

## Synthesis of branched C<sub>8</sub> hydrocarbons by the transformation of isobutanol-isobutane mixture over acid catalysts

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The production of high-octane gasoline on the basis of light paraffin and bio-alcohols, for instance using isobutane and isobutanol, could be interesting as an alternative for exhausting petroleum stores. Natural gas condensate is considered as the main butane source. The development of biobutanol production in the near-term future is planned by DuPont, British Petroleum, and Chevron as it was reported by Reisch (2006) and Ritter (2008).

Currently, two industrial technologies are used in petroleum refining for the production of high-octane petrol fractions on the basis of light hydrocarbons. Namely, hydroisomerization of C<sub>5</sub>-C<sub>6</sub> alkanes over bifunctional acid catalysts (predominantly chlorinated Pd/Al<sub>2</sub>O<sub>3</sub>) and isobutane-isobutene alkylation process with the use of HF and H<sub>2</sub>SO<sub>4</sub> is employed. Concerning bioalcohols, ethanol could be transformed into isoalkanes C<sub>5</sub>-C<sub>6</sub> with 60% yield employing the reaction of hydrogen reducing dehydration on intermetallic hydrides which was written in the article of Tretyakov et al. (2006). Also these authors inform that ethanol to gasoline transformation over HZSM-5 at 400°C allows the production of up to 27% of hydrocarbon (mainly aromatic) fraction. In this communication we present the data on the study of the transformation of isobutane – isobutanol mixture into branched hydrocarbons C<sub>8</sub> over some acidic materials.

### Experimental

The following catalysts have been tested: superacid tungstated zirconia prepared according to the method improved by Brei et al. (2002), HY- faujasite, and ion-exchanged resin Dowex DR 2030 SUPELCO. Isobutanol was dried over the zeolite and distilled. A flow steel reactor with fixed bed catalyst (2–3 cm<sup>3</sup>) was used. The condensed product consisted of two phases: water and hydrocarbons. The yield of obtained liquid organic substances was calculated as the mass ratio of the organic layer of the product to the quantity of spent isobutanol. Gas chromatography (“Chrom-5” with a 50 m capillary column), field mass-spectrometry (“MI-1201”) and <sup>13</sup>C NMR (“Bruker Avance-400”) methods were used for the identification of the reaction

products. 2,2,4-trimethylpentane 98%; 2,3,4-trimethylpentane 98%; 2,4,4-trimethyl-1-pentene 99%; 2,4,4-trimethyl-2-pentene 99%; 2,2-dimethylhexane 98%; 2,4-dimethylhexane 98% (Aldrich) were used as chromatography standards. Octane number of the products was determined according to standard express methods.

## Results and discussion

The performed experiments showed that the reaction products included, as a rule, isobutene, water and mixture of olefin  $C_8'$  and paraffin  $C_8$ . Therefore, the equilibrium contents in the system: isobutane – isobutene - 2,3,4-trimethylpropane - 2,5-dimethylhexene-3 - water have been calculated (Fig. 1). Despite the equilibrium calculations are approximate because of limitations caused by the availability of standard thermodynamic data for branched hydrocarbons  $C_8$ , they predict the complete conversion of isobutanol with the formation of predominantly isooctenes at  $T > 100^\circ\text{C}$ , and also isobutylene and isooctanes (Fig. 1). The total yield of hydrocarbons  $C_8$  could reach 40 mol % from spent isobutanol at 170-200 $^\circ\text{C}$ .

In order to find suitable reaction conditions at which liquid phase of hydrocarbons  $C_8$  could be formed, the experiments at 150–250 $^\circ\text{C}$  and at 0.2 – 1.2 MPa were carried out. Feed rate was varied in the interval 0.8 – 6.0 mmol  $i\text{-C}_4\text{H}_9\text{OH}/g_{\text{cat}}$  h.

The content and yield of  $C_8$  alkylates obtained on  $\text{WO}_3/\text{ZrO}_2$  are presented in the Table. The superacid  $\text{WO}_3/\text{ZrO}_2$  catalyst showed high activity in this process. The yield of  $i\text{-C}_8$  hydrocarbons reached 76 mol % of alcohol spent. The main by-product was isobutene.

