Refinement of Gas Condensate Straight-Run Gasoline on MFI-Type Zeolites Modified with Binary Compounds

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Abstract. The work to the study catalytic properties of high-silica MFI-type zeolite (silicate module 50) modified by Sn₂O₃ + V₂O₅ and Sn₂O₃ + Bi₂O₃ binary system is devoted. In present article influence of the promoting additives concentration on the catalytic properties of high-silica MFI-type zeolite in the process of gas condensate straight-run gasoline conversion into motor fuels high-octane components are investigated. It is shown that the introduction of binary system modifying additives makes it possible to increase in octane number of liquid catalyzate on 2-3 points according to the research method, as well as the yield of the liquid catalyze weight on 6-8 % mass.

1. Introduction

Currently, the main direction of catalytic processes development in oil refining and petrochemistry is the creation of new catalysts and technologies based on them to obtain valuable chemical products from associated gas, natural gas condensate [1-8]. To implement these processes, the most promising are zeolite-based catalysts. At the present day, the greatest application achieve MFI-type zeolite, due to their unique microporous structure and molecular sieve properties exhibit high activity and selectivity in the reactions of dehydrogenation, cracking, isomerization, oligomerization and dehydrocyclization of various hydrocarbons[9-18]. The straight-run gasoline conversion on zeolite catalysts differs from classic reforming that it allows to produce high-octane gasoline of “Euro-4” and “Euro-5” grades with a low content of benzene (no more than 1–2 %), total aromatic hydrocarbons no more than 25-30 % and sulfur is lower than 0,05 – 0,1 % by weight. In addition, preliminary hydrocarbon feedstock hydrotreatment do not required for the process of zeoforming.

The purpose of this work is to study the conversion process of straight-run gasoline of gas condensate in the Tomsk region of the Myldzhinsky deposit. The conversion is carried out into high-octane components of motor fuels on zeolite catalysts that modified with binary systems of Sn₂O₃ + Bi₂O₃ and Sn₂O₃ + V₂O₅ oxides.

2. Experimental procedure

High-silica zeolites were obtained from alkaline aluminosilica gel using an organic structure forming additive hexamethylenediamine (HMDA) as a template at 175-185 °C during 2-4 days [19-20]. According to infrared spectroscopy and X-ray phase analysis, the synthesized zeolites correspond to high-silica MFI-type zeolites.
Studies on the conversion of straight-run gasoline fractions of the gas condensate were carried out on zeolite nanocomposite catalysts on a flowing catalytic installation with a stationary catalyst layer at the 350-550 °C, a feed space velocity – 2 h⁻¹ and atmospheric pressure. Analysis of gaseous and liquid products of the conversion process was carried out by gas chromatography method. The analysis of gaseous hydrocarbons was carried out on a stainless steel packed column (length 3 m, internal diameter 3 mm) filled with 5% NaOH on Al2O3 (fraction 0.25-0.50 mm), liquid hydrocarbons on a quartz capillary column (100 m x 0.25 mm x 0.25 μm) with the fixed phase ZB-1 applied. Quantitative analysis of gaseous and liquid products of the conversion process was carried out by gas chromatography method on a hardware-software complex based on the gas chromatograph "Chromatec-Crystal 5000", using the "Chromatek-Analytic" treatment program. The error in determining the gaseous and liquid hydrocarbons is ± 2.5% by the gas chromatographic method.

According to the fractional composition, the gas condensate of the Myldzhinskoye deposit has the following characteristics: the initial boiling point (IBP) is 31 °C, 82 % of vol. boils out at 200 °C, losses and residue –10 % vol. According to the hydrocarbon group, the straight-run gasoline fraction IBP - 195 °C consists of 35 % n-alkanes, 40 % - isoctanes, 20 % - naphthenes and 4 % - arenas. Octane number of straight-run gasoline fraction is 65 points by research method of gas condensate from Myldzhinskoye field with IBP – 195 °C.

3. Experiments and results

3.1. Effect of additives concentration of tin and vanadium oxides in the binary system on the catalytic properties of zeolite-containing catalysts

