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Dehydration of C₄ alkanols conjugated with a positional and skeletal isomerisation of the formed C₄ alkenes

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Abstract

In the context with our recently published report about skeletal isomerisation of butenes present in C₄ pyrolysis fraction [V. Macho, M. Kralik, L. Jurecek, E. Jurecekova, J. Balazova, Appl. Catal. A: Gen. 203 (2000) 5], the dehydration of C₄ alkanols conjugated with a positional and skeletal isomerisation of the formed C₄ alkenes was studied. Thermally and with diluted sulphuric acid activated gamma-aluminas (A and AA catalysts) were used in a fixed bed reactor at 300–470°C, atmospheric pressure and a catalyst loading GHSW = 0.12–0.8 g cm⁻³ h⁻¹. Under these conditions all the C₄ alkanols were totally dehydrated and underwent subsequent isomerisation, eventually further reactions yielding especially in propene. Depending on the type of origin alcohol and reaction conditions, isobutene was formed mainly from isobutanol and *tert* butanol; *cis*-2-butene was generated dominantly in the case of 2-butanol. The lowest yield of isobutene was in the case of 1-butanol. Distribution of individual butenes is discussed following reaction steps necessary for obtaining a certain butene isomer and its thermodynamic preference. The reported results showed on the possibility to obtain mainly isobutene from all the C₄ alkanols using a simple dehydration–isomerisation catalyst prepared by the acidification of gamma-alumina. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dehydration; Isomerisation; Skeletal isomerisation; C₄ alkanols; Butene; Isobutene; Gamma-alumina; Mixture of alkenes C₂, C₃ and C₅

1. Introduction

Preparation of alkenes, particularly of isobutene, is of great interest of both petrochemical industry and organic synthesis. Isobutene is widely used as a precursor of oxygenates (e.g. methyl-*tert*-butyl ether:

MTBE; ethyl-*tert*-butyl ether: ETBE; and other alkyl-*tert*-butyl ethers) which enhance the octane level of gasoline [2]. Isobutene is also a very good alkylating agent of alkanes, thus enabling to prepare branched hydrocarbons as valuable blends for engine fuels [2]. Alkylating potency of butenes may be capitalised in the preparation of chemical specialities, e.g. antidegradants of polymers, precursors of polyaromatic acids [3], etc. Not the least applications of

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isobutene are in polymer chemistry either directly as a monomer, or as an intermediate for the production of methacrylic acid [3].

Recently [1], we have pointed out catalytic suitability of a micro- and mesoporous gamma-alumina activated with diluted sulphuric acid for the isomerisation of *n*-butenes present in the butadiene and isobutene free pyrolysis C₄ fraction (so called raffinate II: the stream from the synthesis of MTBE, or *tert*-butanol). Skeletal isomerisation of *n*-butenes over natural clinoptilolite zeolites treated with acids (boric, phosphoric or nitric) has been reported by Lee et al. [4]. Catalysts of mesoporous structure were used by Leo et al [5], microporous Mg-ZSM-22 catalysts were employed by Baeck and Lee [6]. The isomerisation over ferrierite zeolites is reported in [7,8], other acid catalysts for this process are described in [9].

Possibility to obtain C₄ alcohols stems from updated well known [10–13] catalysed hydrocondensation of carbon monoxide with hydrogen, or modified Fisher–Tropsch synthesis yielding not only hydrocarbons, but also oxygen compounds, particularly, alcohols with a shorter carbon chain [13,14]. Alkalinated oxides of iron, zinc, copper and chromium [13–15] belong to the most successful catalysts of the latter reaction. Beside methanol, isobutanol is the next alcohol possible to prepare from carbon monoxide and hydrogen [15]. If admixtures of acetylene are present in syngas, it is even possible to obtain lower and higher aliphatic alcohols C₃–C₁₈ over Fe₃O₄–M₂O–V₂O₅/Al₂O₃ (M denotes an alkaline metal) at 170–220°C and pressure 2–20 MPa [14].

