GEOMETRIC FACTOR IN DEHYDRATION OF ALCOHOLS ON X AND Y ZEOLITES

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Geometric conditions for dehydration of alcohols on X and Y zeolites have been studied with the aid of computer constructed models. On the basis of these calculations conditions for two-site adsorption on different pairs of skeletal oxygen atoms in *syn*- and *anti*-elimination course of the reaction are discussed and the most suitable reaction sites are selected. Results of these computations were used to interpret experimental facts such as the preferential formation of *cis*-2-alkenes in the course of dehydration and the dependence of catalyst activity on the size and number of the cations present in zeolite skeleton.

Elimination reactions on polar catalysts have been studied for several decades. Especially in recent years, much information has been collected[1] allowing the deeper insight into regularities controlling these processes. The majority of published works is devoted to dehydration of alcohols[2]. Attention was paid also to the catalytic activity of zeolites[3,4]. In addition to experimental studies also the number of theoretical works increases significantly which are concerned both with heterogeneously catalysed dehydration[5–8] and with surface[9–13] and catalytic[14–16] properties of zeolites.

On the basis of this knowledge one can assume that regardless of the catalyst, the reaction involves two types of adsorption sites, *i.e.* acidic and basic ones[1,2]. In the course of dehydration, the alcohol molecule is first adsorbed *via* oxygen of its hydroxyl groups on the acidic site of the catalyst, which is most likely the proton of surface hydroxyl[4,17–19]. Interaction with acidic site (electron acceptor) induces changes in the alcohol molecule which start dehydration[5–8] — *i.e.* weakening of C_α—O bond and C_β—H bond and distinct increase in the positive charge on the hydrogen atom bonded to the β-carbon atom. The most strongly activated is the hydrogen in antiperiplanar or synperiplanar positions with respect to the hydroxyl[7]. In further stage of the reaction the basic catalyst site (electron donor) interacts with H_{anti} or H_{syn} atom, which results in successive (E1 or E1cB) or concerted cleavage of C_α—O and C_β—H bonds (E2 mechanism)[1,2].

Experimental[20] and theoretical[5–8] studies have demonstrated a great similarity between the course of dehydration of alcohols in the liquid phase catalysed by strong acids and on gas–solid interface. Observed differences, *e.g.* the fact that among primary products of heterogeneously catalysed reaction *cis*-2-alkene is prevailing over thermodynamically more stable *trans*-2-alkene[1,2], can be readily explained by the effect of different geometric conditions acompanying the interaction of alcohol molecule with essentially freely movable solvent molecules in the former case and with the fixed surface sites in the latter case[21,22].

The present work continues our recent study on the geometric conditions in dehydration of alcohols on γ-Al_2O_3 and ThO_2 (ref.[22]). With the aid of computer constructed models we were able to interpret simply several experimental facts which until recently could be explained only with difficulty such as: *a*) the possibility of *anti*-elimination with participation of the pair of surface sites, *b*) the high content of *cis*-2-alkenes in the primary products of the dehydration on γ-alumina, *c*) the high selectivity of ThO_2 with respect to the formation of 1-alkenes from secondary alcohols. The aim of this work was to examine analogously geometric conditions for the dehydration of alcohols on X and Y zeolites and to interpret such experimental facts as the effect of the size of the cation present in zeolites skeleton on dehydration reaction[23-28] and the *cis*/*trans* ratio of 2-alkene isomers which is for primary products of the dehydration of secondary butanol[28-31] quite different from that given by thermodynamic equilibrium.

METHODS

Models

Models used to investigate geometric conditions for the dehydration of alcohols on X and Y zeolites were constructed with the aid of a computer under assumptions, the suitability and justification of which in relation to catalysis were discussed in the previous work[22]. Based on these assumptions, the molecule of alcohol interacts by its oxygen with the proton of skeletal hydroxyl groups and at the same time by the hydrogen bonded to β-carbon with skeletal oxygen.* For this case the two energetically favourable[7] conformations of hydroxyl group with respect to the β-hydrogen to be cleaved off are considered: the mutually antiperiplanar and synperiplanar position corresponding to *anti*-elimination and *syn*-elimination course of the reaction.

