

Dehydration of 2,3-Butanediol over Zeolite Catalysts

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Abstract—2,3-Butanediol as a product of biomass processing is a cheap alternative raw material for synthesis of methyl ethyl ketone (MEK) and butadiene-1,3. The catalytic activity of Al- and Zr-containing BEA zeolites and an alumina-based catalyst in 2,3-butanediol dehydration has been investigated. It has been shown that the presence of Brønsted (H-BEA) or Lewis (Al_2O_3) sites leads to the selective formation of MEK and the combination of two types of sites (Zr-BEA) facilitates the formation of heavy products of condensation.

Keywords: 2,3-butanediol, butadiene, methyl ethyl ketone, zeolites, Zr-BEA, Lewis sites, Brønsted sites

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2,3-Butanediol is a biomass processing product that is produced from sugars by fermentation [1–5]. Butanediol can be used as a solvent, and its esters find applications in pharmaceutical and cosmetic industries [6]. However, 2,3-butanediol products methyl ethyl ketone and butadiene-1,3 are of most interest. Methyl ethyl ketone (MEK) is widely used as an organic solvent and a reactant for synthesis of its peroxide [7–9]. Butadiene is required in synthesis of various synthetic rubbers [10–13]. There is a lack of butadiene on the world market today; thus, alternative processes for its production are of great importance.

Industrial processes for MEK production differ from those of butadiene, but the feedstock for the manufacture of both compounds is C_4 fraction of the oil refining products. Ketone is most often produced from *n*-butylene through formation of 2-butanol [7]. Butadiene is mainly obtained from the pyrolysis C_4 fraction using selective solvents. Besides, a process for butadiene production via butane and butylene dehydrogenation (Houdry-process) is also widely used [10]. The former butadiene production process requires high pyrolysis capacity, and the latter requires high energy expenditure because of high reaction temperatures. Thus, butanediol as a biomass processing product is a cheap alternative feedstock for MEK and butadiene-1,3 synthesis.

Various acid systems (metal oxides, heteropoly acids, zeolites, etc.) can serve as a dehydration catalysts [14–19]. Under certain reaction conditions, high yields of a particular product can be achieved. To reach a high yield of diene, reaction is most frequently carried out at elevated temperatures (350–450°C). Under milder conditions, the main product of 2,3-butanediol dehydration is MEK [15, 17]; however, by varying of catalyst composition, its surface characteristics, and

strength of active sites, it is possible to affect the process selectivity at relatively low temperatures (250–300°C).

The aim of this study was to examine the influence of type and strength of acid sites on the selectivity of 2,3-butanediol dehydration process. As a catalyst with Brønsted acid sites, zeolite BEA with ratio of $\text{Si}/\text{Al} = 75$ was chosen. To obtain a BEA (75)-based system with Lewis acidity, a Zr-BEA catalyst was synthesized. BEA type zeolites are widely used as catalysts of various processes [20–22], and the possibility to modify them with metals, such as tin and zirconium, expand their application area.

EXPERIMENTAL

A commercial zeolite available from Zeolyst (trade name CP 811E-150) with $\text{Si}/\text{Al} = 75$ ratio in H-form (H-BEA) was used as original BEA(75) zeolite.

Zirconium was introduced into catalyst by postsynthetic modification. Zeolite BEA(75) was dealuminated by triple treatment with concentrated HNO_3 followed by treatment with a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution in DMSO. The isomorphous substitution of Zr for Al in tetrahedral positions of the zeolite framework was proved by XPS, NMR, and UV spectroscopy techniques.

Catalyst with low concentration of sites was dealuminated BEA zeolite (deAl BEA), which contained both Brønsted and Lewis sites. A reference catalyst was $\gamma\text{-Al}_2\text{O}_3$ (UOP) as a material with Lewis acidity.

All samples were calcined in a dried air flow at 550°C for 6 h.