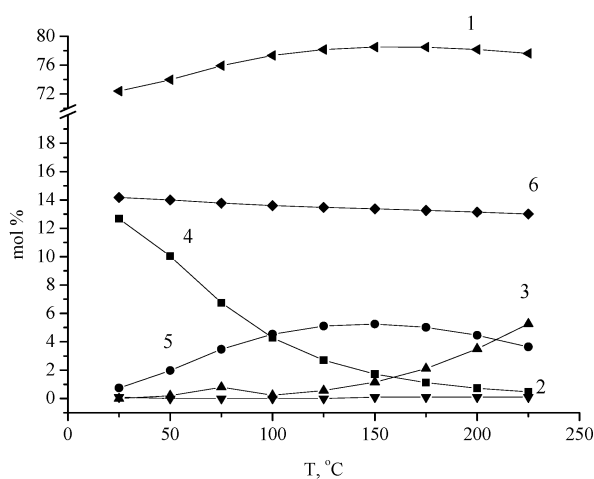


Figure 1. Equilibrium content of the reaction mixture: isobutane (1), isobutanol (2), isobutene (3), 2,3,4-trimethylpentane (4), 2,5-dimethylhexene (5), water (6) at different temperatures ( $P = 0.3\text{Mpa}$ ,  $i\text{-C}_4\text{H}_9\text{OH} : i\text{-C}_4\text{H}_{10} = 1:6$  mol).

Table. The content and yield of liquid hydrocarbons obtained over superacid  $WO_3/ZrO_2$  catalyst

T, °C	P, MPa	Feed rate, mmol (i-C <sub>4</sub> H <sub>9</sub> OH)/g <sub>cat</sub> *h	Yield, mol%	i-C <sub>8</sub> H <sub>18</sub> , %	i-C <sub>8</sub> H <sub>16</sub> , %	i-C <sub>8</sub> H <sub>18</sub> O, %	i-C <sub>4</sub> H <sub>9</sub> OH, %
190	0.3	1,7	23	11.0	89.0	0	0
200	0.7	2	68	14.4	82.9	2.6	0.1
200	0.9	2	76	21.3	78.6	0	0,1
210	1.1	2	56	13.7	85.6	0.6	0.1

The HY sample provided C<sub>8</sub> yield at the level of 10-15 mol %. Dowex DR 2030 sulfated resin was not suitable as a catalyst for this process because the appearance of SO<sub>2</sub> was observed at T > 170°C.

The field mass-spectrum of the reaction product demonstrates the presence of isooctanes (Fig. 2). Diisobutyl ether has also been detected in several experiments. The formation of hydrocarbons heavier than C<sub>8</sub> has not been observed. Measured octane numbers of obtained alkylates were equal to 100-101 (research method) and 90-91 (motor method).

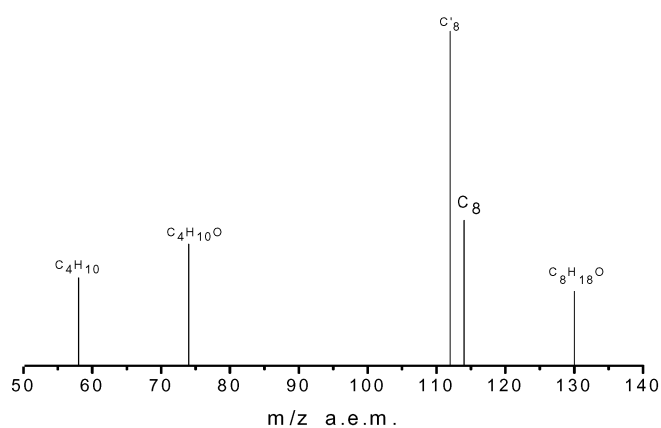


Figure 2. Field mass spectrum of the product obtained over  $WO_3/ZrO_2$  catalyst.

The transformation of isobutane-isobutanol catalyzed by solid acids includes three main reactions. Firstly, isobutene is formed as a result of isobutanol dehydration reaction over acid sites of a catalyst (isobutene was fixed in gas phase using bromine water).



Then isobutene alkylates isobutane with isooctane formation (2) or dimerizes into isooctene (3):



Thus, the process of isobutanol dehydration in the presence of isobutane over  $\text{WO}_3/\text{ZrO}_2$  catalyst results in the formation of not only isobutene and isooctenes but also isooctanes. The yield of the branched hydrocarbones  $\text{C}_8$  as well as the octane/octene ratio depends on the reaction conditions.

### References

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