Acidic and Catalytic Properties of Zeolites Modified by Zinc in the Conversion Process of Lower C\textsubscript{3}–C\textsubscript{4} Alkanes

Vladimir I. Erofeev \textsuperscript{1,*}, Vyacheslav V. Khasanov \textsuperscript{1}, Sofia N. Dzhalilova \textsuperscript{1}, Wladimir P. Reschetilowski \textsuperscript{2}, Anna A. Syskina \textsuperscript{1}\textsuperscript{2} and Lyubov A. Bogdankova \textsuperscript{3}

\textsuperscript{1} National Research Tomsk Polytechnic University, School of Earth Sciences & Engineering, Tomsk 634050, Russia; hasanovvv@tpu.ru (V.V.K.); dzhalilovasn@mail.ru (S.N.D.); saa@tpu.ru (A.A.S.)
\textsuperscript{2} Technical University of Dresden, Department of Mathematics and Natural Sciences, 01062 Dresden, Germany; wladimir.reschetilowski@tu-dresden.de
\textsuperscript{3} Altai State University, Department of Inorganic Chemistry, Barnaul 656064, Russia; krylatova@yandex.ru

* Correspondence: erofeevvi@mail.ru; Tel.: +7-913-812-0990

Received: 28 February 2019; Accepted: 30 April 2019; Published: 5 May 2019

Abstract: The acid and catalytic properties of the modified MFI zeolite catalysts during the conversion of the propane–butane fraction of the associated petroleum gases into the aromatic hydrocarbons were studied. It was established that the high-silica zeolites synthesized with the new structure-forming additive of the alcohol fraction (ZKE-AF) belong to the high-silica MFI zeolites. The resulting zeolites were modified by 1–5 wt. % additives consisting of zinc oxide and sulfide. The influence of the modifying additive concentration containing zinc oxides and sulfides in an amount of 1–5% on the acid and catalytic properties of the catalysts in the conversion process of lower C\textsubscript{3}–C\textsubscript{4} alkanes into liquid hydrocarbons was studied. The research of the acid properties of the modified zeolite catalysts by thermal desorption of ammonia showed that the total concentrations of the acidic centers of H-ZKE-AF modified by 3% and 5% ZnO increased. It was found that the highest yield of liquid hydrocarbons was on the zeolite catalysts modified by 3% and 5% ZnS, and is 60.6% and 60.5%, respectively, which is 9% more than in the initial H-ZKE-AF. The activity of the zeolite catalysts modified by zinc oxide and zinc sulfide was in correlation with their acid properties.

Keywords: zeolite; zinc oxide and sulphide; propane-butane fraction; conversion; arenes

1. Introduction

Lower C\textsubscript{3}–C\textsubscript{4} alkanes are the main components of the propane–butane fraction of natural and associated petroleum gases and cheap hydrocarbon feedstocks for the preparation of lower C\textsubscript{2}–C\textsubscript{4} olefins [1–3], aromatic hydrocarbons [4–8], and other valuable petrochemical products [9–12]. The microporous zeolite catalysts of the MFI type could be the most promising materials for the conversion of lower C\textsubscript{3}–C\textsubscript{4} alkanes to lower olefins and aromatic hydrocarbons, as they exhibit high activity and selectivity in dehydrogenation, isomerization, dehydrocyclization, and cracking reactions of various organic compounds [13–20].

The works [8–14] demonstrate that the high-silica zeolites of the types MFI and ZSM-5 modified by gallium, zinc, molybdenum, and rhenium are most active and selective in the process of conversion of lower C\textsubscript{1}–C\textsubscript{4} alkanes to arenes. The highest yield of the liquid propane conversion hydrocarbons was achieved at 550 °C and 56 wt. % on the catalyst of 3% Zn/ZSM-5 [15–17]. It has also been discovered that the methods for the production of the high-silica zeolites of the type ZSM-5 and introduction of the zeolite additives and their nature influence the yield and selectivity of the aromatic hydrocarbon formation from the lower alkanes [18–21].
In the work [21], the influence of the methods for producing Zn/HZSM-5 on the formation of acidic centers and the catalytic properties of the modified catalysts was studied. In Zn-ZSM-5 obtained by physical mixing of ZnO with the zeolite, zinc is present mainly in the form of ZnO macroparticles and trace amounts of ZnOH⁺, which are formed during solid-phase reactions.

