DEHYDRATION OF DIOLS ON ZEOLITES OF TYPES X AND Y

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ABSTRACT

The transformations of 1,2- 1,3- 1,4- and 1,5-diols on NaX,
NaHX, NaY and NaHY zeolites were studied in a continuous flow reac-
tor, at atmospheric pressure, at 503-623 K. The acidities of the
zeolites were examined by the pyridine adsorption-IR technique, the
Me_2Zn-GC method, and titration with n-butylamine. The two main trans-
formations taking place are dehydration and fragmentation. The ratio
of the two processes is determined by the structures of the diols,
the type of the zeolite and the temperature. The 1,2-diols transform
via the pinacol rearrangement; the 1,3-diols give unsaturated com-
pounds via 1,2-elimination while the 1,4- and 1,5-diols undergo ster-
eoselective ring-closure leading to the formation of cyclic ethers.

The activities of the zeolites in the transformations of diols
proved similar to their activities in the transformations of alco-
hols: NaX < NaY < NaHX < NaHY.

INTRODUCTION

Wide-ranging studies have been reported on the catalytic trans-
formations of alcohols on zeolites [1-3]. The acid centres of zeo-
lites are known to catalyse the elimination of water from alcohols.
The elimination can lead to the formation of both alkenes and ethers,
via intra- or intermolecular dehydration, respectively [4]. Intra-
molecular dehydration on zeolites involves anti elimination, leading
to the formation of alkene mixture with a cis/trans ratio higher than
at equilibrium. These observations have been supported by theoreti-
cal calculations [5]. The activity of a zeolite in the dehydration
process is proportional to the number of its Brönsted acid centres.

On the other hand, only a few data are available on the trans-
formations of dihydroxy compounds (diols) on zeolites. Studies with
2-methyl-2,3-butanediol [6], 1,3-butanediol [7] and 1,4-butanediol [8]
have revealed that the characteristic transformation of diols is

intramolecular dehydration, with the formation of carbonyl compounds, dienes and cyclic ethers. Products formed by fragmentation are also detected.

The aim of our investigations was to establish a correlation between the characteristic transformation directions, the structures of the diols (the orders of the carbon atoms bearing the hydroxy groups, and the relative positions of the hydroxy groups) and the acidities of the zeolites.

EXPERIMENTAL

Materials. The following diols (Fluka products) were used after distillation (GC purity: 100%): 1,2-propanediol (I), 2,3-butanediol (II) (1:1 isomeric mixture), 2,3-dimethyl-2,3-butanediol (III), 2,4-pentanediol (IV) (1:1 isomeric mixture), 2,5-hexanediol (V) (1:1 isomeric mixture), 1,5-pentanediol (VII). ($\pm$)-2,5-Hexanediol (VI) (isomer purity: 98%) was prepared from V via distillation of the isomeric oxepanes [9].

Catalysts. The NaX and NaY zeolites were commercial products (Strem Chemicals, 011878-G and 042578-G, respectively). The NaHX and NaHY zeolites were prepared by Na^+-NH_4^+ ion-exchange, followed by decomposition of the ammonium form at 673 K for 5h [10].

The acidities of the zeolites were determined by three methods. Method A. The IR absorption bands at 1550 cm^{-1} and 1445 cm^{-1} of pyridine adsorbed on zeolites at 473 K are characteristic of the Brönsted and Lewis acid centres, respectively [11]. The values in Table 1 are the ratios peak height/sample quantity, which are proportional to the number of acid centres. Method B. The number of surface protons was determined with the Me_2Zn-tetrahydrofuran reagent via GC determination of methane formed at 363 K [12]. Method C. After heat treatment at 673 K powdered zeolites were titrated with n-butyl-amine in benzene, as in [13].

Table 1

Acidities of zeolites used

| | adsorption of pyridine | | Me_2Zn 10^{20} | n-BuNH$_2$ g^{-1} |
	Brönsted	Lewis		
NaX	1.5	1.5	2.60	1.35
NaHX	6.4	3.0	7.00	2.31
NaY	2.3	1.3	4.55	1.23
NaHY	14.7	4.3	7.86	3.92