Elemental composition was determined by X-ray fluorescence (XRF) analysis. The measurements were made on a Spektroskan MaksGF2E scanning wave-

Table 1. Characterization of samples

Sample	Elemental composition, ω %	Si/Me, mol/mol	Pore volume, cm ³ /g	Micropore volume, cm ³ /g	Amount of adsorbed NH ₃ , μmol/g
H-BEA	Si, 46% Al, 0.5%	86	0.76	0.16	220
deAl BEA	Si, 46% Al, 0.05%	960	0.86	0.16	43
Zr-BEA	Si, 46% Zr, 2%	89	0.81	0.15	270
Al ₂ O ₃	—	—	0.54	0.01	189

length-dispersive X-ray fluorescence spectrometer (Spektron) with operating voltage of 40 kV and a current of 50 μA. Powdered samples were pressed as 200-mg tablets. Metal content was determined by calibration.

Structure and phase composition of samples were defined by X-ray diffraction analysis on a Bruker D2 Phaser (CuKα) diffractometer in the 2θ range of 5°–80°.

Acid–base properties of samples were studied using temperature-programmed desorption of ammonia (NH₃ TPD) on a Unisit USGA-101. Sample of 0.1 g mass was placed in a quartz reactor and calcined in a dry air flow at 500°C for 1 h and with subsequent purging of reactor with nitrogen. Samples were saturated in a stream of dry ammonia diluted with nitrogen (1 : 20) for 30 min. Physisorbed ammonia was removed at 100°C in a dry helium stream (at a flow rate of 30 mL/min) for 1 h; then, sample was cooled to room temperature. To obtain a TPD curve, temperature was linearly increased up to 800°C at rate of about 8°C/min.

The nature of acid sites was studied by IR spectroscopy of adsorbed CO. IR spectra were recorded on a Nicolet Protege 380 spectrometer with 4 cm⁻¹ resolution. A low-temperature cell for IR measurement under static conditions was used for CO adsorption. Adsorption of probe molecules was conducted in vacuum, equipped with an absolute pressure sensors, at an operating vacuum of 5 × 10⁻⁴ Pa. Tablet mass was 0.02 g. Prior to experiment, catalyst samples were degassed, heated up to 450°C at a rate of 0.5°C/min, and calcined at this temperature until a vacuum ≤ 1 × 10⁻³ Pa. Adsorption of probe molecules was performed at –173°C. Pressure was monitored with a Barocell transducer.

Adsorption measurements were made on a Micromeritics ASAP 2010 instrument. Before measurement, all samples were degassed at 120°C and a pressure of 10–1 mmHg for 2 h. Nitrogen adsorption

isotherms were quantitatively processed using the program software.

Thermogravimetric analysis of catalysts was performed on a TA Instruments SDT Q600 apparatus with heat flux and corresponding mass change detection. Samples were heated at a rate of 10°C/min in temperature range of 25–800°C in a dry air flow of 100 mL/min.

Catalytic activity of systems were investigated in 2,3-butanediol dehydration reaction. Reaction was conducted in a flow reactor at atmosphere pressure and 250°C; the feedstock weight hourly space velocity was varied with the interval of 1–10 h⁻¹. Nitrogen was used as a carrier gas with a flow rate of 25 mL/h. The products were determined on a gas chromatograph with a FFAP capillary column (40 m). Methane and dioxane-1,4 were used as external standards for analysis of gaseous and liquid products, respectively.

RESULTS AND DISCUSSION

Characteristics of samples are given in Table 1.

To control dealumination process and subsequent introduction of zirconium, mass concentration of metals was determined in all samples. Results showed that dealumination of the initial BEA zeolite was incomplete, deAl BEA sample contained 0.05 wt % aluminum.

Zirconium introduction procedure proposed in this study made possible to obtain a sample with high zirconium content of 2%.

Different methods for synthesis of Zr-BEA system are reported in literature [23, 24], in particular, hydrothermal synthesis of zeolite when zirconium salt is introduced into reaction mixture or incipient wetness impregnation with aqueous solutions of zirconium salts. However, it is often impossible to introduce zirconium in a large quantity by these methods, and metal loading does not exceed 1 wt % [23].