In the catalysts Zn-ZSM-5 obtained by ion exchange method and direct hydrothermal synthesis, zinc is present only in the form of ZnOH⁺. The catalysts Zn-ZSM-5 synthesized by impregnation, contain most of ZnOH⁺ and ZnO nanoparticles dispersed in the pores and channels of the zeolite. Thus, zinc in the zeolites depends on the methods of its introduction into the catalyst in various surface oxygen-containing thermostable structures. It was also shown that in the acidic centers of ZnOH⁺ the reactions of dehydrogenation of light hydrocarbons to aromatic compounds and the suppression of hydrogen transport reactions and the formation of alkanes predominantly occur.

There are physical, chemical, acid, and catalytic properties of the microporous high-silica MFI zeolite synthesized using a new multicomponent structure-forming additive (alcohol fraction was a byproduct of caprolactam production) researched in the present work. The catalyst samples were modified by 1–5 wt. % ZnO and ZnS and their properties were studied in the conversion process of the propane-butane fraction of associated petroleum gases into aromatic hydrocarbons.

2. Results and Discussion

2.1. Synthesis and Characterization of Catalysts

The microporous high-silica zeolites were obtained by hydrothermal synthesis with an silicate module 45 45 from alkaline alumina-silica gel using a multicomponent organic structure-forming additive of the alcohol fraction (a byproduct of caprolactam production) in the autoclaves made of stainless steel at 170–175 °C for 4–5 days (ZKE-AF), described in [22]. To synthesize the zeolite, the organic structure-forming additive of alcohol fraction is taken in excess of no more than 2–3%. After receiving the zeolite, it is removed during calcination at 600 °C for 4–6 h.

The physical and chemical properties of the obtained zeolites were studied by X-ray diffraction analysis and IR spectroscopy. The X-ray patterns of the obtained zeolites show the lines with the interplanar distances (d, Å): 11.05; 10.00; 4.29; 4.07; 3.87; 3.83; 3.73; 3.66; 3.45; 3.06; 2.99; 2.02, which are characteristic of the ZSM-5 type zeolite (Figure 1) [23]. Due to a small amount of ZnO and ZnS (1–5%) in the zeolite, the X-ray patterns of the zeolites modified by 1–5 wt. % ZnO and ZnS correlate with the pattern of the pure H-ZKE-AF zeolite.

![X-ray spectrum of H-ZKE-AF zeolite catalyst.](image)
The IR spectra of the synthesized zeolites have intense absorption bands at 451, 541, 794, and 900–1300 cm\(^{-1}\) (Figure 2). The absorption band at 541 cm\(^{-1}\) corresponds to 5-rings in the zeolite framework and is characteristic of the ZSM-5 type zeolites. The strong absorption band at 1000–1200 cm\(^{-1}\) in the IR spectrum corresponds to the antisymmetric stretching vibrations of TO\(_4\) tetrahedra, the absorption band at 794 cm\(^{-1}\) refers to the stretching vibrations of SiO\(_4\) tetrahedra. According to the data of X-ray phase analysis and IR spectroscopy, the obtained zeolite samples in the decationized form of H-ZKE-AF refer to the microporous zeolites of the ZSM-5 type [23].

![Figure 2. IR spectrum of H-ZKE-AF zeolite catalyst.](image)

### 2.2. Catalytic Activity

The studies of the conversion process of propane–butane fraction (PBF) on the initial H-ZKE-AF zeolite showed that with the increase in the process temperature from 525 to 600 °C and the volume flow rate of PBF equal to 240 h\(^{-1}\), the yield of liquid products increased from 46.1 to 51.4% due to a rise in the conversion of PBF from 82.3 to 88.8% (Table 1).

The yield of the gaseous products with an increase in the reaction temperature of the PBF conversion decreases from 53.8 to 48.6%, the main gaseous hydrocarbon products were methane and ethane, the total content of which is 58–63%. Besides, with a growth of the reaction temperature of the gaseous products PBF conversion, the yield of lower olefins–ethylene and propylene rose, and the total content of C\(_2\)–C\(_3\) olefins increased from 6.6 to 12.6% due to the intensification of dehydrogenation and cracking reactions of alkanes.

