates in Table II, nonlinear but it differs for the individual reactions and can be approximately expressed by a logarithmic dependence. Since we have found (Table I) a linear relationship between the weight percentage of Na in the catalyst and its total acidity $\sum A_1$ ($\mu\text{mol m}^{-2}$) we have correlated the rate constants directly with total catalyst acidity using the equation

$$\log k = a + b(\sum A_1).$$

The sensitivity of the individual reactions to the catalyst acidity is expressed by the slopes b for which the following values were found:

Reaction	(1)	(2)	(3)	(4)	(5) + (6)
Slope b , $\text{m}^2 \mu\text{mol}^{-1}$	2.47	3.17	2.53	1.85	6.2

The order of sensitivity of the reactions to catalyst acidity resulting from the b values is in accord with the order estimated from relative reaction rates (Table II), with the exception of reactions (1) and (3); the difference of the b values for these reactions is, however, negligible.

Adsorption coefficients K_i in Table III reveal different trends. The adsorption coefficient of 1-butanol in the ether formation reaction (1) increase with sodium content of the catalyst (with the exception of the catalyst with 0.5 wt. % Na), whereas in the olefin formation reaction (2) this coefficient decreases. The adsorption coefficient of di-(1-butyl) ether in the olefin-forming reaction (3) increases (again except for the catalyst with 0.5 wt. % Na) while in the disproportionation reaction (4) it remains almost constant. The increase of K_A values in the ether-forming reaction

TABLE III
Rate equations and their parameters

Reaction <i>j</i> (see Schemes 1 <i>a</i> and 1 <i>b</i>)	Right hand side of the rate equation $r_j^0 = f_j(p_i^0)$	Param- eter ^a	Catalyst (Na content, wt. %)				
			0.0	0.09	0.17	0.31	0.5
(1)	$k_1(K_A p_A^0)^{0.5}/[1 + (K_A p_A^0)^{0.5}]$	k_1	390	55.5	43.2	25.5	5.4
		K_A	0.13	0.17	0.19	0.43	0.21
(2)	$8k_2 K_A p_A^0/[1 + (1 + 8K_A p_A^0)^{0.5}]^3$	k_2	953	81.6	43.4	20.7	4.15
		K_A	0.17	0.11	0.07	0.03	0.01
(3)	$k_3 k_D p_D^0/[1 + 2(K_D p_D^0)^{0.5}]^3$	k_3	387	147	81.5	55.4	6.4
		K_D	0.13	0.26	0.34	0.47	0.14
(4)	$k_4(K_D p_D^0)^2/(1 + k_D p_D^0)^2$	k_4	39.2	17.5	12.6	—	1.9
		k_D	0.29	0.30	0.29	—	0.33
(5)	$k_5 p_B^0(1)$	k_5	1.57	0.12	0.013	—	—
(6)	$k_6 p_B^0(1)$	k_6	0.316	0.041	0.0055	—	—

^a Dimensions: k_1, k_2, k_3, k_4 ($\text{mol h}^{-1} \text{kg}^{-1}$); K_A, K_D (kPa^{-1}); k_5 and k_6 are products of rate constant and adsorption coefficient and have dimension $\text{mol h}^{-1} \text{kg}^{-1} \text{kPa}^{-1}$.

of 1-butanol can be explained by the enhancement of alcohol chemisorption with increasing catalyst basicity what is in agreement with the mechanism of ether-forming reaction proposed by Figueras et al.⁴². On the contrary, the reason of the decrease of K_A values in the olefin-forming reaction (2) might be in the decrease of the number of stronger acidic centers which are, together with the weakly basic centers, necessary for alcohol chemisorption leading to olefin formation⁴².

Selectivity

It follows from the different sensitivity of individual reactions of Schemes 1a and 1b to catalyst acidity that also the selectivity must significantly vary in dependence on sodium deactivation. Besides, the different kinetics of individual reactions result in an effect of partial pressure of starting reactants on the selectivity. The situation is demonstrated for 1-butanol transformation in Fig. 3. Here the selectivities $S_{2/(1+2)}$ of butene formation defined as $r_2^0/(r_1^0 + r_2^0)$ are plotted in dependence on 1-butanol initial partial pressure for aluminas deactivated to a different degree. With pure alumina and alumina with 0.09 wt. % Na the selectivity of butene formation monotonously decreases with 1-butanol partial pressure while for more poisoned aluminas this dependence passes through a maximum. The form of these curves results from different kinetics of olefin-forming and ether-forming dehydrations of 1-butanol (see Fig. 1 and the corresponding rate equation in Table III). Analogous curves for the selectivity $S_{3/(3+4)}$ in the transformation of di-(1-butyl) ether defined as $r_3^0/(r_3^0 + r_4^0)$ present very similar features: they monotonously descend for less deactivated aluminas and pass through a maximum for more deactivated aluminas. The selectivity of *cis*- and *trans*-2-butene formation in the isomerization of 1-butene does not practically vary with the reactant partial pressure; this is a consequence