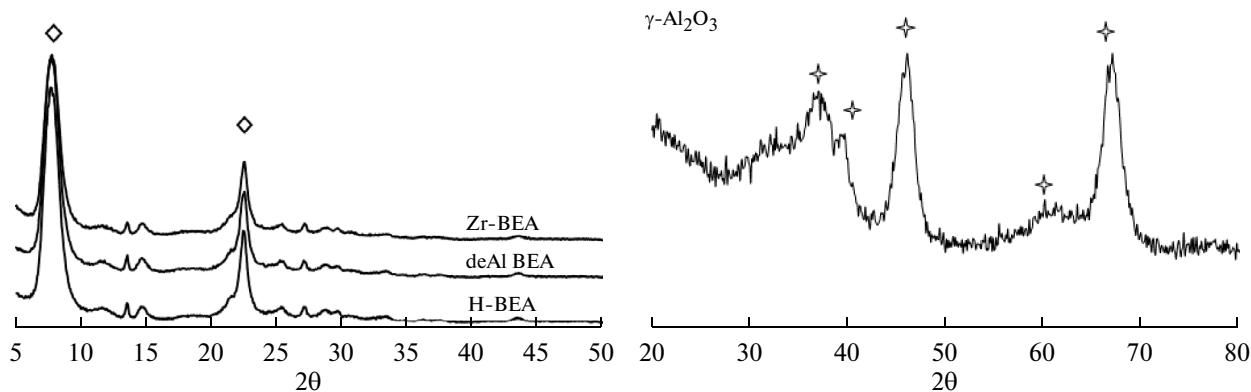


Fig. 1. X-ray diffraction analysis of catalysts.

Phase composition of samples was studied by XRD technique (Fig. 1). All zeolite samples had BEA zeolite structure. Sequential dealumination and introduction of zirconium into framework of material does not affect the crystallinity of systems and type of diffraction pattern [24–26].

Diffraction patterns of samples have reflections at 2θ of 7.74 and 22.1 characteristic of BEA zeolite. Intensity of these reflections for the deAl BEA sample is lower. This decrease can be due to the formation of small defects on sample surface, that is quite likely caused by aggressive treatment of zeolite with concentrated acid. Zr-BEA material can also be characterized by some decrease in the intensity of diffraction maximums in comparison with the initial BEA.

The diffraction pattern of γ - Al_2O_3 exhibits characteristic reflections of this oxide at 2θ of 37–39, 46, 62, and 67 in good agreement with published data and confirms modification and phase composition of this catalyst [27].

Acid properties of systems were studied using techniques of NH_3 TPD and IR of adsorbed CO. The total amount of acid sites and their distribution by strength was investigated by temperature-programmed desorption of ammonia (Fig. 2a).

The shape of NH_3 TPD curves for H-BEA and deAl BEA samples is similar, it is characterized by two peaks in temperature regions of 150–180°C and 330–380°C. The first peak is associated with physisorption of ammonia and formation of $\text{NH}_4^+(\text{NH}_3)_n$ ($n \geq 1$) groups [17]. This peak can be also due to ammonia desorption from weak acid sites; however, it is known that the temperature at its maximum and its area strongly depend on ammonia venting conditions before the experiment. The high-temperature peak at 350°C corresponds to ammonia desorption from strong acid sites and sites of medium strength. For deAl BEA, the total amount of acid sites is in five times lower than that of the initial zeolite (Table 1), a difference that is associated with a high degree of dealumination of this sample.

Curves for Zr-BEA and Al_2O_3 samples are characterized by a more blurred profile, which indicates less homogeneous distribution of sites.

