

Transformation of isobutanol-isobutane mixture into branched C₈ hydrocarbons over acid catalysts

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It was shown, that isobutanol-isobutane mixture transforms into mixture of isooctenes and isooctanes as a result of isobutanol dehydration and isobutane-isobutene alkylation consecutive reactions over superacid WO₃/ZrO₂.

1. INTRODUCTION

The development of new routes of obtaining high-octane gasoline on the basis of light paraffin and bio-alcohols, e.g. using isobutane and isobutanol, can be of interest in connection with exhaustion of petroleum stores. Butane-propane fraction is formed as by-product in fluid-cracking process of gasoline. Natural gas condensate also contains a considerable quantity of butane. Recently, well-known corporations such as DuPont, British Petroleum and Chevron claimed the development of biobutanol production in the near future [1].

Currently, two industrial technologies in petroleum refining for production of high-octane petrol fractions on the basis of light hydrocarbons are used. They are hydroisomerization of C₅-C₆ alkanes over bifunctional acid catalysts and isobutane-isobutene alkylation process with the use of HF and H₂SO₄ [2].

Concerning bioalkohols, the reaction of hydrogen reducing dehydration of C₅-C₆ alcohol for obtaining of branched alkanes has been studied [3]. For instance, ethanol could be transformed into isoalkanes C₅-C₆ with 60% yield over intermetallic hydrides [3]. Transformation of ethanol over HZSM-5 at 400 °C (like MTG process) gives up to 27% of hydrocarbon (mainly aromatic) fraction [3].

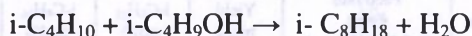
In this paper, results of the study of the reaction of isobutane alkylation with isobutanol over acidic catalysts as well as search for acceptable reaction conditions for obtaining of branched hydrocarbons C₈ are presented.

2. EXPERIMENTAL

Superacid tungstated zirconia, whose synthesis was described earlier [4], and ion-exchanged resin Dowex DR 2030 SUPELCO were used as catalysts. Isobutanol was dried under zeolite and distilled. A flow steel reactor with fixed bed catalyst (2–3 cm³) was used. Reaction products were condensed in a receiver cooled with ice. The condensed product included two phases: water and hydrocarbons (upper layer). The yield of liquid organic products was calculated as mass ratio of the upper layer to the quantity of used isobutanol. Gas chromatography (Chrom-5 with a 50 m capillary column), field mass-spectrometry (MI-1201) and ¹³C NMR (Bruker Avance-400) methods were used for the identification of the reaction products. 98% 2,2,4-trimethylpentane, 98% 2,3,4-trimethylpentane; 99% 2,4,4-trimethyl-1-pentene, 99% 2,4,4-trimethyl-2-pentene; 98% 2,2-dimethylhexane; 98% 2,4-dimethylhexane (Aldrich) were used as chromatography standards. Octane number of the products was determined according to the standard express method.

3. RESULTS AND DISCUSSION

The reaction of isobutane alkylation with isobutanol



is not forbidden thermodynamically. Equilibrium yield of isooctane can reach 40 mol % at 200 °C (Figure 1).

Experiments at 150–250 °C and at 1.5–11 Bar were carried out to determine suitable reaction conditions at which one liquid phase of hydrocarbons C₈ was formed. Different (3:1, 6:1, 8:1 and 10:1) mole ratios of reactive i-C₄H₁₀: i-C₄H₉OH mixture were used. Load feed rate was varied in the interval 0.8–6.0 mmol i-C₄H₉OH/g_{cat}h.

Content and yield of obtained liquid organic fractions are presented in the Table 1. The superacid WO₃/ZrO₂ showed high activity in the reaction. Yield of hydrocarbons i-C₈ reached 76 mol % of used alcohol (Table 1). Dowex DR 2030 resin is not suitable as a catalyst for this process because the appearance of SO₂ has been observed at T > 170 °C.

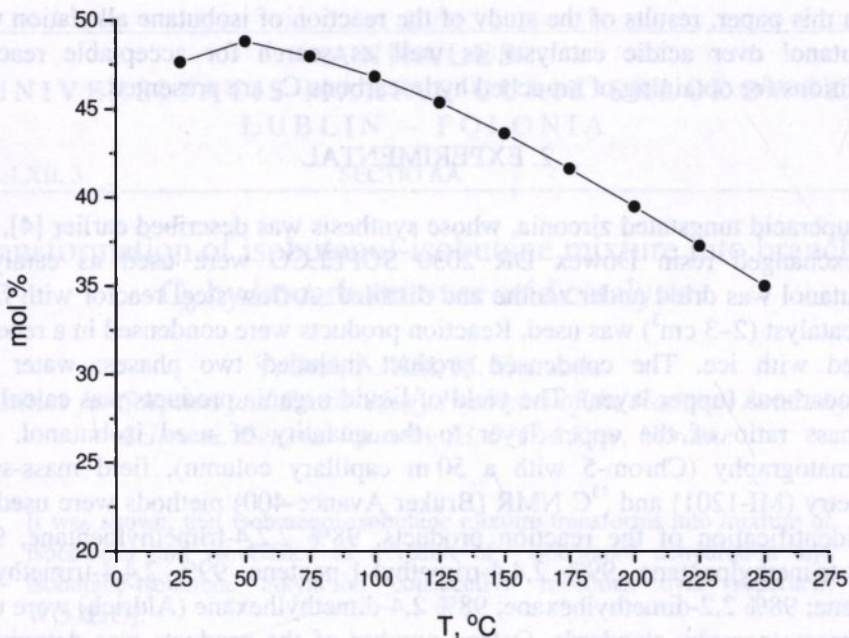


Fig.1. Equilibrium content of isooctane formed in alkylation reaction of isobutane with isobutanol at different temperatures.