In constructing the models of alcohol molecules and of skeletal hydroxyl, standard bond lengths were used[32] (O—H 96 pm, C—H 109 pm, C—O 143 pm, C—C 154 pm). The distance between oxygen and hydrogen in the hydrogen bond equaled to 160 pm (ref.[33]). Bond angles in the alcohol molecules were tetrahedral. Except for the C_α—O bond, all the dihedral angles in the molecule of the alcohol corresponded to staggered conformations. Models of three different parts of zeolite skeleton were constructed with the use of the structural data obtained by X-ray diffraction[34]. Metal cations were placed into the zeolite skeleton to appropriate positions[35,36] in the distances from skeletal oxygen given by ion radii[37].

Geometric models of the reactant-catalyst complexes were constructed with computer in the following way: *a*) Provided that the adsorption proceeds *via* two hydrogen bonds (between skeletal hydroxyl and oxygen of the alcohol and between skeletal oxygen and β-hydrogen, the O_{skel}—H...O_{alc} and O_{skel}—H...C_β atoms being colinear), by rotation around the C_α—O bond

* Simultaneous interaction with two catalyst sites is selfevident requirement in the case of concerted *anti*-elimination proceeding by E2 mechanism. Nevertheless, even for successive cleavage of the key bonds by E1 and E1cB mechanisms, the molecule passes necessarily through the stage in which it is adsorbed on two sites. In the course of breaking the first of the bonds cleaved, in utmost case, the adsorption bond to the remaining part of the molecule must be formed to ensure the adsorption of the molecule.

such a conformation has been found in which both catalytic sites (O_{skel}—H and O_{skel}) have the distance which is identical with that of the chosen pair of oxygens of zeolite skeleton. From Fig. 1 which demonstrates this situation, it is evident that the alcohol molecule in the conformation suitable for *anti-* and *syn*-eliminations can be adsorbed only on the pairs of sites, the distance between which lies within a certain interval. Under the structural conditions accepted, this interval is 101—560 pm for *syn*-elimination and 557—671 pm for *anti*-elimination[22]. *b)* Molecule of the alcohol obtained by the above method is, as such, subjected to translation and rotation so that the presumed positions of skeletal oxygens (Fig. 1) are identified with the position of the chosen pair of oxygen atoms in the model of zeolite. *c)* By rotation of the alcohol molecule around the joint of the two skeletal oxygen atoms which are adsorption sites in this case, such a configuration of the whole system is sought for which the distance between the reactant and the catalyst is maximal. In this work, the reactant-catalyst distance is defined as the distance between the centres of the two closest atoms of the reactant and of the catalyst from which the sum of the radii of these atoms is substracted. Similarly as in our previous work[22], the radii of these atoms were chosen so that the atoms connected *via* chemical bond be in mutual contact. The above radii so defined differ significantly from the ion radii[37] widely used in depicting crystal structures. On the the other hand, their values are close to valence radii with which they share a similar definition[38]. The sum of the so defined radii of two atoms corresponds to the length of their chemical bond and in this work it is understood as the minimal distance to which both atoms can approach each other.

Calculations

For writting the programme realizing the above operations, several relations were derived which are valid in the case of rotation of the alcohol molecule around the joint of catalytic sites identified with the y coordinate. The distance between the pair of the reactant and catalyst atoms depends on the rotation according to the following relation (*1*)

$$l_{ij} = [r_i^2 + r_j^2 + 2(P_1 \sin \omega - P_2 \cos \omega - P_3)]^{1/2} \qquad (1)$$

$P_1 = x_i z_j - z_i x_j$; $P_2 = x_i x_j + z_i z_j$; $P_3 = y_i y_j$; $r_i^2 = x_i^2 + y_i^2 + z_i^2$; $r_j^2 = x_j^2 + y_j^2 + z_j^2$, where x_i, y_i, z_i, x_j, y_j and z_j are the coordinates of both atoms prior to rotation and ω is the corresponding angle of rotation. By differentiation of Eq. (*1*) one can derive the relation for the maximal and minimal distance between the centres of a given pair of atoms (Eq. (*2*))

$$(l_{ij})_{min}^{max} = \{r_i^2 + r_j^2 + 2[\pm(P_1^2 + P_2^2)^{1/2} - P_3]\}^{1/2} \qquad (2)$$

and also the relation for the upper and lower boundary of the interval in which the distance of a given pair of atoms is greater than a certain limit value l_{lim} (Eq. (*3*)).