The main liquid hydrocarbon products were aromatic hydrocarbons: benzene, toluene, and xylenes; the content of benzene increases with a rise in the conversion temperature of PBF from 13.5 to 16.4% [24–26]. The main aromatic hydrocarbon product was toluene, the content of which increased with a rise of the PBF conversion temperature from 36.9 to 39.8% (Table 1). It is important to note that the total content of the xylenes and naphthalene derivatives decreased with the rise of the PBF conversion temperature due to the dealkylation reactions of xylenes and methylnaphthalenes.

The addition of 1–5% zinc oxide (1–5% ZnO/99–95% H-ZKE-AF) to the initial H-ZKE-AF zeolite led to the yield decrease in gaseous hydrocarbons and the yield increase in liquid hydrocarbons (arenes) with a rise in the reaction temperature of the PBF conversion from 550 to 600 °C. The yield of the gaseous products with an increase in temperature of the PBF conversion reaction from 550 to 600 °C falls for all samples of H-ZKE-AF modified by 1–5% ZnO. The maximum reduction in the yield of the...
The main gaseous hydrocarbon products were methane and ethane, the total content of which was 51.5–59.5%. In addition, with a rise of the reaction temperature of the gaseous products PBF conversion, the yield of lower olefins—ethylene and propylene increased, the total content of C₂–C₃ olefins rose from 6.6 to 12.6% due to the intensification of dehydrogenation and cracking reactions of alkanes. The modification of the initial H-ZKE-AF zeolite with 1–5% zinc oxide (1–5% ZnO/99–95% H-ZKE-AF) led to an increase in the liquid hydrocarbon amount (arenes with a rise in reaction temperature of the PBF conversion from 550 to 600 °C) in comparison with the initial H-ZKE-AF (Table 1). The highest yield of the liquid PBF conversion products was achieved at 600 °C on the catalysts of 1% ZnO/99% H-ZKE-AF and 3% ZnO/97% H-ZKE-AF and was 56.8% and 54.7% respectively at 600 °C and at a feed space velocity of 240 h⁻¹. A further increase in the content of zinc oxide to 5% in the H-ZKE-AF zeolite reduced the yield of liquid hydrocarbons with an increase in the reaction temperature from 550 to 600 °C from 49.2 to 48.8% (Table 1). It should be noted that the addition of zinc oxide from 1 to 5 wt. % in the H-ZKE-AF zeolite led to an increase in the content of benzene in the liquid PBF conversion products up to 23.9% by 1% ZnS/99% H-ZKE-AF up to 23.5% by 5% ZnS/95% H-ZKE-AF at 600 °C, compared with 16.4% of benzene formed in the original H-ZKE-AF at 600 °C. The main liquid

### Table 1. Effect of temperature on composition of products (wt. %) of propane–butane fraction (PBF) conversion process on H-ZKE-AF modified by 1–5% ZnO at a feed space velocity of 240 h⁻¹.

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Initial H-ZKE-AF</th>
<th>1% ZnO</th>
<th>3% ZnO</th>
<th>5% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>550</td>
<td>575</td>
<td>600</td>
<td>550</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>82.3</td>
<td>86.2</td>
<td>88.8</td>
<td>79.5</td>
</tr>
<tr>
<td>Yield of gas products, %</td>
<td>53.9</td>
<td>51.9</td>
<td>48.6</td>
<td>48.1</td>
</tr>
<tr>
<td>Yield of liquid products, %</td>
<td>46.1</td>
<td>51.4</td>
<td>51.9</td>
<td>54.7</td>
</tr>
</tbody>
</table>

| Composition of gas products, normalized by wt. % | | | | | | | | | | | | |
| Methane | 34.4 | 38.5 | 40.9 | 31.2 | 33.5 | 36.5 | 18.7 | 23.5 | 23.9 | 20.9 | 20.8 | 16.5 |
| Ethane | 24.1 | 23.5 | 22.0 | 20.3 | 21.7 | 23.0 | 27.6 | 34.7 | 33.6 | 34.1 | 31.8 | 22.5 |
| Ethylene | 3.7 | 5.6 | 7.9 | 3.2 | 4.2 | 5.7 | 1.6 | 1.8 | 2.7 | 1.3 | 2.1 | 3.4 |
| Propane | 31.6 | 25.9 | 22.4 | 41.6 | 34.6 | 32.7 | 47.5 | 34.9 | 32.0 | 37.5 | 36.5 | 42.9 |
| Propylene | 2.9 | 3.8 | 4.7 | 2.0 | 2.4 | 3.5 | 2.6 | 3.8 | 6.4 | 4.2 | 6.5 | 11.1 |
| Isobutane | 1.0 | 0.7 | 0.3 | 0.5 | 0.2 | 0.1 | 0.4 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 |
| Butane | 1.4 | 1.0 | 0.6 | 1.0 | 0.5 | 0.5 | 1.3 | 0.7 | 0.7 | 1.2 | 1.2 | 1.8 |