Availability of isobutanol and *tert*-butanol favours a straightforward synthesis of alky-*tert*-butyl ethers directly from a lower alkanol, e.g. methanol, and butanols [16], and in this connection dehydration of butanols which is supposed to be a step preceding the alkylation is important subject of studying.

In planning experiments over activated gamma-alumina, we were aware of the fact that isomerisation requires a higher temperature (about 450°C) than is the temperature sufficient for the dehydration (in the range of 100–320°C; depending on the type of alkanol and a catalyst). Moreover, at such a high temperature dialkyl ethers can exist only at a very limited extent due to the thermodynamics [17,18], and if some precursors of them could be formed on a catalyst surface, these precursors are immediately turn out to alkenes

and water. Recently [1], we have carried out a thermodynamic analysis showing on distribution of reaction products in the isomerisation of *n*-butenes neglecting other reactions like methathesis, co-methathesis, dehydrogenation and hydrogenation, cracking, etc. Of course, besides thermodynamic preferences, kinetic pathways of transformation of intermediates formed by the dehydration of alcohols influence a composition of the resulting reaction mixture significantly. All these outlined aspects have formed a basis for the start of investigation reported in this paper.

2. Experimental

All the used alcohols (1-butanol, 2-butanol, isobutanol and *tert*-butanol) were of analytical grade purity, or containing 99.5 wt.% of alcohol with admixtures being formed mainly by water.

Preparation and physicochemical properties of the gamma-alumina and gamma-alumina activated with a diluted sulphuric acid (0.5 wt.%) were the same as in [1]. Hereafter, pure activated gamma-alumina and gamma-alumina activated with sulphuric acid are denoted as the catalysts **A** and **AA**, respectively.

Main parts of an experimental apparatus were also described in [1]. Liquid alcohols were dosed by a micropump, and evaporation before entering the reactor was ensured by 50 cm³ of silica wool heated to 295 ± 5°C (the temperature close, but always lower than that in the reactor). After evaporation, alcohols flowed through the 150 cm³ layer of Rashig rings heated to the same temperature as in the reaction part consisted of 50 cm³ of the dehydration–isomerisation catalyst.

Output from the reactor was cooled, a gas part was directly analysed by a GC using MCH-112 apparatus from Satalice–Prague, and the liquid (mainly water phase) was extracted with hexane and also analysed by GC. The GC analytical details including retention times are in [1]. Water was not considered in characterisation of the composition of reaction mixture.

A reactivation of the catalyst was carried out every 6 h at 430–470°C for 1 h with dry air.

3. Results and discussion

In accordance with thermodynamic preferences [17,18], all the butanols were totally dehydrated at

Table 1

Selectivities to products in the dehydration of butanols accompanied with the isomerisation and other transformation reactions (GHSV = $0.18 \pm 0.02 \text{ g cm}^{-3} \text{ h}^{-1}$).