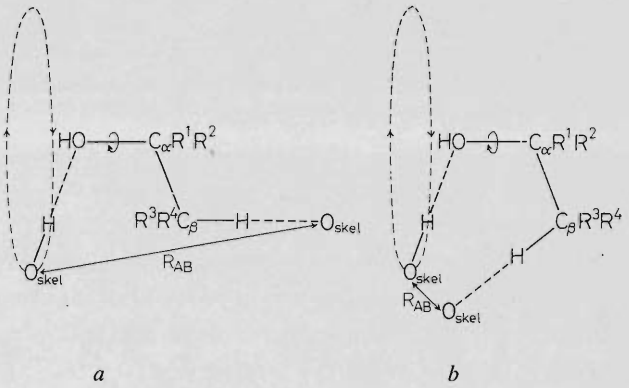
$$(\omega)_{lower}^{upper} = \text{arctg}\,\{[-AP_1 \pm P_2(P_1^2 + P_2^2 - A^2)^{1/2}]/[AP_2 \pm P_1(P_1^2 + P_2^2 - A^2)^{1/2}]\}$$

$$A = 0{\cdot}5(r_i^2 + r_j^2 - l_{lim}^2) - P_3\,. \qquad (3)$$

In the operation of the programme, the reactant and catalyst atoms were divided into two groups. The first group was formed by the atoms which are prerequisite for the course of the reaction (atoms of zeolite skeleton and the atoms of alcohol molecules, C_α, C_β, H_β, O and H_{OH}). The second group comprised the atoms, the presence of which was not prerequisite (metal cations present in zeolite skeleton and hydrogen atoms or methyl groups bonded to the α- or β-carbon atoms). In the first stage of the calculations we examined by using Eq. (*2*) whether the maximal

distance between the centres of all the possible pairs of reactant and catalyst atoms belonging to the first group is greater than the sum of the corresponding atom radii.

The further stage involved the determination of the overlap of all the intervals of the angle of rotation calculated according to Eq. (*3*) for all the possible pairs of reactant and catalyst atoms, the limit distance l_{lim} being given by the sum of corresponding atom radii. With the use of Eq. (*1*) the configurations with maximal distance between reactant and catalyst were systematically sought for in the intervals determined above. At the same time also all the possible combinations of the present atoms belonging to the second group (metal cations, methyl groups) were systematically taken into account. With regard to the fact that for a given distance between catalyst sites (except for the maximal and minimal distance) one can find always two conformations of the C_α—O bond in alcohol molecule (Fig. 1 — positions of the O_{skel}—H groups lying symmetrically



a *b*

FIG. 1

Schemes illustrating change in the distance of the pair of acidic (O_{skel}—H) and basic (O_{skel}) catalytic site on rotation around the C_α—O bond of the alcohol molecule *a* for *anti*-elimination reaction; *b* for *syn*-elimination reaction. Presented conformations correspond to minimal possible distance between the above sites

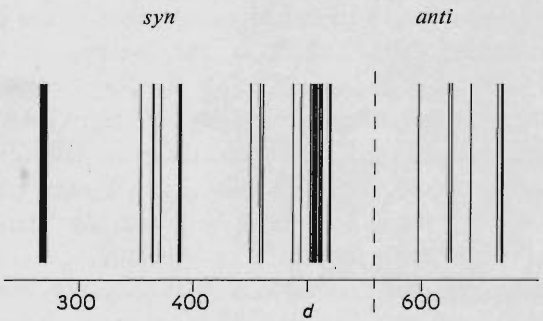


FIG. 2

Spectrum of distances between skeletal oxygen atoms (in pm) in X and Y zeolite with designation of regions of the pairs of sites suitable for *syn*- and *anti*-elimination