| Composition of liquid products, normalized by wt. % | | | | | | | | | | | | |
| Benzene | 13.5 | 14.5 | 16.4 | 17.8 | 20.7 | 21.0 | 18.6 | 21.0 | 21.6 | 18.8 | 20.7 | 19.2 |
| Toluene | 36.9 | 37.6 | 39.8 | 40.9 | 40.4 | 37.8 | 42.2 | 41.5 | 39.0 | 40.0 | 40.0 | 38.9 |
| Ethylbenzene | 2.4 | 2.2 | 2.3 | 2.2 | 1.9 | 1.6 | 1.2 | 0.9 | 0.9 | 1.0 | 1.1 | 1.6 |
| m-Xylene | 11.3 | 10.8 | 10.5 | 10.6 | 8.8 | 7.4 | 10.9 | 8.9 | 7.8 | 8.9 | 8.1 | 7.4 |
| p-Xylene | 5.1 | 4.8 | 4.7 | 4.8 | 4.1 | 3.4 | 5.2 | 4.4 | 4.2 | 5.7 | 5.7 | 6.0 |
| α-Xylene | 5.3 | 5.1 | 5.0 | 4.9 | 4.2 | 3.5 | 4.7 | 3.8 | 3.2 | 3.5 | 3.2 | 3.1 |
| Pseudocumene | 1.2 | 1.1 | 1.0 | 1.0 | 0.7 | 0.6 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Naphthalene | 8.5 | 7.8 | 7.7 | 7.0 | 8.3 | 9.5 | 8.0 | 9.8 | 10.1 | 11.1 | 9.4 | 7.5 |
| α-methylnaphthalene | 2.1 | 1.9 | 1.7 | 1.6 | 1.7 | 2.2 | 1.1 | 1.0 | 1.1 | 0.4 | 0.3 | 0.6 |
| β-methylnaphthalene | 5.4 | 4.7 | 4.2 | 4.0 | 4.3 | 5.9 | 4.1 | 4.7 | 6.2 | 6.3 | 5.7 | 5.7 |

The main gaseous hydrocarbon products were methane and ethane, the total content of which was 51.5–59.5%. In addition, with a rise of the reaction temperature of the gaseous products PBF conversion, the yield of lower olefins—ethylene and propylene increased, the total content of C₂–C₃ olefins rose from 6.6 to 12.6% due to the intensification of dehydrogenation and cracking reactions of alkanes. The modification of the initial H-ZKE-AF zeolite with 1–5% zinc oxide (1–5% ZnO/99–95% H-ZKE-AF) led to an increase in the liquid hydrocarbon amount (arenes with a rise in reaction temperature of the PBF conversion from 550 to 600 °C) in comparison with the initial H-ZKE-AF (Table 1). The highest yield of the liquid BPF conversion products was achieved at 600 °C on the catalysts of 1% ZnO/99% H-ZKE-AF and 3% ZnO/97% H-ZKE-AF and was 56.8% and 54.7% respectively at 600 °C and at a feed space velocity of 240 h⁻¹. A further increase in the content of zinc oxide to 5% in the H-ZKE-AF zeolite reduced the yield of liquid hydrocarbons with an increase in the reaction temperature from 550 to 600 °C from 49.2 to 48.8% (Table 1). It should be noted that the addition of zinc oxide from 1 to 5 wt. % in the H-ZKE-AF zeolite led to an increase in the content of benzene in the liquid products to 21.6% at 600 °C for the catalyst of 3% ZnO/97% H-ZKE-AF compared to 16.4% of the aromatic hydrocarbons formed on the initial H-ZKE-AF at 600 °C. The introduction of 1–5% zinc sulphide (1–5% ZnS/99–95% H-ZKE-AF) to the initial H-ZKE-AF zeolite led to an increase in the yield of liquid hydrocarbons (arenes) in comparison with the initial H-ZKE-AF with a rise in the reaction temperature of the PBF conversion from 550 to 600 °C (Table 2). The maximum yield of the liquid PBF conversion products was 59.8–60.5% at 600 °C on the catalysts of 1–5% ZnS/99–95% H-ZKE-AF, which is significantly higher than the pure H-ZKE-AF (51.4%) at 600 °C and a feed space velocity of 240 h⁻¹. Besides, the modification of the H-ZKE-AF zeolite of 1–5% ZnS resulted in a significant increase in the benzene content of the liquid PBF conversion products up to 23.9% by 1% ZnS/99% H-ZKE-AF up to 23.5% by 5% ZnS/95% H-ZKE-AF at 600 °C, compared with 16.4% of benzene formed in the original H-ZKE-AF at 600 °C. The main liquid
conversion products of PBF on the zeolite catalysts modified by 1–5% ZnS were toluene and xylenes, the content of which was 38.0–41.4% and 14.2–22.2%, respectively (Table 2). The total content of toluene, xylenes, and naphthalene derivatives with an increase in the conversion temperature of PBF was likely to decrease due to the intensive dealkylation reactions.