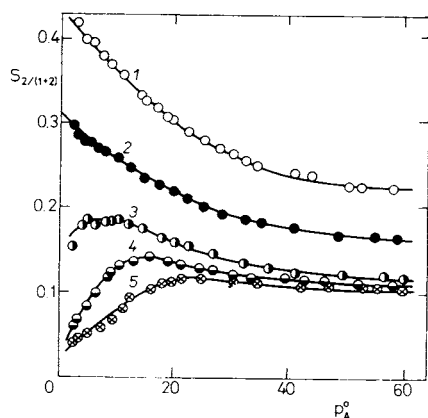


FIG. 3

Dependence of the selectivity $S_{2/(1+2)}$ on initial partial pressure of 1-butanol p_A^0 (kPa) on aluminas with different sodium content. Denotation of the curves see Fig. 1

of very similar kinetics of the two reactions closely approaching a first order rate law.

Fig. 3 also reveals how strong is the effect of sodium content in the catalyst on the selectivity $S_{2/(1+2)}$ of butene formation from 1-butanol. The decline of the catalyst selectivity for olefin-forming dehydration of 1-butanol with increasing Na content is much more pronounced at low partial pressure of the starting reactant; a similar feature is revealed by the selectivity of olefin-forming reaction $S_{3/(3+4)}$ in di(1-butyl) ether transformation. Table IV presents the selectivities $S_{2/(1+2)}$ and $S_{3/(3+4)}$ calculated from experimental rate data measured for partial pressures of starting reactants equal to 10 kPa on aluminas deactivated to a different degree. The selectivity decrease of olefin-forming elimination with sodium poisoning is more pronounced in the case of 1-butanol dehydration than in the case of di-(1-butyl) ether transformation. In the 1-butene isomerization where the effect of reactant partial pressure on selectivity was not significant, the selectivity of *cis*-2-butene formation slightly decreases with Na content in the catalyst in favour of *trans*-2-butene; the decrease is approximately linear.

TABLE IV

Effect of sodium content in alumina on the selectivity

Na content C_{Na} , wt. %	Selectivity				
	Parallel reactions ^a			Consecutive reactions ^b	
	$S_{2/(1+2)}$ ^c	$S_{3/(3+4)}$ ^d	$S_{5/(5+6)}$ ^e	$S_{(5+6)/2}$ ^f	$S_{(3+4)/1}$ ^g
0.0	0.363	0.406	0.825	0.170	0.177
0.09	0.259	0.370	0.778	0.137	0.488
0.17	0.182	0.301	0.735	0.033	0.403
0.31	0.127	0.277	—	—	0.407
0.5	0.071	0.205	—	—	0.380

^a Expressed as the fraction of the total initial rate of the reactant transformation corresponding to the given reaction branch at the initial partial pressure of the starting reactant equal to 10 kPa;

^b expressed as the ratio of the total initial rate of the transformation of the given reaction intermediate to the initial rate of its formation by the reaction indicated, measured separately at the initial partial pressure of the corresponding reactants equal to 10 kPa; ^c selectivity of the olefin formation (reaction (2)) in 1-butanol dehydration; ^d selectivity of the olefin-forming reaction (3) in the di-(1-butyl) ether transformation; ^e selectivity of *cis*-2-butene formation in 1-butene isomerization; ^f selectivity of 1-butene isomerization related to its formation by reaction (2); ^g selectivity of di-(1-butyl) ether transformations by reactions (3) and (4) related to its formation by reaction (1).

Besides the effect of catalyst deactivation in the above mentioned parallel reactions, also the selectivity in some systems of consecutive processes can be estimated, namely the formation and subsequent isomerization of 1-butene and the formation and subsequent decomposition of di-(1-butyl) ether. Of course, these selectivities could be evaluated only from the r^o ratio of reactions investigated separately at equal initial partial pressure of the starting reactant. Since the isomerization of 1-butene is more suppressed by the addition of sodium to the catalyst than its formation from 1-butanol (see Table II), the participation of the subsequent olefin isomerization in 1-butanol dehydration becomes negligible at higher sodium content (see the values $S_{(5+6)/2}$ in Table IV). The selectivity in the consecutive system of di-(1-butyl) ether formation and decomposition ($S_{(3+4)/1}$) vary irregularly and not very markedly with Na content of the catalyst. However, the selectivity of ether formation in the complex system of reactions occurring when 1-butanol is dehydrated will very probably increase with progressive catalyst deactivation, because particularly the selectivity of its formation from 1-butanol (reaction (1)) is enhanced at the expense of the olefin-forming reaction (2) (see the values of $S_{2/(1+2)}$ in Table IV).