above and below the plane of drawing) and further with regard to the two possible absolute configurations of the bonds on the oxygen of the alcohol molecule (we deal with four differently occupied bonds pointing to the corners of tetrahedron - free electron pair, proton, α-carbon and hydroxyl of zeolite skeleton), for a given distance between adsorption sites one can construct four geometrically different configurations of adsorbed alcohol molecule. The calculation examining geometric conditions for adsorption on the pair of centres with a given distance was then done for each of these structures, *i.e.* four times. Of the three models of zeolite skeleton, we selected always that for which the vicinity of the studied pair of catalytic sites was as wide as possible.

RESULTS AND DISCUSSION

In the regions of the competent distances 7 pairs of oxygen atoms have been found in zeolite skeleton to be located in the distance corresponding to *anti*-elimination and 28 pairs with the distance corresponding to *syn*-elimination, as documented by Fig. 2. Let us pay attention first to the energetically more favourable *anti*-elimination[7].

Results of calculations relating to the *anti*-elimination are summarized in Table I which presents data for 4 pairs of skeletal oxygens. On the remaining three pairs shown in Fig. 2, *i.e.* O2–O3 (597·1 pm), O3–O4 (623·6 pm) and O3–O4 (669·8 pm), no alcohol molecule can be adsorbed, as proved by calculation; this holds even for the case when all the neighbouring positions of metal cations remain unoccupied.

The quality of geometric conditions for two-site adsorption can be evaluated on the basis of both types of quantities presented in Table, *i.e.* the maximal possible distance between the reactant and the catalyst (for definition see Methods) and the deviation of the adsorption bond from optimal direction[9,34]. One should take into account also the affinity to proton of the skeletal oxygens forming the pair of adsorption sites. As documented by extensive experimental[34,35,39–42] and theoretical[9,10] study, the affinity to proton is highest for oxygens of the O1 and O3 type[34]. At the same time, the proton on atom O1 is located in the easily accessible position since it is oriented into a large cavity of the zeolite. The proton on atom O3 occurs within hexagonal prism, which is the inaccessible position for reactant[9,10,34,35,39–42].

Suitable acidic catalytic site is therefore mainly the hydroxyl HO1, the accessibility of which is much greater compared to HO3 and the frequency of its occurrence is substantially greater compared to HO2 and HO4. For the same reason, the atom O1 can be regarded as being the most suitable basic site. As follows from deviations of the adsorption bond from the optimal direction, atom O3 is accessible only from the site opposite to that regarded as suitable. Atoms O2 and O4 are not ready proton acceptors. These atoms accept proton at most only temporarily, before being transferred to the energetically more suitable O1 or O3 position[39,43].

If one considers the three above mentioned factors (*i.e.* the type of skeletal oxygen, maximal possible distance between the reactant and the catalyst and the deviation

TABLE I

Geometric conditions of two-site adsorption of alcohols on the pair of *anti*-elimination sites. Adsorption sites are hydroxyl group and oxygen atom, which are constituents of the skeleton of X and Y zeolite containing Na of K cations in positions S_{II} and S_{III}[35,36] (Fig. 6). Stereoscopic figures of all the structures presented in the table are available on request