Table 2. Effect of temperature on product composition (wt. %) of PBF conversion process on H-ZKE-AF modified by 1–5% ZnS at a feed space velocity of 240 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H-ZKE-AF</th>
<th>1% ZnS</th>
<th>3% ZnS</th>
<th>5% ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modifier</td>
<td>Initial H-ZKE-AF</td>
<td>550</td>
<td>575</td>
<td>600</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>550</td>
<td>575</td>
<td>600</td>
<td>550</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>550</td>
<td>575</td>
<td>600</td>
<td>550</td>
</tr>
<tr>
<td>Yield of gas products, %</td>
<td>550</td>
<td>575</td>
<td>600</td>
<td>550</td>
</tr>
<tr>
<td>Yield of liquid products, %</td>
<td>550</td>
<td>575</td>
<td>600</td>
<td>550</td>
</tr>
</tbody>
</table>

2.3. Acid Properties of Catalysts

The research of the acid properties of the zeolite catalysts modified by ZnO and ZnS showed that the initial H-ZKE-AF has two forms of the ammonia desorption: the low-temperature and high-temperature peaks. The low-temperature peak emerged on the thermal desorption spectrum in the region of 100–300 °C with a peak temperature of 180 °C and associated with the desorption of ammonia from the weakly Lewis acidic sites of the zeolite, which are coordinately unsaturated aluminum ions in H-ZKE-AF. The high-temperature peak in the 300–600 °C region with a peak temperature of 435 °C associated with the desorption of ammonia with the strongly Bronsted acidic centers of the zeolite, hydrogen ions of which are bridged hydroxyl groups [4,18,26–30]. The concentration of weakly acidic centers for H-ZKE-AF determined by the amount of the desorbed ammonia was 607 µmol/g, and for strongly acidic sites was 213 µmol/g (Figure 3, Table 3).
The low-temperature ammonia desorption peaks from the H-ZKE-AF zeolites modified by 1–5% ZnO shifted to the higher temperatures and were 195 and 190 °C, respectively. For 1% ZnO/99% H-ZKE-AF, the low-temperature peak of the ammonia desorption shifted slightly to the high temperatures up to 185 °C in comparison with the initial H-ZKE-AF zeolite (Figure 3). In contrast, the high-temperature ammonia desorption peaks from H-ZKE-AF zeolites modified by 1–5% ZnO were shifted to the lower temperatures from 435 °C for H-ZKE-AF to 420–425 °C for the H-ZKE-AF samples modified by 1–5% ZnO.

The concentration of weakly acidic centers for 1% ZnO/99% H-ZKE-AF decreased to 561 μmol/g compared to 607 μmol/g for H-ZKE-AF. With a further increase in the additive content from 1 to 5% ZnO in H-ZKE-AF, on the contrary, there was an increase in the concentration of the weakly acidic centers from 561 to 638 μmol/g (Table 3). The concentration of the strongly acidic centers for H-ZKE-AF was 213 μmol/g, and with an increase in the additive content from 1 to 5% ZnO in H-ZKE-AF the concentration of strongly acidic centers decreased from 213 to 129 μmol/g (Table 3).