The type of acid sites of samples were determined using IR spectroscopy of adsorbed CO (Fig. 2b). IR spectrum of the initial H-BEA zeolite has three characteristic bands at 2174, 2156, and 2138 cm^{-1} . The 2174- cm^{-1} band corresponds to vibrations of CO adsorbed on Brönsted acid sites of zeolite, and 2156- and 2138- cm^{-1} bands to CO adsorbed on surface OH groups and physisorbed CO, respectively [23, 28, 29]. These bands are retained in the spectrum for deAl BEA sample; however, the intensity of 2174- cm^{-1} band is lower than that for initial zeolite, indicating that the amount of Brönsted sites decreased.

Along with the bands listed above, Zr-containing sample is characterized by the presence of a band at 2190 cm^{-1} due to CO molecules adsorbed on Lewis acid sites. 2174- cm^{-1} band was also observed for this material. Thus, it can be concluded that this system is characterized by a high concentration of Lewis sites and insignificant contribution of Brönsted sites.

γ -Alumina has pronounced Lewis acidity which is in good agreement with published data [28]. During CO adsorption on this sample, band at 2195 cm^{-1} shifted to lower frequencies (2186 cm^{-1}). Kondo et al. [28] explains this behavior by either dipole–dipole interactions (unlikely in case of Al_2O_3) or inhomogeneity of active sites when CO is first adsorbed on stronger sites (2195 cm^{-1}) and then on weaker sites (2186 cm^{-1}).

Besides 2195–2186 cm^{-1} band, there is a band at 2168 cm^{-1} and a shoulder at 2145 cm^{-1} for Al_2O_3 . The 2168- cm^{-1} band is attributed to CO vibrations on nonacid hydroxyl groups of oxide, and shoulder at 2145 cm^{-1} is associated with physisorbed CO.

There is a quite distinct band at 2228 cm^{-1} for Zr-BEA and Al_2O_3 samples. This band can also be observed for systems with Brönsted acidity, although with a lower intensity. According to published data

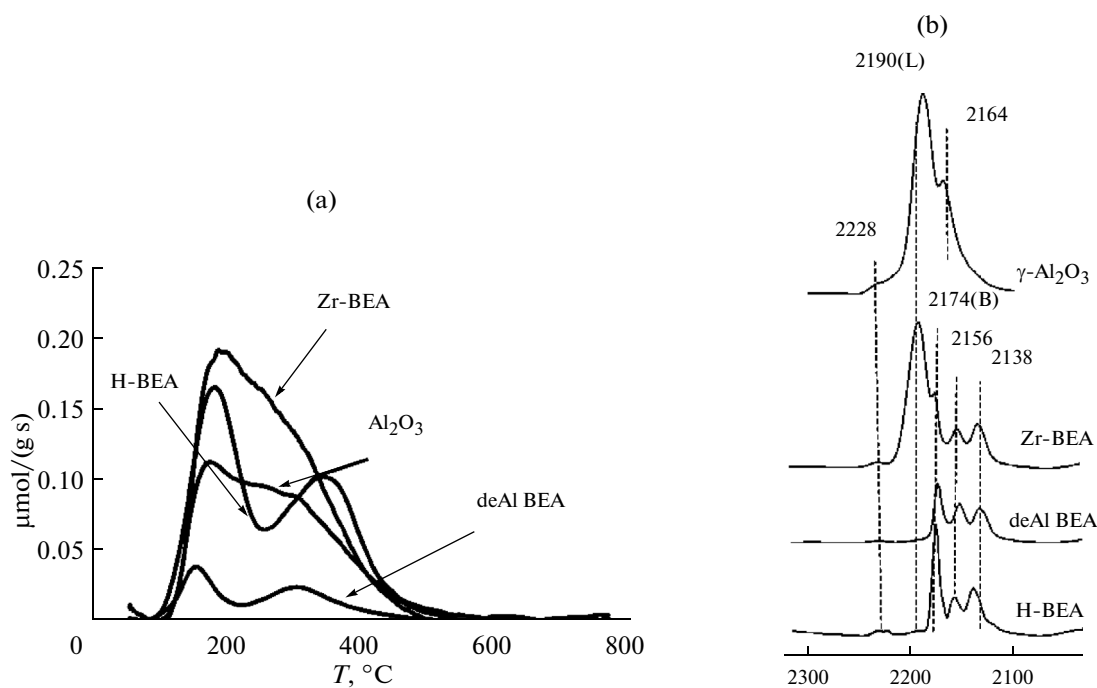


Fig. 2. (a) NH₃ TPD curves; (b) IR spectra of adsorbed CO.