R_{AB}[a]	A—B[b]	Vacancy	Type of site	Na			K		
				l_{max}[c]	Θ_A[d]	Θ_B[d]	l_{max}	Θ_A	Θ_B
626·2	O1—O1	S_{III}	1[e]	65·5	59	78	65·5	59	78
			C[e]	60·8	58	79	43·1	49	56
			T[e]	21·4	80	65	21·4	80	65
	O1—O1	S_{II}, S_{III}	1	65·5	59	78			
			C	65·5	59	78		see Na	
			T	21·4	80	65			
642·9	O1—O2	S_{II}	1	27·8	64	44	22·8	61	41
			C	27·8	64	44	22·8	61	41
			T	7·3	60	8	7·3	60	8
	O2—O1	S_{II}	1	41·1	31	75	30·9	26	71
			C	12·5	44	69	—	—	—
			T	10·2	45	69	—	—	—
	O2—O1	S_{II}, S_{III}	1	49·2	37	80			
			C	36·2	40	83		see Na	
			T	11·1	44	87			
666·3	O3—O2	S_{III}	1	19·9	173	106			
			C	2·5	164	109		see Na	
			T	—	—	—			
	O2—O3	S_{III}	1	21·2	102	164			
			C	—	—	—		see Na	
			T	—	—	—			
671·0	O4—O4′	S_{III}	1	25·5	63	55	9·7	55	60
			C	4·3	93	83	—	—	—
			T	—	—	—	—	—	—
	O4—O4′	S_{II} S_{III}	1	25·5	63	53			
			C	13·5	82	51		see Na	
			T	2·7	79	51			
	O4′—O4	S_{III}	1	34·5	55	62	16·2	64	51
			C	14·4	83	45	—	—	—
			T	14·4	83	45	—	—	—
	O4′—O4	S_{II}, S_{III}	1	45·1	53	68			
			C	19·6	51	86		see Na	
			T	14·4	83	45			

[a] Distance of the pair of catalytic sites (in pm); [b] type of oxygen atoms[34] forming the pair of acidic (A) and basic (B) catalytic site; [c] maximal possible distance between the catalyst and the reactant (in pm, for definition see Methods); [d] deviation of the adsorption bond direction from optimal direction (in degrees); [e] possible formation of at most: 1 1-alkenes, C *cis*-2-alkenes and T *trans*-2-alkenes.

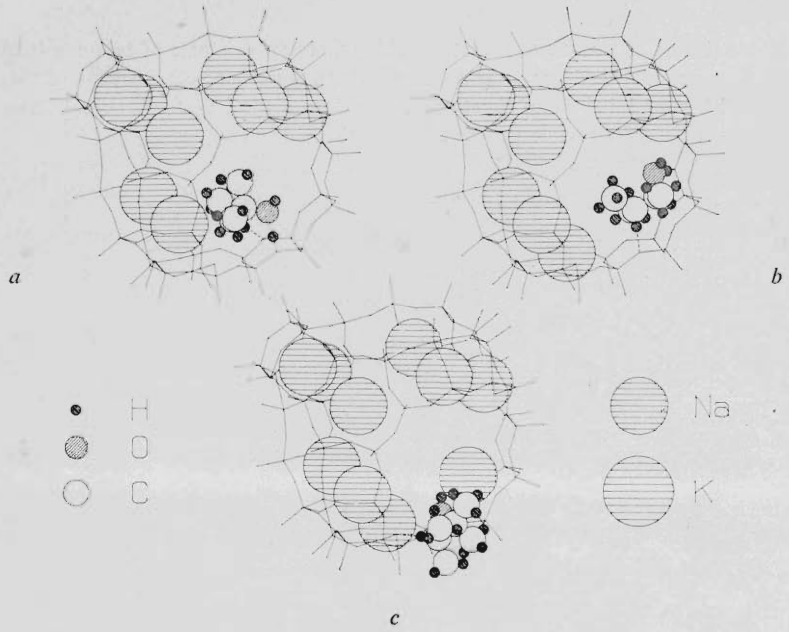


FIG. 3

Molecules of alcohols adsorbed on two sites in a large cavity of X and Y zeolites in configurations suitable for formation of *trans*-2-alkenes, *i.e.* on the pairs of skeletal oxygens O1—O1 with mutual distance *a* 371·4 pm; *b* 626·2 pm; *c* 504·2 pm. Circles on the sides of the lower part of the figure define the way by which atoms are depicted in this and in all the following figures. The choice of atomic radii is explained in Methods