Entry	Catalyst	T (°C)	C ₄ OH ^a	Selectivity (%)											
				1-C ₄ ''	c-2-C ₄ ''	t-2-C ₄ ''	i-C ₄ ''	CH ₄	C ₂	C ₂ ''	C ₃	C ₃ ''	n-C ₄	i-C ₄	≥C ₅
1	A	400	n	21.4	26.7	40.5	7.4	0.1	0.07	0.5	0.02	1.33	0.42	0.05	1.1
2	AA	400	n	16.4	16.4	19.9	18.2	0.3	0.39	0.21	0.21	6.12	0.93	0.93	6.7
3	A	474	n	15.9	16.3	22.8	27.4	0.7	0.48	0.18	0.18	7.01	0.89	0.89	3.2
4	AA	472	n	12.1	12.9	18.3	31.1	0.9	1.90	0.37	0.37	9.60	2.01	2.01	6.1
5	A	400	2	21.1	25.0	36.7	14.4	0.2	0.01	0.20	0.01	1.21	0.20	0.08	1.1
6	AA	400	2	14.3	16.1	26.3	31.8	0.6	0.06	0.44	0.39	3.59	0.24	0.09	4.5
7	A	471	2	16.6	16.5	23.3	30.2	0.4	0.17	0.83	0.08	6.52	0.53	0.94	3.4
8	AA	471	2	10.8	15.3	23.5	33.3	0.8	0.08	0.66	0.67	7.61	0.31	0.91	6.8
9	A	400	i	14.3	15.6	23.5	40.1	0.2	0.01	0.10	0.01	0.13	0.33	0.12	1.8
10	AA	400	i	13.4	14.5	22.9	39.9	0.5	0.03	0.29	0.06	3.91	0.08	0.14	3.3
11	A	470	i	12.9	13.4	18.4	39.8	0.5	0.16	0.52	0.11	5.98	0.25	1.64	5.4
12	AA	472	i	10.3	14.5	21.7	38.7	0.9	0.05	0.36	0.06	5.83	0.16	0.16	6.9
13	A	400	t	4.1	4.9	7.0	81.1	0.3	0.01	0.02	0.02	0.24	0.07	1.32	1.1
14	AA	400	t	5.6	6.7	9.7	75.3	0.5	0.00	0.03	0.02	1.93	0.00	0.29	0.8
15	A	470	t	12.9	13.9	15.2	41.6	0.8	0.07	0.06	0.6	5.36	0.11	1.35	5.5
16	AA	470	t	13.5	15.0	22.4	33.4	0.8	0.04	0.30	0.05	6.60	0.32	1.39	6.0

^a C₄: alkanol; n: 1-butanol; 2: 2-butanol; i: *iso*-butanol; t: *tert*-butanol.

a temperature higher than 300°C, and GHSV < $0.8 \text{ g cm}^{-3} \text{ h}^{-1}$. A kinetic and thermodynamic control of this dehydration accompanied with an isomerisation of the formed butenes is illustrated by Table 1 and Fig. 1.

Comparison of data in Tables 1 and 2 implies much higher tendency to equilibrium composition when the more active AA catalyst was used. At a lower temperature (400°C), a kinetic control was governing the process and a butene isomer which mostly resembled structure of the original C₄ alkanol was formed. Thus, from *n*-butanol, *trans*-2-butene was the main product, and similarly, but in lower extent, *trans*-2-butene was formed from 2-butanol. Due to the supposed starting secondary carbenium cation on the beta-carbon

Table 2

The theoretical equilibrium composition in the system with reactions $1\text{-C}_4\text{H}_8 \rightleftharpoons \text{cis-2-C}_4\text{H}_8 \rightleftharpoons \text{trans-2-C}_4\text{H}_8 \rightleftharpoons \text{iso-C}_4\text{H}_8$; calculated from data in [17,18]

Compound	Composition (mol.%)	
	400°C	470°C
1-C ₄ H ₈	0.099	0.123
cis-2-C ₄ H ₈	0.154	0.162
trans-2-C ₄ H ₈	0.241	0.244
iso-C ₄ H ₈	0.506	0.471