It is worth noting that all the mentioned trends in selectivities resulting from the addition of sodium to the catalyst are very similar to the selectivity changes caused by the addition of water to the reactant feed¹. Water exerted the strongest inhibiting effect on relative participation of isomerization reactions and less strong effect on that of olefin-forming reactions; the less influenced was the disproportionation of ether. Also the difference in the sensitivities of alcohol and ether transformations to the addition of water as well as the trend in the selectivity of *cis*- and *trans*-2-butene formation are similar to those resulting from the addition of sodium to the catalyst. As it has been already mentioned, the addition of sodium to alumina causes changes of acid-base properties of its surface (the total acidity decreases). The reversible inhibiting effect of water on the individual reactions of the system under study can be explained by chemisorption of water on catalytically active sites¹. For these reasons, it can be deduced from the similarity between the effect of the modification of surface acidity by sodium and the reversible effect of water added to the reactant feed on the selectivities that the reversible adsorption of water might be associated with acidic sites of alumina.

It follows from the presented results that the modification of alumina by sodium and the proper selection of reactant partial pressure can be used in praxis as efficient tools for influencing the selectivity in 1-butanol dehydration. If di(1-butyl) ether is to be prepared, the selectivity of its formation can be enhanced when a not very acidic or even slightly basic catalyst is used. A similar effect exert lower reaction temperature, higher 1-butanol partial pressure and the selection of such a value of time variable (space time) at which the conversion of 1-butanol does not exceed 50% (for details see^{4,3}). Changing the catalyst and reaction conditions in an opposite way would stimulate the formation of butenes. When the content of 2-butenes should

be minimized in the preparation of butenes, a weakly acidic alumina is to be used with which the subsequent isomerization of 1-butene is less important but which is active enough to catalyze the dehydration of 1-butanol at temperatures below 300°C and at reasonably low values of time variable. The addition of water is also able to suppress isomerization. At any case, the requirements on the purity of 1-butene and the admissible lowering of 1-butanol conversion to butenes have to be balanced.

Separability or Non-separability of the Kinetics

The results of this study enable us to discuss the problem of separability or non-separability of the kinetics of 1-butanol dehydration when the catalyst is progressively poisoned by sodium ions. According to Bakshi and Gavalas²¹, the nonseparable kinetics manifests itself by the following effects:

- a) the ratio $r(c, m)/r(c, n)$, where m and n represent two different poisoning states, is markedly changed with varying concentration c of reaction components;
- b) the selectivity of formation of individual products changes with the extent of poisoning;
- c) the values of the constants of rate equations vary significantly with the extent of poisoning.

As it can be deduced from the Figs 1 and 2, the ratio of the rates of each of the investigated single reactions for any different poisoning states is strongly dependent on the partial pressure of 1-butanol and di-(1-butyl) ether, resp. Thus, the criterion a) is complied with, which is considered in the literature^{13,25} to be the most important proof of nonseparable kinetics. Therefore, the results in Figs 1 and 2 allow us to claim that the kinetics of reactions, occurring when 1-butanol is dehydrated on alumina successively poisoned by sodium, is of the nonseparable type. This conclusion is supported also by the results in Fig. 3: they demonstrate a strong dependence of the ratio of the selectivity olefin/ether for any different poisoning states on the initial partial pressure of 1-butanol. The same was found for the ratios of the selectivity of reactions (3) and (4) in di-(1-butyl) ether transformation.

Table IV demonstrates the dependence of the selectivities on the extent of catalyst poisoning (point b)). However, Forzatti et al.¹³ doubt that this point is an unambiguous proof of nonseparable kinetics.

On the contrary, point c), even though it is considered in the literature to be a less direct proof of the nonseparability¹³ than point a), is complied with in our case. As we have already discussed, the constants of the rate equations of individual reactions occurring in the investigated system strongly depend on the poisoning degree. Especially the variations of the values of adsorption coefficients in reactions (1), (2) and (3) can be considered as an evidence of the nonuniformity of active centers. Thus, the basic assumption of the nonseparable model of the kinetics is fulfilled.

Our results allow us, therefore, to conclude definitely that the deactivation kinetics in 1-butanol dehydration on alumina progressively deactivated by sodium ions cannot be described by the simplified model of the separable type.

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LIST OF SYMBOLS

a	absolute term in the linear relation between $\log k$ and total acidity $\sum A_1$
A_1, \dots, A_4	acidity in the regions of acid strength defined in Table I
$\sum A_1$	total acidity of the catalyst
b	slope of the linear relation between $\log k$ and $\sum A_1$
c	concentration
k	rate constant
K_A, K_D	adsorption coefficient of 1-butanol and di-(1-butyl) ether, resp.
m, n	poisoning states
r_{rel}	relative reaction rate
r^0	initial reaction rate
p^0	initial partial pressure
S	selectivity

Substances

A	1-butanol
B(1)	1-butene
B(<i>cis</i> -2)	<i>cis</i> -2-butene
B(<i>trans</i> -2)	<i>trans</i> -2-butene
D	di-(1-butyl) ether
W	water

Indices (subscripts)

i	reaction component
$j (= 1, \dots, 6)$	reactions in Schemes 1a and 1b
$l (= 1, \dots, 4)$	region of acid strength defined in Table I

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