The acid characteristics for H-ZKE-AF modified by 1–5% ZnS differ from the acid characteristics of H-ZKE-AF modified by 1–5% ZnO. The low-temperature ammonia desorption peaks from the H-ZKE-AF zeolites modified by 1–5% ZnS also shifted to the higher temperatures and were 190 and 185 °C for 1% ZnS/99% H-ZKE-AF and 5% ZnS/95% H-ZKE-AF, respectively, compared with the initial

Table 3. Acid properties of catalysts with various additives of zinc sulphide and oxide according to thermal desorption spectra of NH3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T_{peak}, °C</th>
<th>Concentration, μmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_I</td>
<td>T_II</td>
</tr>
<tr>
<td>H-ZKE-AF</td>
<td>180</td>
<td>435</td>
</tr>
<tr>
<td>1% ZnO</td>
<td>195</td>
<td>420</td>
</tr>
<tr>
<td>3% ZnO</td>
<td>185</td>
<td>425</td>
</tr>
<tr>
<td>5% ZnO</td>
<td>190</td>
<td>420</td>
</tr>
<tr>
<td>1% ZnS</td>
<td>190</td>
<td>415</td>
</tr>
<tr>
<td>3% ZnS</td>
<td>180</td>
<td>435</td>
</tr>
<tr>
<td>5% ZnS</td>
<td>185</td>
<td>420</td>
</tr>
</tbody>
</table>

* T_I, T_II—peak temperatures for forms I and II; C_I, C_II, and C_Σ—concentration of acidic centers in forms (I), (II), and total, respectively.

**Figure 3.** Thermal desorption spectrum of ammonia on H-ZKE-AF modified by 1–5% zinc oxide: (1) pure H-ZKE-AF, (2) 1% ZnO additive, (3) 3% ZnO additive, (4) 5% ZnO additive.
H-ZKE-AF zeolite (Figure 3, Table 3). The high-temperature ammonia desorption peaks from the H-ZKE-AF zeolites modified by 1% and 5% ZnS were shifted to the lower temperatures from 435 °C for H-ZKE-AF to 415 and 420 °C for the H-ZKE-AF samples modified by 1% and 5% ZnO, respectively. For 3% ZnS/97% H-ZKE-AF the low-temperature and high-temperature ammonia desorption peaks from the H-ZKE-AF zeolites modified by 3% ZnS, as well as for the initial H-ZKE-AF are 180 and 435 °C, respectively. For the modified zeolites with an increase in the content from 1 to 5% ZnS in H-ZKE-AF, the concentrations of the weakly acidic and strongly acidic centers decreased from 607 to 571 and 213 to 110 μmol/g, respectively (Figure 4, Table 3).

![Figure 4](image-url)  
**Figure 4.** Thermal desorption spectrum of ammonia on H-ZKE-AF modified by 1–5% zinc sulfide: (1) pure H-ZKE-AF, (2) 1% ZnS additive, (3) 3% ZnS additive, (4) 5% ZnS additive.

It should be noted that the total concentrations of the acidic centers of H-ZKE-AF modified by ZnO increased from 1 to 5% ZnO, from 732 to 767 μmol/g, mainly due to an increase in the concentration of the weakly acidic centers. For H-ZKE-AF modified by ZnS, with an increase in ZnS concentration from 1 to 5% ZnS, on the contrary, the total concentrations of the acid sites in the samples of the zeolite catalysts decreased from 795 to 681 μmol/g.

It is important to note that the activity of the zeolite catalysts modified by zinc oxide and zinc sulfide was in correlation with their acid properties. This behavior of the modified zeolite catalysts may be explained by the different structure of the electron shells of zinc oxide and sulfide, as well as by the formation of the different surface types of zinc oxide and sulfide with the acidic centers and their zeolite pore and surface position. The presence of the free 3d orbitals in zinc sulfides makes the electrons more mobile and reactive when these electrons interact with the acid sites of the zeolites, especially at the high temperatures of dehydrogenation, cracking, and dehydrocyclization of the lower C3–C4 alkanes as compared to the zeolite catalysts modified by zinc oxide [1,27–31]. Therefore, the zeolite catalysts modified by zinc sulfide are more active and selective in the reactions of dehydrogenation, cracking, oligomerization, and aromatization of lower C3–C4 alkanes of PBF, which results in a higher yield of methane and aromatic hydrocarbons than on the zeolites modified by zinc oxide.