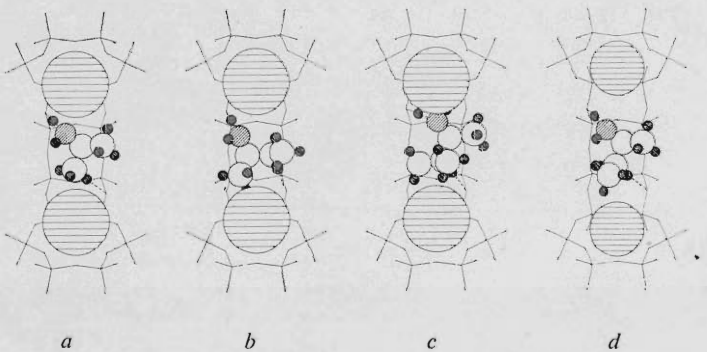


FIG. 4

Molecules of alcohols adsorbed on two sites in a large cavity of X and Y zeolite, *i.e.* on the pair of skeletal oxygen atoms O1—O1 with the distance 626·2 pm in the configuration suitable for formation of at most: *a* 1-alkene; *b cis*-2-alkene; *c trans*-2-alkene; *d cis*-2-alkene. The view from the centre of the cavity

of the adsorption bond direction), according to Table I the least suitable position for the adsorption appears to be the pair O3–O2 (666·3 pm). On this pair one could expect formation of the least sterically demanding 1-alkenes. However, geometric conditions for their formation are extremely unfavourable. Further pair, *i.e.* O4–O4′ (671·0 pm), creates conditions only somewhat better. But the oxygen of the type O4 cannot be expected to function readily as the acidic or basic centre. Of a certain usability in the real reaction can be the pair O1–O2 (642·9 pm) since the hydroxyl HO1 is readily accessible and sufficiently frequent acidic centre. However, geometric conditions allow here only *cis*-2-alkene formation. Undoubtedly best conditions for the reaction can be found for the pair O1–O1 (626·2 pm) (Fig. 3*b*). This is due to the high affinity of oxygens of the type O1 to proton as well as to favourable geometric conditions. The easy process is especially 1-alkene (Fig. 4*a*) and *cis*-2-alkene formation (Fig. 4*b*), *trans*-2-alkenes being markedly less favoured (Fig. 4*c* and Fig. 3*b*).

Concerning *syn*-elimination, the calculations were performed only for the pairs composed of atoms of the type O1 and O3 which exhibit relatively high affinity to proton. It was found that on pairs O3–O3 (364·9 om), O3–O3 (387·1 pm) and O1–O3 (458·1 pm) the alcohol molecule cannot be adsorbed, not even in the case when all the neighbouring positions of cations remain unoccupied. Data calculated for the remaining 4 couples of oxygens of the type O1 and O3 are presented in Table II.

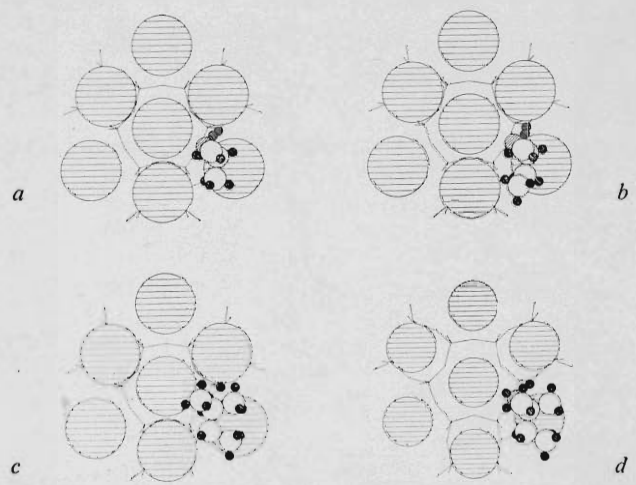


FIG. 5

Molecules of alcohols adsorbed on two sites in a large cavity of X and Y zeolite, *i.e.* on the pair of skeletal oxygens O1—O1 with the distance 504·2 pm in configuration suitable for formation of at most: *a* 1-alkene; *b* *cis*-2-alkene; *c* *trans*-2-alkene; *d* *trans*-2-alkene. The view from the centre of the cavity