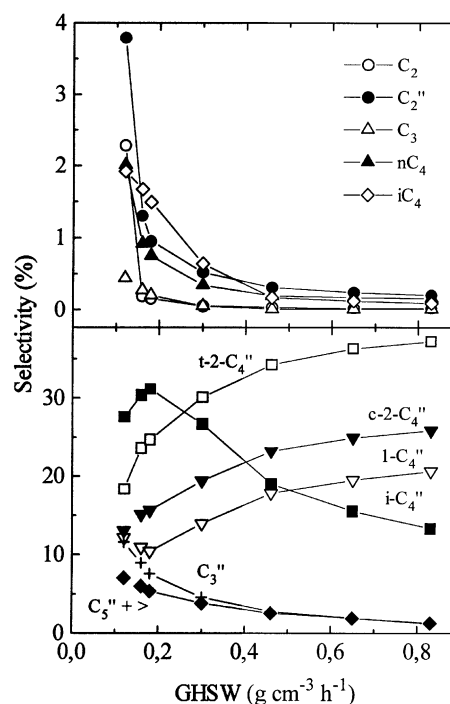


Fig. 1. Effect of loading (GHSV) in the total dehydration of *n*-butanol accompanied by the isomerisation and other reactions (acidified gamma-alumina: the catalyst AA; atmospheric pressure; $T = 472 \pm 2^\circ\text{C}$).

in the course of dehydration of 2-butanol, an easier transformation to isobutene proceeds in comparison with 1-butanol, where the starting primary-carbenium cation is supposed. Closer structure of isobutanol to isobutene resulted in a higher formation of isobutene. Expectedly, the highest formation of isobutene was under kinetic control from *tert*-butanol.

A higher activity of the catalyst **AA** has brought up a larger extent of side reactions yielding in lower and higher than C_4 hydrocarbons. This situation is fairly illustrated by the selectivity to propene, e.g. 1.33 and 6.12% over the **A** and **AA** catalysts, respectively, in experiments with *n*-butanol at 400°C.

Using *n*-butanol as a most arduous substrate to convert to isobutene, we searched for an optimal loading GHSV with respect to a maximum yield of isobutene. The found value of $GHSW = 0.18 \text{ g cm}^{-3} \text{ h}^{-1}$ of *n*-butanol (Fig. 1) is significantly lower than the $GHSW = 0.6 \text{ g cm}^{-3} \text{ h}^{-1}$ reported for the pure isomerisation reaction carried out over the catalyst **AA** [1]. Necessity of a higher residence time in the dehydration–isomerisation process stems from three main factors:

1. dilution of the butene mixture with water (lowering in activity of butenes);
2. chemisorption of water on the hydrophilic surface of catalysts (decrease in number of active sites available for butenes);
3. more complicated reaction pathways of transformation of *n*-butanol to isobutene (see Fig. 6).

A higher extent of cracking, methathesis and co-methathesis reactions at higher residence time (lower loading) is also evident from Fig. 1. Similarly, as discussed about the influence of temperature, propene is mainly formed at the higher residence time.

A more detailed temperature dependence of the dehydration–isomerisation of *n*-butanol is presented in Fig. 2. At the total conversion of *n*-butanol, the selectivity to 1-butene dramatically decreases at a change of temperature from 300 to about 360°C. At this temperature, a maximum yield of 2-butenes over the less active catalyst **A** was monitored, whereas a higher yield of the *cis* isomer than the *trans* isomer could be prescribed to geometrical restrictions on the catalyst surface. Isobutene has started to be assuredly registered from the temperature 360°C and a yield of isobutene gradually increased. However, the more

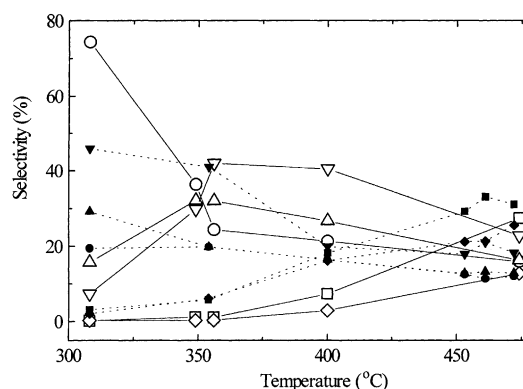


Fig. 2. Effect of temperature on the selectivity in the total dehydration of *n*-butanol accompanied by the isomerisation and other reactions. Empty and full symbols denote the catalysts **A** and **AA**, respectively; circle: 1-butene, up triangle: *cis*-2-butene; down triangle: *trans*-2-butene; square: isobutene; diamond: others; atmospheric pressure; $GHSW = 0.18 \pm 0.02 \text{ g cm}^{-3} \text{ h}^{-1}$.