3. Material and Methods

3.1. Catalysts Preparation

The microporous high-silica zeolites were obtained by hydrothermal synthesis with an oxide module 45 from alkaline alumina-silica gel using a multicomponent organic structure-forming additive of the alcohol fraction (a byproduct of caprolactam production) in the autoclaves made of stainless
steel at 170–175 °C for 4–6 days (ZKE-AF) described in [22]. The synthesis of caprolactam, all products and their composition meet the technological regulations (Joint-stock company "Nitrogen", Kemerovo, Russia). The alcoholic fraction, a by-product of caprolactam production with the final boiling point of 80–150 °C, has the following structure (wt. %): amyl alcohol—40–53; isomyl alcohol—0.5–1.7; cyclohexanone—2–22; cyclopentanone—1–3; butyl alcohol—0.3–0.6; isobutyl alcohol—0.5–2.5; 2-heptanone—0.2–2.5; 2-propanol—0.3–0.6; cyclohexanol—0.1–2.3; ethylcyclohexyl ether—1.4–9.7; higher-boiling compounds—0.2–1.3; water—the remainder. Due to the fact that the organic agent is plentiful, the process of the zeolite crystallization is slightly dependent on the possible change in cyclohexanone concentration. The zeolites of the MFI type have an orthorhombic structure (Pnma, a = 20.1; b = 19.9; c = 13.4 Å. The crystal lattice consists of the 5-membered rings and 10-membered channels with the internal diameter from 5 to 5.6 Å [32].

Modification of the H-ZKE-AF zeolite with zinc oxide in an amount of 1–5 wt. % was carried out by the method of imbibition considering the moisture capacity of the zeolite. The zeolite pellets (2 × 3 mm, the same for each sample) were imbibed with an aqueous solution of Zn(NO$_3$)$_2$ considering the moisture capacity of the zeolite, then dried for 4 h at 110 °C and calcined for 6 h at 600 °C.

The addition of zinc sulphide in the amount of 1–5 wt. % was performed by dry mixing of the calculated amounts of the H-ZKE-AF powders with ZnS powder synthesized by self-propagating high-temperature synthesis using the method described in the KM-1 vibratory ball mill at a temperature of 20–25 °C for 6 h, the modified zeolite catalysts were dried at 110 °C for 4 h and calcined at 600 °C for 6 h [24].

3.2. Characterization Techniques

The physical and chemical properties of the obtained zeolites were studied by X-ray diffraction analysis (X-ray DRON-3, Mo-anode, Ni-filter) and IR spectroscopy (Nicolet 5700 Fourier spectrometer).

3.3. Acid Properties of Catalysts

The acid properties of the zeolite catalysts modified by 1–5% ZnO and ZnS were studied at the thermal desorption device by adsorption of ammonia in a stream of helium carrier gas in the range of 50–650 °C with a linear heating rate of 10 °C/min according to the procedure described in [25]. The concentration of acid sites (μmol/g catalyst) in the zeolite catalysts modified by 1–5% ZnO and ZnS was determined by the amount of ammonia in the desorption peaks, the accuracy of determining the amount of the adsorbed ammonia by the gas chromatography method was ±2.5%.

3.4. Catalytic Activity Test

The conversion of a mixture of lower C$_3$–C$_4$ alkanes (propane–butane fraction) of the composition (wt. %) methane—0.3%; ethane—3.0%; propane—80.9%; butanes—15.8%, was carried out on the zeolite catalysts modified from 1 to 5 wt. % ZnO and ZnS in a continuous flow reactor with a stationary catalyst bed (6 cm$^3$) in a temperature range of 525–600 °C, a feed rate of 240 h$^{-1}$, atmospheric pressure and a test duration of 2 h at each specific reaction temperature (Figure 5). The composition analysis of the propane–butane fraction (PBF) and the reaction products of the PBF conversion was carried out by gas chromatography using the Chromatek-Crystal 5000M gas chromatograph.

The analysis of the gaseous hydrocarbons was carried out on the quartz glass packed column (3 m long, 3 mm internal diameter) filled with 5% NaOH on Al$_2$O$_3$ (0.25–0.50 mm fraction) using the thermal conductivity detector, the carrier gas is helium.