Apparatus. The experiments were carried out in a glass flow reactor (lenght: 160 mm, inner diameter: 20 mm) (Figure 1). The dead space of the reactor tube was filled with glass beads 3 mm in diameter. The liquid products were collected in a condenser (5), while the quantity of gaseous products was measured with a gas burette (9).
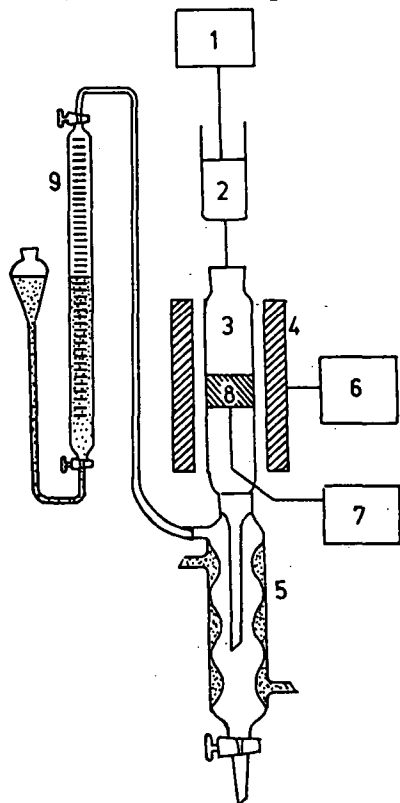
1 Feeding motor
2 Syringe
3 Reactor tube
4 Heating jacket
5 Condenser
6 Temperature controller
7 Temperature meter
8 Catalyst sample
9 Gas burette

Fig. 1. Apparatus

Measurements. The catalyst samples of 2 ml were kept at 673 K for 1 h before use, then cooled to the temperature of the experiment. The diols were fed into the reactor at a feeding rate of 0.6 ml/ml h. After the first 2 ml of diol, a constant catalyst activity was reached, and all the measurements were carried out in this range.

Analysis. The composition of the reaction products was determined by GC. Before analysis, the heterogeneous products (aqueous and organic layers) were homogenized by adding an appropriate amount of diglyme to the mixture. The columns were as follows (length: 1.8 m, solid support: Merck Kieselguhr with a grain size of 0.2-0.3 mm): 10% PEG 20M (for determination of the conversions), 15% Reoplex 400 (for determination of the composition of the liquid products), and 10% squalane (for determination of the composition of the gaseous products). Authentic compounds and calibration curves were used for the identification of products and the calculations, respectively.

RESULTS

Tables 2-5 present data on the transformations of the diols examined.

Table 2

Product compositions (mol %) of 1,2-diols on NaHY zeolite
(623 K, 100% conversion)

I		II		III	
Acetaldehyde	4	1,3-Butadiene	28	2,3-Dimethyl-	
Propionaldehyde	67	Acetaldehyde	6	-1,3-butadiene	20
Acetone	13	Acetone	4	3,3-Dimethyl-	
2-Propanol	5	2-Butanone	62	-2-butanone	71
2-Propen-1-ol	5			Unidentified	9
Unidentified	6				

Table 3

Conversions (%) of 2,3-butanediol at 503 K

NaX	NaHX	NaY	NaHY
33	89	36	94

Table 4

Product compositions (mol %), conversions and transformation
directions pf 2,4-pentanediol (IV). (X=NaX, HX=NaHX, Y=NaY, HY=NaHY)

|	523 K				548 K				573 K			
	X	HX	Y	HY	X	HX	Y	HY	X	HX	Y	HY
Dienes	79	70	37	34	90	53	36	25	95	39	36	11
Propene		4	7	8	2	2	6	12		6	8	18
Acetaldehyde		4	8	7		2	7	15		7	10	23
Acetone		6	10	8	2	7	11	13	2	14	12	11
Ethanol		3	11	8		4	8	12		12	8	15
2-Pentanone	1	3	4	4	2	1	4	6	2	1	3	6
4-Penten-2-ol	20	3	23	22	6	29	28	10	1	14	20	7
3-Penten-2-one		7		9		2		7		7	3	9
Conversion	53	90	77	95	90	93	93	95	97	98	98	100
Dehydration	100	89	77	81	98	90	80	66	98	75	74	53
Fragmentation	0	11	21	19	2	10	20	34	2	25	26	47

Table 5

Product compositions (mol%) of 2,5-hexanediols (V, VI) and 1,5--pentanediol (VII) (NaHY, 573 K, 100% conversion)

		V	VI		VII
2,5-Dimethyltetra-	cis	45	96	Tetrahydropyran	95
hydrofurans	trans	49	4	Unidentified	5
Unidentified		6			

DISCUSSION

The main reaction directions in the transformations of 1,2--diols on zeolites are the two different forms of dehydration (Table 2). The pinacol rearrangement leads to the formation of carbonyl compounds, and 1,2-elimination to an unsaturated alcohol or dienes (Scheme 1).