active **AA** catalyst enabled to form isobutene even at 310°C with the yield of about 3 wt.%. The yield of isobutene almost linearly increased over the **AA** catalyst up to 460°C, then a slight drop was monitored which could be prescribed to a higher extent of side reactions.

tert-Butanol (Fig. 3) converts to isobutene much easier than *n*-butanol, but at increasing temperature isobutene undergoes the skeletal isomerisation to

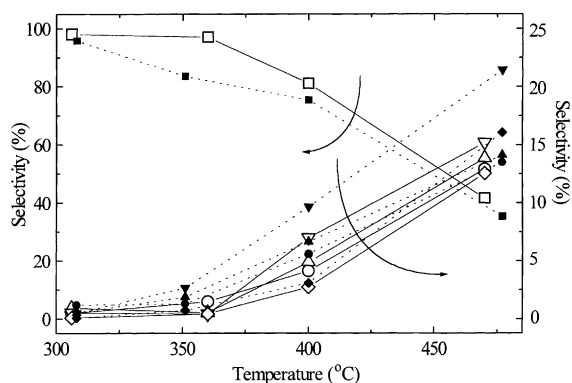


Fig. 3. Effect of temperature on the selectivity in the total dehydration of *tert*-butanol accompanied by the isomerisation and other reactions. Empty and full symbols denote the catalysts **A** and **AA**, respectively; circle: 1-butene, up triangle: *cis*-2-butene; down triangle: *trans*-2-butene; square: isobutene; diamond: others; atmospheric pressure; $GHSW = 0.18 \pm 0.02 \text{ g cm}^{-3} \text{ h}^{-1}$.

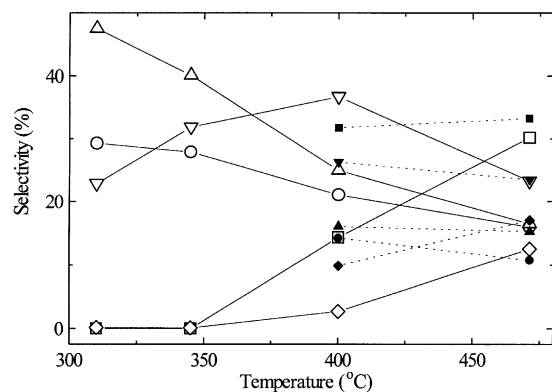


Fig. 4. Effect of temperature on the selectivity in the total dehydration of 2-butanol accompanied by the isomerisation and other reactions. Empty and full symbols denote the catalysts **A** and **AA**, respectively; circle: 1-butene; up triangle: *cis*-2-butene; down triangle: *trans*-2-butene; square: isobutene; diamond: others; atmospheric pressure; GHSW = $0.18 \pm 0.02 \text{ g cm}^{-3} \text{ h}^{-1}$.

2-butenes, and other reactions at further increased temperature. In comparison with *n*-butanol, thermodynamically more stable *trans*-2-butene is formed preferentially on the both less and more active catalysts **A** and **AA**. Such a behaviour could be also explained by a “geometrical favorisation” for the transformation of isobutene to 2-butenes (see Fig. 6). The amount of other products besides butenes is in the whole temperature range rather higher in experiments with the more active **AA** catalyst. This difference is increased at increased temperature.

Experiments with 2-butanol (Fig. 4) rendered similar selectivity curves like in the case of 1-butanol, but the formation of butenes was high even at 310°C. Due to geometrical aspects, *cis*-2-butene was mainly formed at lower temperature. Thereafter (from 400°C), thermodynamic preferences caused a dominant formation of *trans*-2-butene (geometrical isomerisation) and at increased temperature, a higher yield of isobutene formed by the skeletal isomerisation appeared.