[28], this band is due to CO vibrations on strong Lewis sites that were formed from Brönsted sites during dehydration (all samples were evacuated at 450°C).

To summarize, we can conclude that H-BEA and deAl BEA samples exhibit pronounced Brönsted acidity and differ only in total amount of acid sites. Zr-BEA system contains a large quantity of weak Lewis sites and an insignificant amount of Brönsted and strong Lewis sites. Alumina Al₂O₃ is characterized by the presence of a large amount of Lewis sites of different strengths.

Catalytic properties of samples were studied in 2,3-butanediol dehydration reaction. Reaction was conducted in a flow reactor at atmospheric pressure. Temperature and feed weight hourly space velocity were varied in order to find optimal conditions of the experiment.

At elevated temperature ($\geq 300^\circ\text{C}$) and a low feed space velocity ($\geq 10\text{ h}^{-1}$), all catalysts under investigation showed high activity; the butanediol conversion was 100%.

For a more correct comparison of catalysts, temperature of 250°C was chosen.

Figure 3 shows butanediol conversion versus time over all systems concerned. H-BEA catalyst with a high concentration of Brönsted sites was the most active. Its dealuminated analogue deAl BEA showed a lower activity, with both of catalysts being characterized by fast deactivation during the experiment. For systems with Lewis acid sites time-on-stream stability

of catalysts significantly increases; aluminum oxide remains stable in operation over the entire time on stream.

Thermogravimetric analysis of catalysts after reaction showed that the maximum amount of coke (15%) was accumulated over the H-BEA and Zr-BEA samples characterized by the maximal concentration of acid sites (Fig. 4).

The total loss on ignition of the samples is similar; however, condensation products differ in type. In the case of H-BEA, coke burns off at 380–540°C, but coke combustion temperature in the case of Zr-BEA is

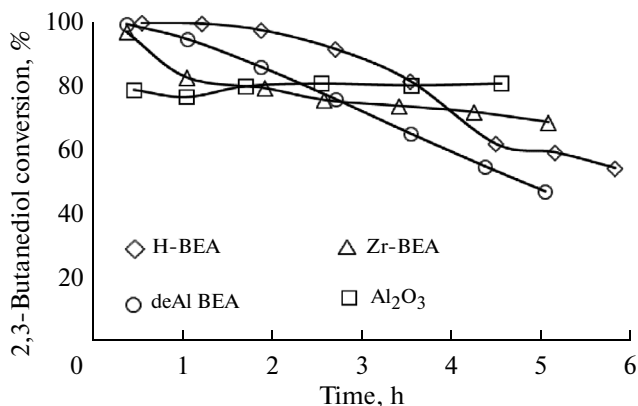


Fig. 3. Dehydration of 2,3-butanediol over catalysts (250°C, 1 atm, 2,3-butanediol WHSV = 10 h⁻¹).