The carbenium ion formed in the first step may be stabilized in two ways: after 1,2-anionotropic migration of an α-substituent (in the examined 1,2-diols H or Me), carbonyl compounds are formed as a result of proton elimination (pinacol rearrangement); alternatively, unsaturated alcohols may be formed through elimination of an α-proton, and these give the diene end-product through the
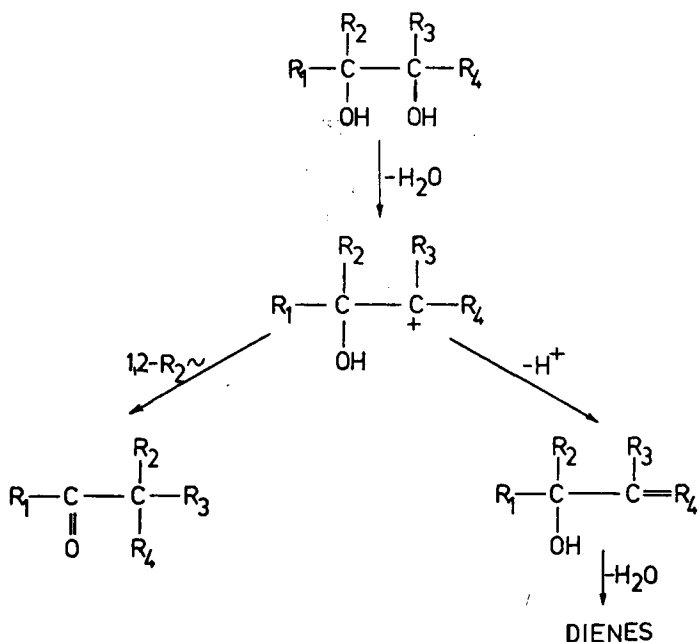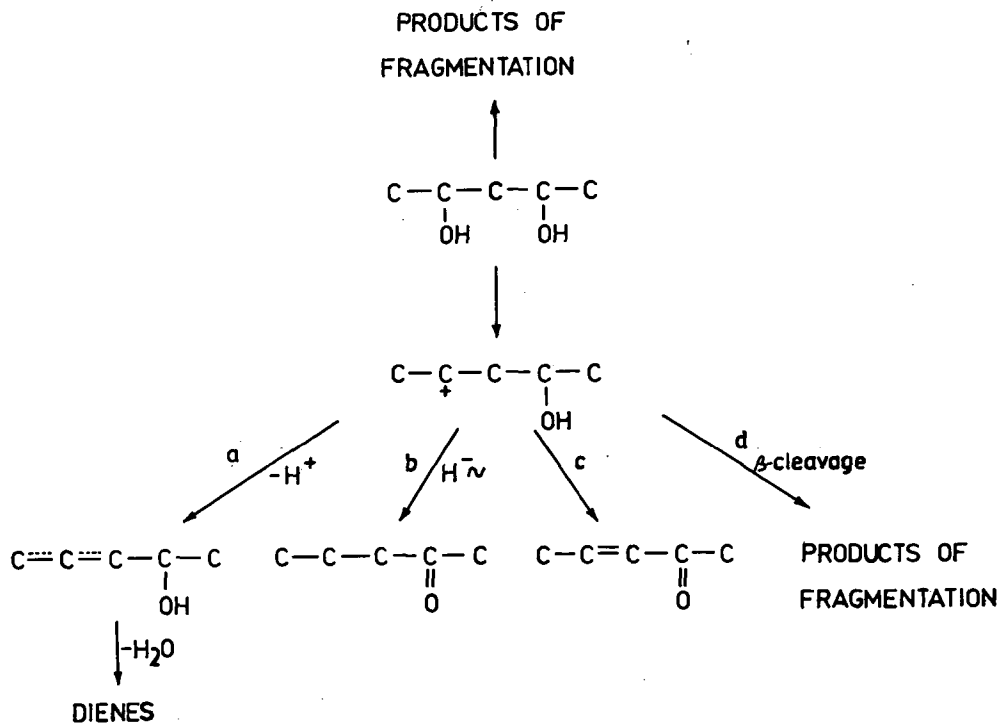

Scheme 1

elimination of a further molecule of water via a similar mechanism.