Geometrical preferences for the formation of isobutene are also nicely demonstrated in experiments with isobutanol (Fig. 5). Even with the less active catalyst **A**, the yield of isobutene is very high up to 350°C. Then, thermodynamic driving force with a temperature activated kinetics enables the conversion to butenes (the skeletal isomerisation) whereas the most stable *trans*-2-butene is formed mainly. In

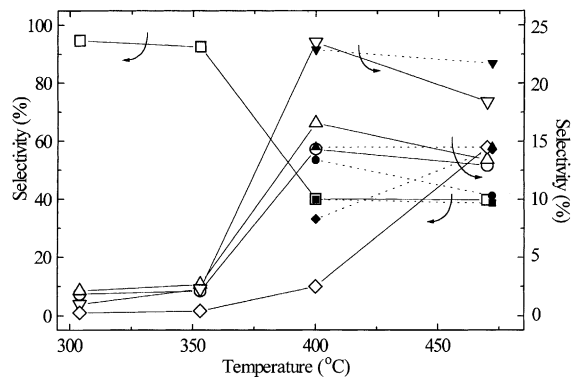


Fig. 5. Effect of temperature on the selectivity in the total dehydration of isobutanol (2-methyl-propanol) accompanied by the isomerisation and other reactions. Empty and full symbols denote the catalysts **A** and **AA**, respectively; circle: 1-butene, up triangle: *cis*-2-butene; down triangle: *trans*-2-butene; square: isobutene; diamond: others; atmospheric pressure; GHSW = $0.18 \pm 0.02 \text{ g cm}^{-3} \text{ h}^{-1}$.

accordance with thermodynamic preferences and necessity to undergo the position isomerisation (shift of the double bond from the position “2” to the position “1”) 1-butene is formed at the lowest extent with values close to thermodynamic ones.

Thermal activation of both pure and sulphated gamma-aluminas (catalysts **A** and **AA**, respectively) in air stream is accompanied by the dehydration of these materials. Due to effect of water formed by the dehydration of alkanols, a reverse process, i.e. hydration with water may be supposed. In addition, removal of sulphate groups by reaction with water is possible for the catalyst **AA**. Consequently, a stronger deactivation would appear and not such a full regenerability of these catalysts like in the case of their utilisation in the isomerisation of butenes [1] could be supposed. However, re-utilisation of the catalysts **A** and **AA** showed more than 200 h operation time (regeneration every 6 h as described in Section 2) without monitoring any significant decrease in their activity. This observation implies that at temperatures higher than 300°C, vapour water acts as a diluter of the gas reactants, it occupies a part of catalytic sites, decreases the reaction rate (see above), but does not destroy the catalytic sites.

On the basis of reported experimental results, thermodynamics, geometrical restrictions on the catalyst surface and the stability of carbenium cations, we have

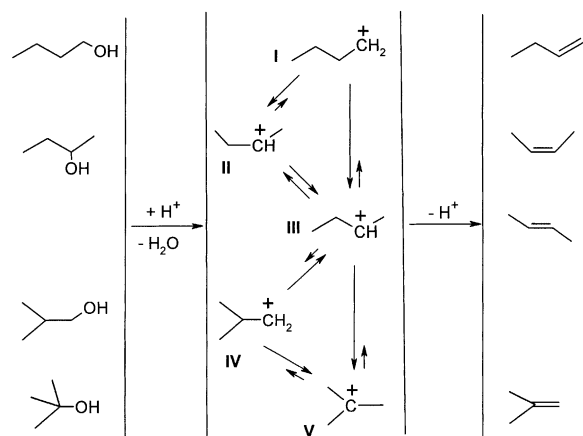


Fig. 6. Probable reaction pathways in the dehydration of C₄ alcohols followed by the isomerisation of the formed carbenium cations.