The analysis of the liquid conversion products of PBF was carried out on the quartz glass capillary column (100 m × 0.25 mm × 0.5 μm) with the fixed ZB-1 phase deposited on the flame ionization detector. The quantitative analysis of gaseous and liquid hydrocarbons was carried out on a hardware-software complex based on the Chromatek-Crystal 5000 M gas chromatograph using the results-based analysis program Chromatek-Analytic [25]. The error in determining the gaseous and liquid hydrocarbons by the gas chromatographic method is ±2.5%.
The study of the acid properties of the modified zeolite catalysts by the thermal desorption and IR spectroscopy analyses showed that the synthesized high-silica zeolites using the new multicomponent structure-forming additive belong to the high-silica zeolites of the MFI type. The study of the acid properties of the modified zeolite catalysts by the thermal desorption of ammonia showed that the total concentrations of the acidic centers of H-ZKE-AF modified by ZnO densifying from 1 to a 5% ZnO rise from 732 to 767 μmol/g mainly due to an increase in the concentration of the slightly acidic centers.

For H-ZKE-AF modified by ZnS, with an increase in ZnS concentration from 1 to 5% ZnS, on the contrary, the total concentrations of acid sites in the samples of the zeolite catalysts decreased from 795 to 681 μmol/g. It was found that the highest yield of the liquid hydrocarbons was observed on the zeolite catalyst modified by 3% and 5% ZnS, and was 60.6% and 60.5% respectively, which is 9% more than in the initial H-ZKE-AF. With an increase in the content of ZnO in the zeolite catalyst during the process of the propane-butane fraction conversion, the reactions of cracking and polycondensation occur mainly, it leads to an increase in the yields of alkenes and alkynaphthalenes. On the contrary, the acidity of the zeolites modified by ZnS is lower than the one of zeolites modified by ZnO, the contribution of cracking and polycondensation reactions is much smaller, it leads to an increase in the yield of liquid products.

The activity of the zeolite catalysts modified by zinc oxide and zinc sulfide was in correlation with their acid properties. This behavior of the modified zeolite catalysts can be explained by the different structure of the electron shells of zinc oxide and sulphide, as well as by the formation of the different surface types of zinc oxide and sulphide with the acidic centers and their zeolite pore and surface position. The presence of the free 3 d-orbitals in zinc sulfides makes the electrons more mobile and reactive when these electrons interact with the acid sites of the zeolites, especially at the high temperatures of dehydrogenation, cracking, and dehydrocyclization of the lower C₃–C₄ alkanes.

### 4. Conclusions

In the present work, the physical, chemical, acid, and catalytic properties of the modified MFI zeolite catalysts were studied during the conversion of the propane-butane fraction of the associated petroleum gases to the aromatic hydrocarbons. The X-ray diffraction and IR spectroscopy analyses showed that the synthesized high-silica zeolites using the new multicomponent structure-forming additive belong to the high-silica zeolites of the MFI type.

Figure 5. Diagram of catalytic process plant: (1) operator’s workplace; (2) pressure regulator; (3) cylinder with PBF; (4) pressure reducer; (5) thermocouple; (6) temperature regulator; (7) reactor; (8) heating element; (9) water cooler; (10) liquid products collector; (11) dispenser valve; (12) gas meter.
Therefore, the aromatization of lower C₃–C₄ alkanes of PBF on the zeolite catalysts modified by zinc sulfide results in a higher yield of methane and aromatic hydrocarbons than on the zeolites modified by zinc oxide.

**Author Contributions:** V.I.E. and V.P.R. planned and designed the experiments. V.I.E. and L.A.B. synthesized and characterized the catalyst. V.V.K. and S.N.D. performed the catalytic activity tests. V.I.E. and V.P.R. characterized the catalyst by X-ray diffraction analysis and IR spectroscopy. V.I.E. and A.A.S. wrote the manuscript. V.P.R. revised the manuscript. V.I.E. supervised the project and revised the manuscript. All authors discussed the results and approved the final version of the manuscript.

**Funding:** The research is funded from Tomsk Polytechnic University Competitiveness Enhancement Program grant. This work was supported by the Ministry of Education and Science of the Russian Federation (project no. 2011-1-9-519-024-068).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

11. Asachenko, E.V.; Rodina, O.V.; Ordomskii, V.V.; Gurev, Y.V.; Ivanova, I.I. Specifics of the deactivation of acid and zinc-containing propane aromatization catalysts. *Petroleum Chem.* 2008, 48, 100–104. [CrossRef]


23. Breck, D.W. *Zeolite Molecular Sieves*; Publisher World: Moscow, Russia, 1976.


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).