About 70% of the carbenium ions are stabilized through the pinacol rearrangement, which is in good agreement with the results found on other acid-type catalysts, e.g. Na_2HPO_4 [14] and $Ca_3(PO_4)_3$ [15].

In the case of 1,2-propanediol (I), the results of the pinacol rearrangement can be acetone or propionaldehyde, depending on whether the primary or secondary OH group is eliminated in the first step. Their ratio (acetone:propionaldehyde = 1:5) corresponds to the difference between the rates of decomposition of hydroxonium ions bound to the primary and secondary carbon atoms [16]. Diene formation is not observed in the case of I, for the cumulated diene obtained from it (1,2-propadiene) is thermodynamically unstable under such conditions.

The data in Table 4 show that the main reaction direction for 2,4-propanediol (a typical 1,3-diol) is dehydration through 1,2-elimination, which is accompanied by fragmentation too, depending on the temperature and the zeolite type. The observed transformations are depicted in Scheme 2.

Scheme 2

The secondary carbenium ion formed by elimination of one of the OH groups can react further in four ways:

a) Elimination of an α-proton, with the formation of unsaturated alcohols, which can be further dehydrated to dienes (1,2-elimination);

b) formation of 2-pentanone during hydride ion migration processes;

c) formation of 3-penten-2-one by an unknown route;

d) fragmentation (β-cleavage).

Of these four processes, 1,2-elimination predominates. It may be mentioned that on NaX zeolite, at a conversion of 100%, pentadienes are formed with a yield of 95%. Of the two possible pentadiene isomers, the thermodynamically more stable conjugated 1,3--pentadiene is formed to an extent of nearly 90%.

The large number of fragmentation products to be found in the catalyst demonstrate that, besides the β-cleavage occurring in the carbenium ion, fragmentation also takes place in the diol molecule itself. The latter process was also observed by Mazet et al. [17] during the acid catalysis of 2,2-disubstituted-1,3-propanediols under homogeneous conditions.

It is worth stressing that the 1,2-diols, in contrast with the 1,3-diols, barely undergo fragmentation. The explanation of this may be that the α-OH-containing carbenium ion formed in the first step (Scheme 1) participates much more quickly in 1,2-anionoid migration than in β-cleavage of a C-C bond.

Areshidze et al. [8] found that 1,4-butanediol is converted to tetrahydrofuran on zeolites, i.e. intramolecular ether formation occurs. Our results show that the main reaction for 1,4- and 1,5-diols is cyclodehydration (Table 5). It follows from the tabulated data that, similarly to the cyclodehydration taking place on other heterogeneous catalysts and under homogeneous conditions [9] , the ring closure is stereospecific and is accompanied by inversion. The stereospecific nature of the process permits the conclusion that the
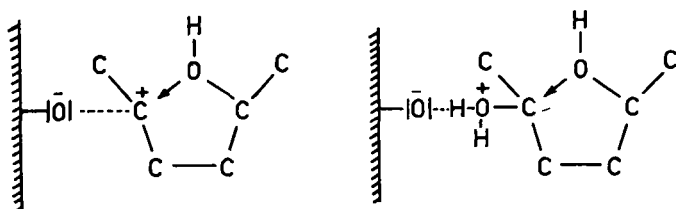
Scheme 3

cation formed in the first step, which may be either a carbenium ion or an oxonium ion, is bound to the surface of the zeolite following intramolecular S_N2 attack by the OH group (Scheme 3), as assumed by other authors for zeolites [18]. This process ensures the occurrence of inversion on one of the asymmetry centres.

The results of measurements of the zeolite acidities (Table 1) and comparisons of the conversions of the diols (Tables 3 and 4) reveal that (as in zeolite-catalysed processes in general) a higher acidity results in a higher activity. Both the activities and the acidities of the zeolites vary in the sequence:

NaX < NaY < NaHX < NaHY

Apart from this sequence, no more exact correlation can be found between the acidity and the activity, which demonstrates that the activity of a zeolite in the dehydration processes is influenced not only by the acidity, but by other effects too. It can also be seen, however, that the increase of the acidity within the pairs NaX-NaHX and NaY-NaHY results in a higher extent of fragmentation of 2,4-pentanediol (Table 4). It can also be stated that the Y-type zeolites cause more fragmentation than do those of X type. Since stronger electrostatic fields develop in the Y-type zeolites than in those of X type [19], this indicates that the electrostatic fields play some direct role in the occurrence of fragmentation.

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