proposed a reaction scheme (Fig. 6) describing the conversion of C₄ alkanols to butenes. *n*-Butanol is supposed to form the primary carbenium cation (I) by the cleavage of the hydroxyl group. This primary cation is stabilised on the catalyst surface and it can be either transformed to 1-butene by leaving the protonic catalytic site, or the point of chemisorption can be shifted yielding more stable secondary carbenium cation (II, or III). Due to steric obstacles, the *cis*-isomer (II) with methyl groups upstanding from the catalyst surface is more probable, but the *trans*-isomer (III) is more thermodynamically stable. The *cis*-isomer is supposed to be generated as the first one also in the case of the formation of the secondary carbenium cation directly from 2-butanol. Despite the relatively high temperature, we do not suppose an extensive formation of 1-butene from the secondary carbenium cation II, or III because of much higher C–H binding energy in the –CH₃ group in comparison with the energy in the –CH₂– group. The skeletal isomerisation of secondary butene carbenium cation is also more probable from the *trans*-isomer (III), which can straightforwardly possess methyl–cyclopropyl carbenium cation and consequently rearrangement to the *tert*-butyl carbenium cation (V) (monomolecular mechanism), or the *trans*-isomer of secondary butene cation can react with another molecule of butene and undergoes rearrangement and splitting (bimolecular mechanism). Rates of reactions in bimolecular mechanism are also

higher in the case the *trans*-isomer because of a better geometrical arrangement for an attack on the secondary carbon. Besides isomers of butenes, dimers of butene can be split to other hydrocarbons, and according with our results (Table 1, Fig. 1), mainly propene and pentenes are formed. A predominant formation of isobutene from iso-butanol is caused by a quick shift of the positive charge from the primary carbon (IV) to the tertiary one (V); the reaction which is indicated in the lower part of Fig. 6. Expectedly, *tert*-butanol gives directly tertiary carbenium cation (V), which is either converted to isobutene (under a kinetic control), or it enters other reactions yielding in other isomers of butenes (thermodynamic control). As discussed about the bimolecular mechanism of the isomerisation, each of carbenium cations depicted in Fig. 6 can undergo further reactions from which hydrocarbons with shorter and longer chains can result. A hydrogenation–dehydrogenation process also takes part in the reaction system, thus, giving chance to generation of alkanes, even a little proportion of methane as illustrated by Table 1.

While acidity of pure alumina (the catalyst A) is established only by Al(III) atoms (Lewis centers) and hydroxyl groups (Brønsted centres), the alumina activated with sulphuric acid (the catalyst AA) bears additional protonic centres represented by the sulphate groups bound to surface atoms of aluminum in alumina. Therefore, the higher dehydration (not reported directly in this paper), as well as, isomerisation activity [1,19] is not surprising. This high activity is of great potential also for other acid-catalysed reactions, e.g. dehydration of 1,4-butanediol to tetrahydrofuran, catalytic cracking of paraffines [20] and others.

Improvement of an activity by treatment with sulphuric acid is well known for zirconia, titania and other applications of oxide metals [21–25]. For example, catalysts used for the alkylation of isobutane with 1-butene [25] would be probably active for the skeletal isomerisation of alkenes, and alkanes, too.

4. Conclusions

A higher activity of sulphated gamma alumina (the catalyst AA) than the activity of original commercial alumina (the catalyst A) for the dehydration of C₄ alkanols conjugated with positional, geometrical and

skeletal isomerisation was proved. The isomers of butenes are formed following the kinetic, geometric and thermodynamic conditions of the process. A reaction scheme enabling qualitative and semi-quantitative description of the formation of carbenium ion intermediates and corresponding butene isomers, has been proposed. Thus, all the butene isomers may be prepared from each of the C₄ alkanols. Besides the reactions resulting in butenes, reactions which product lower and higher hydrocarbons take part, too, whereas the extent of these reactions is highest with the most reactive primary carbenium cation formed from 1-butanol.

A potentiality of the developed sulphated gamma alumina, as well as suitability of other oxides activated by this way, for other acid catalysed reactions is pointed out.

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