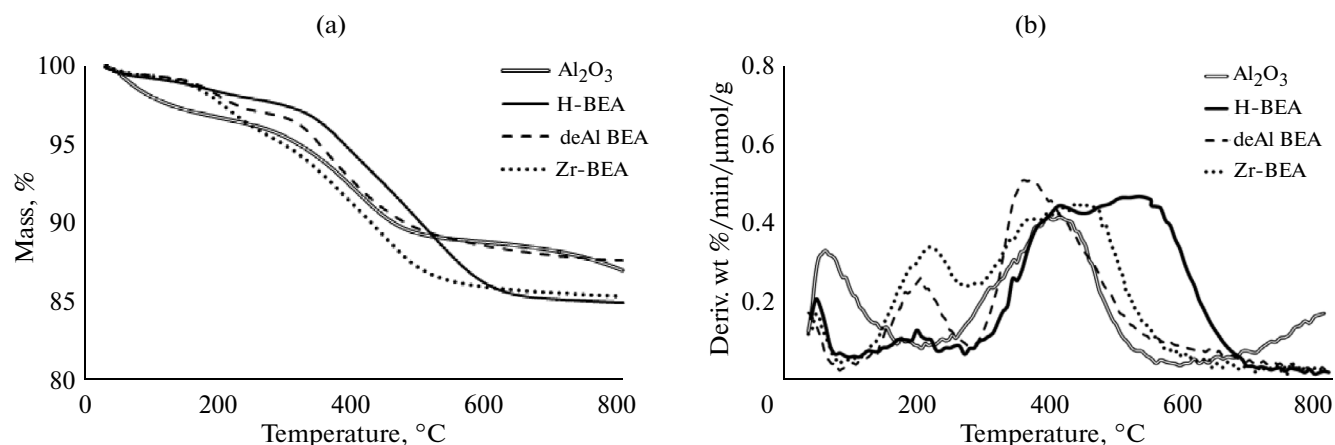


Fig. 4. Thermogravimetric curves of catalysts after 2,3-butanediol dehydration reaction (catalyst venting at 250 °C, 25 mL/min N₂, 30 min).

significantly lower (380–440 °C). It is apparently for this reason Zr-BEA zeolite has a higher deactivation stability.

Alumina is characterized by a lower coke/active site ratio. Temperature of coke combustion over this catalyst is 380 °C, corresponding to formation of light condensation products. This result is in agreement with data for Zr-BEA (Fig. 4) and confirms that the light products formed over Lewis sites are easy removable from catalyst surface.

It should be also noted that the texture of this catalyst strongly differs from that of zeolite catalysts. Alumina does not contain micropores, which can be blocked by condensation products. This is a likely cause of high time-on-stream stability of this catalyst (Fig. 3).

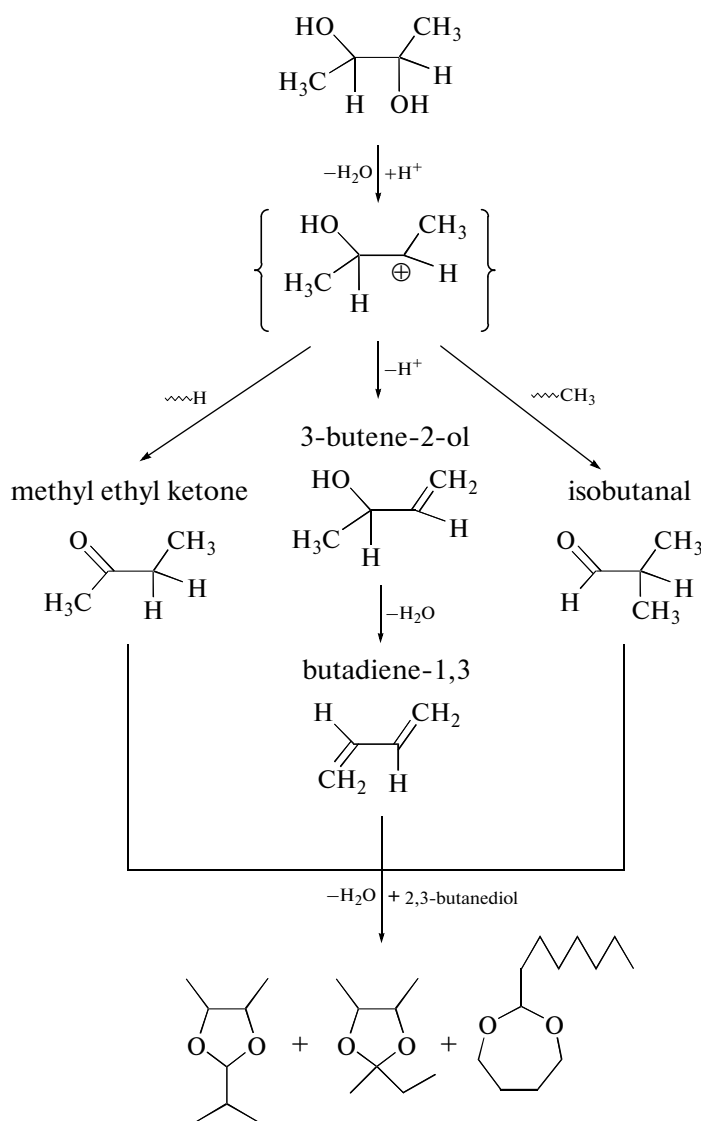
The main products of reaction on all catalysts were methyl ethyl ketone, isobutanol, and butadiene-1,3. In addition, heavy dioxolanes (C₈–C₁₂) were found in significant amount. According to literature [15, 18, 19], MEK is produced as a result of elimination of water molecule followed by hydride ion migration (scheme). In the case of isobutanol, methyl group migrates. Butadiene-1,3 is produced via the successive elimination of two water molecules involving the step of formation of unsaturated alcohol 3-butene-2-ol. Heavy products are formed as a result of interaction of primary products of reaction with initial butanediol.

