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# Research and Application of Modified ZSM-5 for the Process of Alkylation of Oil Distillate Fractions

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**Abstract**

In the oil distillate fraction alkylation process, a modified Zr zeolite ZSM-5 was obtained and studied. The modification was executed using a method that impregnated ZSM-5 with a 5% solution of $ZrOCl_2 \cdot 6H_2O$. X-ray diffraction studies were conducted on zeolite ZSM-5, zirconyl chloride modifier $ZrOCl_2 \cdot 6H_2O$, and modified zeolite ZSM-5-$ZrO_2$, which was calcined at temperatures of 200, 400, and 550°C. The results revealed that the phase composition of modified ZSM-5-$ZrO_2$ zeolite samples varied depending on the calcination temperature. It was determined that only at a temperature of 550°C did the modified ZSM-5 catalyst contain three phases belonging to $ZrSi_{24}O_{50}$, $ZrO_2$, and ZSM-5. The emergence of the $ZrO_2$ phase occurred at a calcination temperature of 550°C. An increase in temperature from 200 to 550°C facilitated the transition of the amorphous phase to the crystalline phase. The crystal structure of the ZSM-5-$ZrO_2$ catalyst, calcined at 550°C, contributed to a rise in its activity. Consequently, during alkylation with catalytic cracking gases, the viscosity-temperature properties of the T-30 turbine oil distillate fraction significantly improved (the viscosity index increased from 49.9 to 137). An increase in zeolite ZSM-5 activity was demonstratd due to the introduction of zirconium and an elevated calcination temperature to 550°C.

**Keywords**
ZSM-5; modified zeolite ZSM-5-$ZrO_2$; X-ray diffraction; phase composition; alkylation; viscosity index

## 1. Introduction

As is widely recognized, base oils derived from Azerbaijani sources often display unsatisfactory viscosity-temperature characteristics (low viscosity index). From these oils, hydrocarbon restructuring can only achieve low-viscosity with high viscosity indices. The main avenue for enhancing these properties involves implementing production processes that modify the chemical composition, favoring the formation of hydrocarbons with higher viscosity indices. Enriching oil fractions with isoparaffinic hydrocarbons improves their rheological properties, diminishes volatility, enhances thermal-oxidative stability, and augments several performance indicators. Therefore, alkylation is one method to increase isoparaffinic hydrocarbons by transforming normal paraffin into isoparaffins.

For alkylation processes, various modifications of zeolite-containing catalysts are utilized. Numerous alkylation methods involving isobutane, gasoline fractions, and aromatic compounds with olefins or olefin fractions on various zeolite catalysts are well-documented. Alkylation of oil fractions with olefins has primarily been studied on homogeneous systems containing $AlCl_3$. For the alkylation of oil fractions with catalytic cracking gases, we have previously examined industrial catalysts such as Seokar 2, Seokar 600, and Omnikat 210P [1-6]. The alkylation of oil fractions aims to enhance their viscosity-temperature properties (increase in viscosity index).

In prior studies on alkylation processes using Zeocar 600 and Omnikat 210P catalysts, turbine oil distillates with kinematic viscosities at 40°C of 27.8 and 76.4 $mm^2/s$ and viscosity indices of 32 and 55, respectively, were used as distillate oil fractions [1-6]. A low-viscosity industrial oil fraction with a kinematic viscosity at 40°C of 9.85 $mm^2/s$ and a viscosity index 79 was also used. Conducting the alkylation process with the Zeokar-600 catalyst at a temperature of 50°C, a pressure of 0.6 MPa, and an oil:gas ratio of 1:1 led to an increase in the viscosity index of the turbine oil distillate fraction from 32 to 75. With other zeolites, the viscosity indices of the resulting alkylates were significantly lower, ranging from 45 to 33. With a kinematic viscosity at 40°C of 76.4 $mm^2/s$, the viscosity index on the Zeokar-600 catalyst increased from 55 to 70. On other zeolites, it only reached 60. These studies have demonstrated that alkylation becomes less active as the viscosity of oil fractions increases.