A measure of catalytic activity of the catalyst is the amount of formed aromatic hydrocarbons. The results of catalytic studies are presented in Table 1. The investigations of the temperature effect have made it possible to establish that the growth of the temperatur from 350 to 425 °C and the volume feed rate of straight-run petrol 2 h⁻¹ occurs a decrease in the yield of high-octane gasolines from straight-run petrol on all catalysts due to an rise in depth hydrocarbons conversion of raw materials. On HSZ, the catalytic yield drops from 65.1 % at 350 °C to 54.9 % at 425 °C by weight. First of all, the output of gaseous products increases for paraffins C₃-C₄ from 34.9% at 350 °C to 45.1% at 425 °C, and the yield of Arenes C₅-C₉ in liquid products rise from 24% to 33.3% by weight. Toluene and dimethylbenzene predominate among the Arenas, the yield of benzene and olefins C₅+ increases from 1.3 % and 1 % at 350 °C to 2.9 % and 1.7 % at 425 °C, respectively. The coming out of naphtene, n-paraffin, isoparaffin hydrocarbons decreases with increasing temperature (Table 1). Propane and butanes predominate among the gaseous products of the straight-run gasoline fraction, the materials can be used to produce commercial liquefied propane-butane gases or as an initial crude hydrocarbons for petrochemistry and gas-to-chemicals. The total yield reaches 90-95 % by weight. The coming out of propane among gaseous products rises from 47.8 % to 51.2 % at 350 °C to 425 °C, respectively.

The dependence of the octane number on temperature is presented in Fig. 1a.

![Figure 1a](image1.png)

![Figure 1b](image2.png)

**Figure 1.** The influence of temperature on the obtained catalysate octane number (a) and catalyze yield (b) in the conversion straight-run gasoline with zeolite-containing catalyst. 1 — HSZ, 2 — 96.2 % HSZ / (3 % Sn₂O₃, 0.8 % V₂O₅), 3 — 96.8 % HSZ / (3 % Sn₂O₃+0.2 % Bi₂O₃).
### Table 1. The conversion products composition of straight-run gasoline of gas condensate to catalysts: 1 - HSZ, 2 - 96.2 % HSZ / (3 % Sn<sub>2</sub>O<sub>3</sub>, 0.8 % V<sub>2</sub>O<sub>5</sub>), 3 - 96.8 % HSZ / (3% Sn<sub>2</sub>O<sub>3</sub> + 0.2 % Bi<sub>2</sub>O<sub>3</sub>).

|                     | Catalyst 1 | Catalyst 2 | Catalyst 3 |
|---------------------|------------|------------|------------|
| **Temperature, °C** | 350        | 375        | 400        |
| **Gas phase, % mass** | 34.9       | 36.8       | 42.9       |
| **Liquid phase, % mass** | 65.1       | 63.2       | 57.1       |
| **Gas phase composition, % mass** | Methane | 0.3        | 0.5        |
|                     | Ethane     | 0.9        | 1.5        |
|                     | Ethylene   | 0.3        | 0.6        |
|                     | Propane    | 56.9       | 57.6       |
|                     | Propylene  | 0.8        | 1.5        |
|                     | Isobutane  | 21.1       | 19.6       |
|                     | N-butane   | 18.7       | 17.2       |
|                     | Isobutene  | 0.9        | 1.3        |
| **Liquid phase composition, % mass** | Aromatic | 21.7       | 23.4       |
|                     | Benzene    | 1.2        | 1.5        |
|                     | Isoparaffines | 42.9       | 41.8       |
|                     | Naphthenes | 18.8       | 19.1       |
|                     | Paraffines | 15.6       | 14.5       |
|                     | Olefines   | 1.00       | 1.2        |
| **Octane number (research method)** | 87.3       | 89.7       | 91.7       |

Both catalysts that modified with binary compounds of tin and vanadium oxides make it possible to obtain catalyst with octane number by the research method more on 2-3 points than with the initial
zeolite as shown in figure. The octane numbers obtaining on the modified zeolites are close in values and they vary from 89 points at 325 °C to 94 points at 425 °C.

Figure 1b) shows the effect of the temperature of the conversion process on the yield of the catalyst in straight-run gasoline.

The highest coming out of liquid products is observed on a sample 3 - 96.8% HSZ / (3% Sn2O3 + 0.2% Bi2O3) but there is a fall from 73.1 % to 61.0% at the temperature range 350 - 425 °C.

4. Conclusion
It was studied catalytic properties of the original high-silica zeolite and zeolite catalysts that modified with binary compounds of tin (III) and vanadium (V) oxides. It is established that an increase in the amount of formed aromatic hydrocarbons and a decrease in the yield of the target product due to a rise in the depth of raw material conversion are typical for all catalysts under study. Isoparaffins, arenes and naphthenes predominate in the composition of high-octane liquid catalyst, obtaining after the raw materials conversion. Propane and butanes prevail in the gaseous reaction products. The provision of modifying additives allows increasing the octane number in the initial zeolite by the research method of the obtained catalyst by 2-3 points. Also, the modification of the zeolite leads to a rise in the yield of the liquid catalyst by 6-8 % by weight.

Thus, the most coming out of liquid products and the largest octane number of the produced catalyst is observed on a zeolite that modified with a binary oxide system (3% Sn2O3 + 0.2% Bi2O3).

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**Acknowledgments**

The research is carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.