Tab. 1. Content and yield of liquid hydrocarbons obtained over different catalysts.

Catalyst	T, °C	P, Bar	Feed rate mmol ($i\text{-C}_4\text{H}_9\text{OH}$)/ $g_{\text{cat}}\cdot\text{h}$	Yield mol%	$i\text{-C}_8\text{H}_{18}$ mol%	$i\text{-C}_8\text{H}_{16}$ mol%	$i\text{-C}_8\text{H}_{16}\text{O}$ mol%	$i\text{-C}_4\text{H}_9\text{OH}$ mol %
WO_3/ZrO_2	190	3	1,7	23	11	89	0	0
WO_3/ZrO_2	200	7	2	68	14,4	82,9	2,6	0,1
WO_3/ZrO_2	200	9	2	76	21,3	78,6	0	0,1
WO_3/ZrO_2	210	11	2	56	13,7	85,6	0,6	0,1
DR2030	180	3	3,2	15	55	44,5	0,5	0

Organic fractions include isooctenes and isooctanes (Table 1, Figures 2 and 3). Diisobutyl ether has also been detected in several experiments. The formation of hydrocarbons heavier than C_8 was not observed. Measured octane numbers of obtained alkylates were equal to 100–101 (research method) and 90–91 (motor method).

At the first stage of this process, isobutene is formed as a result of isobutanol dehydration reaction over acid sites of the catalyst. We have fixed isobutene in

the gas phase after reactor using bromine water. Then isobutene could alkylate isobutane with isooctane formation or dimerize to isooctene.

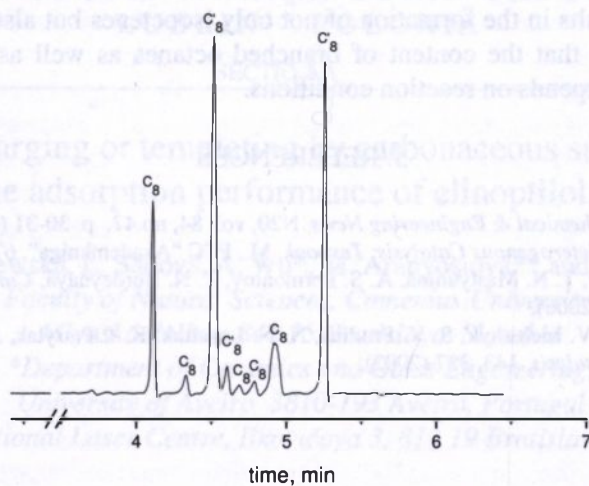


Fig. 2. Chromatogram of liquid hydrocarbon fraction (WO_3/ZrO_2 , $T = 200\text{ }^\circ\text{C}$, $P = 6\text{ Bar}$, $i\text{-C}_4\text{H}_{10} : i\text{-C}_4\text{H}_9\text{OH} = 6:1$).

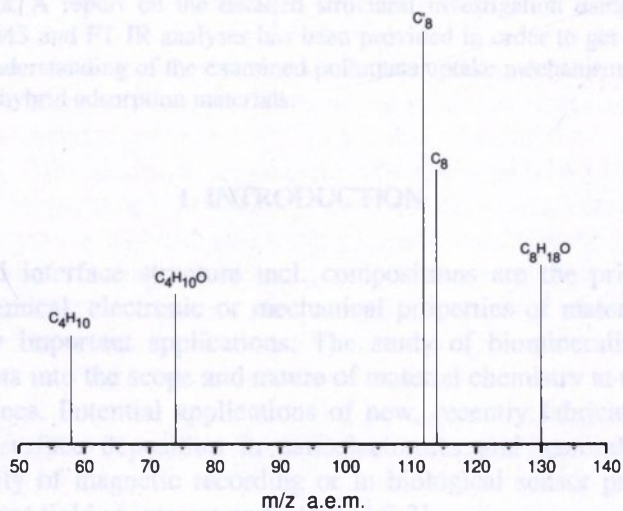


Fig. 3. Field mass spectrum of the product obtained over WO_3/ZrO_2 catalyst.

4. CONCLUSIONS

It has been shown that reaction of isobutanol dehydration in isobutane atmosphere results in the formation of not only isooctenes but also isooctanes. It has been found that the content of branched octanes as well as octane/octene ratio strongly depends on reaction conditions.

5. REFERENCES

- [1] M. S. Reisch, *Chemical & Engineering News*, N20, vol. 84, no 47, p. 30-31 (2006).
- [2] O. V. Krylov, *Heterogenous Catalysis: Textbook*, M., PTC "Akademkniga", 679 pp. (2004).
- [3] V. F. Tretyakov, T. N. Mastyunina, A. S. Lermontov, T. N. Burdeynaya, *Catalysis in Industry*, no 4, p. 12-17 (2006).
- [4] V. V. Brei, O. V. Melezhyk, S. V. Prudius, N. N. Levchuk, K. I. Patrylak, *Studies in Surface Science and Catalysis*, 143, 387 (2002).