TABLE II

Geometric conditions of two-site adsorption of alcohols on the pair of *syn*-elimination sites. Adsorption sites are hydroxyl group and oxygen atoms which are constituents of the skeleton of X and Y zeolites containing Na or K cations in positions S_{II} and S_{III}[35,36] (Fig. 6). Stereoscopic figures of all the structures presented in the table are available on request

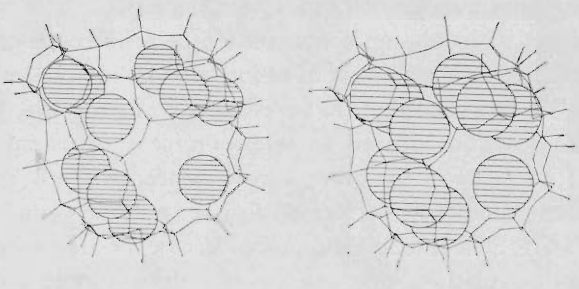
R_{AB}[a]	A—B[b]	Vacancy	Type of site	Na			K		
				l_{max}[c]	Θ_A[d]	Θ_B[d]	l_{max}	Θ_A	Θ_B
268·3	O1—O3	S_{III}	1[e]	16·4	85	161			
			C[e]	2·3	95	163		see Na	
			T[e]	2·3	95	163			
	O1—O3	S_{II}, S_{III}	1	16·4	85	161			
			C	11·7	100	161		see Na	
			T	11·7	100	161			
	O3—O1	S_{III}	1	33,4	163	80	33·4	163	80
			C	33·4	163	80	18·1	153	72
			T	21·1	159	77	8·1	154	73
371·4	O1—O1	S_{III}	1	57·0	65	58	41·2	64	60
			C	57·0	65	58	41·2	64	60
			T	51·6	66	56	27·8	65	58
	O1—O1	S_{II}, S_{III}	1	59·9	92	59			
			C	59·9	92	59		see Na	
			T	59·9	92	29			
504·2	O1—O1		1	46·2	31	28	34·1	38	12
			C	46·2	31	28	18·8	36	16
			T	38·0	39	10	15·0	47	5
	O1—O1	S_{III}	1	55·1	32	60			
			C	55·1	32	60		see Na	
			T	55·1	32	60			
505·9	O1—O3	S_{III}	1	14·6	85	151			
			C	9·6	86	154		see Na	
			T	9·6	86	154			
	O3—O1	S_{III}	1	33·2	164	37			
			C	33·2	164	37		see Na	
			T	33·2	164	37			

[a] Distance of the pair of catalytic sites (in pm); [b] type of oxygen atoms[34] forming the pair of acidic (A) and basic (B) catalytic site; [c] maximal possible distance between the catalyst and the reactant (in pm, for definition see Methods); [d] deviation of the adsorption bond direction from the optimal direction (in degrees); [e] possible formation of at most: 1 1-alkenes, C *cis*-2-alkenes and T *trans*-2-alkenes.

Pairs of sites containing oxygen O3, *i.e.* O1 – O3 (268·3 pm) and O1 – O3 (505·9 pm) show too great deviations of the adsorption bond on the O3 oxygen, similarly to analogous *anti*-elimination pairs, this deviation being about 160 degrees. Also calculated maximal reactant-catalyst distances are not favourable. Therefore, these pairs of sites do not create suitable conditions for the reaction. Distinctly better conditions have been found for pairs O1 – O1 (371·4 pm) (Fig. 3*a*) and O1 – O1 (504·2 pm) (Fig. 3*c*) on which 1-alkenes (Fig. 5*a*), *cis*-2-alkenes (Fig. 5*b*) and also *trans*-2-alkenes (Fig. 5*c*) can be formed with comparable ease.

According to calculations, geometric conditions for the most suitable *syn*- and *anti*-elimination pairs of sites are comparable, which allows to conclude that in dehydration of alcohols on X and Y zeolites *anti*-elimination is preferred process since it is energetically more favourable[7]. On the basis of the aspects discussed in the present work, the most suitable pair of sites for the reaction is the pair of skeletal oxygens O1 – O1 with the distance 626·2 pm (Fig. 3*b* and Fig. 4).