Table 2 shows data on reaction products distribution at similar conversions.

Table 2. Distribution of selectivity for 2,3-butanediol dehydration products (250 °C, 1 atm, 2,3-butanediol WHSV = 10 h⁻¹)

	H-BEA	deAl BEA	Al ₂ O ₃	Zr-BEA
Acid site type*	B	B	L	L + B
2,3-Butanediol conversion, %	81.6	75.9	82.8	80.0
Product selectivity, wt %				
butadiene-1,3	4.6	4.2	3.2	2.3
isobutanol	16.3	17.4	2.8	7.2
MEK	51.9	50.5	73.3	25.7
3-butene-2-ol	0.2	0.2	0.0	0.1
C ₈ –C ₁₂	26.1	27.6	19.9	63.1

* B and L symbolize Brönsted and Lewis sites, respectively.



Scheme of the 2,3-butanediol dehydration reaction.

Zeolites H-BEA and deAl BEA having Brønsted acidity appeared to be close in selectivity. The main dehydration product in this case is MEK ($\approx 50\%$ selectivity), the most stable product, which is formed via elimination of one water molecule and subsequent hydride shift. Butadiene-1,3 is formed in an insignificant amount under the given experimental conditions, as well as unsaturated alcohol. The amount of isobutanal is 16–17%, indicates on significant contribution of the route involving methyl shift. Besides dehydration products, significant amounts of heavy condensation products (C₈–C₁₂) were observed.

In the case of Al_2O_3 , selectivity for MEK is substantially higher than that for zeolites with Brønsted acid sites (about 70%) mainly because of the decrease in the contribution of isobutanal and heavy dioxolanes. Probably Lewis acid sites likely promote hydride shift.

Zr-BEA sample strongly differs from the other systems. Main products of reaction over this catalyst were C₈–C₁₂ heavy condensation products (63%). MEK content was about 20%, and the contribution of isobutanal decreases to 2%. It is likely that combination of Brønsted and Lewis sites leads to a large contribution of condensation products with 2,3-butanediol and, hence, to a smaller contribution of desired products.

CONCLUSIONS

The main product of 2,3-butanediol dehydration over catalysts with Brønsted or Lewis sites is methyl ethyl ketone, which forms as a result of elimination of a water molecule and subsequent hydride transfer. Lewis acid sites give rise to higher catalyst selectivity and resistance to deactivation.

The combination of two types of acid sites with the prevalence of Lewis sites leads to the formation of a large amount of heavy condensation products.

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