From the results of calculations one can draw also conclusions about the product composition in the dehydration of secondary butanol on X and Y zeolites which are in good agreement with experiment. Similarly as earlier[22] for γ-Al_2O_3, we found also for zeolites that steric demands concerning the formation of alkene isomers increase in the sequence 1-alkene, *cis*-2-alkene and *trans*-2-alkene. Differences in the ease of formation of individual isomers on zeolites are not, however, so distinct as are in the case of γ-Al_2O_3 for which we found[22] a significant difference in the frequency of the occurrence of the sites suitable at most for formation of *cis*-2-alkenes o the sites suitable for *trans*-2-alkene formation. On zeolites such specialized sites have not been observed. The differences stated above relate only to the greater ease with which *cis*-2-alkenes are formed on the sites participating also in formation of *trans*-2-alkenes (Fig. 4 and Fig. 5). This means that, when compared to γ-Al_2O_3,



a *b*

FIG. 6

A large cavity of X and Y zeolite (one of the three models of skeleton used in the present work) with positions of the type S_{II} and S_{III} fully occupied by cations *a* Na; *b* K

one can expect the less distinct preference of *cis*-2-alkenes in the products of dehydration on X and Y zeolites. This conclusion comports with experiment, since comparing with γ-Al_2O_3 (refs[1,2]) on which *cis*/*trans* ratio was close to 10, on zeolites[28–31] this ratio changed from 0·9 to 1·6. It is worthy of note that for thermodynamic equilibrium[44] this value is 0·44. In this connection one should add that experimentally observed composition of reaction products can in the case of zeolites be to a great extent distorted by consecutive isomerization of alkenes[44–46]. For that reason, the composition of products of dehydration itself should be determined experimentally by using the shortest contact times as possible[29], to suppress consecutive isomerisation.

Further conclusion drawn from the results of performed calculations is also the experimentally observed[23–28] effect of the size of cations on the catalyst activity. The diminuation of the vacant space in the large cavity of zeolite due to the exchange of Na cation for bulkier K cations is documented in Fig. 6. From comparison of data summarized in Tables I and II for Na and K, it is evident that geometric conditions for dehydration of alcohols on X and Y zeolites are on the whole more favourable in the presence of Na cations than in the presence of K cations. This fact is illustrated in Fig. 4*b*,*d* and Fig. 5*c*,*d*.

Finally, from Tables I and II it becomes clear that geometric conditions in the dehydration are also affected by the amount of cations located in the zeolite skeleton. It is of interest that, except for one case (O1–O1; 504·2 pm), the alcohol molecule cannot be adsorbed on a given pair of sites without the existence of at least one vacancy of the cation which lies in the close vicinity. This vacancy is most frequently required in position S_{III}, which is obviously fulfilled as far as the zeolites used are concerned. For energetical suitability of cation positions it holds that $S_I > S_{II} > S_{III}$, the amount of cations (given by the number of Al atoms present in skeleton) being sufficient at most for the occupation of positions S_I and S_{II} (ref.[35]). Experimentally found increase in the catalytic activity accompanying decationization or exchange of cations for the smaller number of cations with higher charge includes in addition to the dominant effect of increasing concentration of acidic catalytic sites[4,39] obviously also the steric effect of the amount of cations present in skeleton.

In conclusion it can be stated that the investigation of geometric factor in heterogeneously catalysed reactions proved to be profitable since, similarly as earlier[22] for γ-Al_2O_3 and ThO_2, also in the present work concerned with X and Y zeolites, the study of geometric conditions performed with the aid of a computer made it possible to quantify steric demands which can otherwise be only roughly evaluated. Furthermore, from calculations one can directly draw simple conclusions about some phenomena which have as yet been interpreted only with difficulty, such as the possibility of *anti*-elimination course of reactions on solid phase surface, which have been the matter of discussion for many years or the high production of *cis*-isomers in most heterogeneously catalysed eliminations studied so far, which does not

correspond to thermodynamic equilibrium. Also in the case of dehydration of alcohols on X and Y zeolites, the study of geometric factor aided in classifying the present knowledge and in getting a deeper insight into regularities controlling this reaction.

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