It is widely acknowledged that the surface of catalysts during catalytic processes should possess a porous structure, as the activity, stability, strength, and other physicochemical properties of catalysts depend on their surface's morphological structure (porosity). Accordingly, a significant focus is placed on studying their acid-base surface properties.

By modifying catalysts with various anions and cations—effectively altering the surface properties—we can control the characteristics and yield of the resulting product.

The selected ZSM-5 zeolite for research possesses a porous structure and high acidity created by Bronsted acid sites. The integration of metal ions into the zeolite framework results in the

neutralization of some proton centers (Bronsted centers) and the emergence of new Lewis acid centers.

## 2. Experimental Part

Zeolite ZSM-5 was modified using a salt zirconyl chloride ($ZrOCl_2 \cdot H_2O$) solution via the impregnation method, then dried at 110°C for 4 hours. The zirconium-modified zeolite ZSM-5 underwent calcination in a muffle furnace at temperatures of 200°C, 400°C, and 550°C, each for 4 hours.

X-ray diffraction was employed to study the phase composition of the zeolite ZSM-5 and the zirconium-modified ZSM-5.

The alkylation of the distillate fraction of T-30 oil with catalytic cracking gases on a modified ZSM-5-$ZrO_2$ catalyst was conducted in an autoclave with a stirrer, at a temperature of 50°C, and a pressure of 0.9 MPa, established by gases at a temperature of 50°C. The amount of catalyst used was 1.5 grams [7]. The reaction time was 1 hour. The catalytic cracking gases comprised 56.09 vol% olefinic hydrocarbons, primarily C3-C4. The composition of the catalytic cracking gases is provided in Table 1. The principal properties of the distillate fraction of T-30 oil are presented in Table 2.

**Table 1** Composition of catalytic cracking gases.

| Hydrocarbons | Gas composition, % vol. |
|---|---|
| Ethylene-ethane | 0.07 |
| Propylene | 32.73 |
| Propane | 11.08 |
| Iso-butane | 21.89 |
| butene-1 | 11.74 |
| Butane | 8.43 |
| trans-butene-2 | 6.59 |
| sis-butene-2 | 4.63 |
| 3-methylbutene-1 | 0.24 |
| iso-pentane | 2.28 |
| 2-methylbutene-1 | 0.14 |
| pentene-1 | 0.10 |
| Pentane | 0.03 |
| Trans-pentene-2 | 0.03 |
| sis-pentene-2 | 0.01 |
| 2-methylbutene-2 | 0.02 |

**Table 2** The main properties of the distillate fraction of oil T-30.

| Indicators | Method | Distillate oil T-30 |
|---|---|---|
| Kinematic viscosity, $mm^2/s$, at temperatures | | |
| 40°C | ASTM D445 | 49.870 |
| 100°C | ASTM D445 | 6.1284 |
| Index viscosity | ASTM D445 | 49.9 |
| Flash point in open evaporating basin, °C | QOST 4333-87 | 173 |
| Freezing point, °C | QOST 20287-91 | minus 30 |
| Density at 20°C, $kg/m^3$ | ASTM D 5002 | 910.8 |

The kinematic viscosities at 40°C, and 100°C, and the viscosity index of the oil fraction and alkylates were determined by ASTM D445. Densities at 20°C were determined according to ASTM D 5002.

## 3. Results and Discussion

Given that the structure of surface centers fundamentally depends on the temperature of zeolite calcination and the nature of the modifier, we investigated the surface of zirconium-modified zeolite ZSM-5 catalysts calcined at temperatures of 200°C, 400°C, and 550°C.

The X-ray patterns of zirconium-modified zeolite ZSM-5, calcined at temperatures of 200°C, 400°C, and 550°C, are presented in Figure 1.

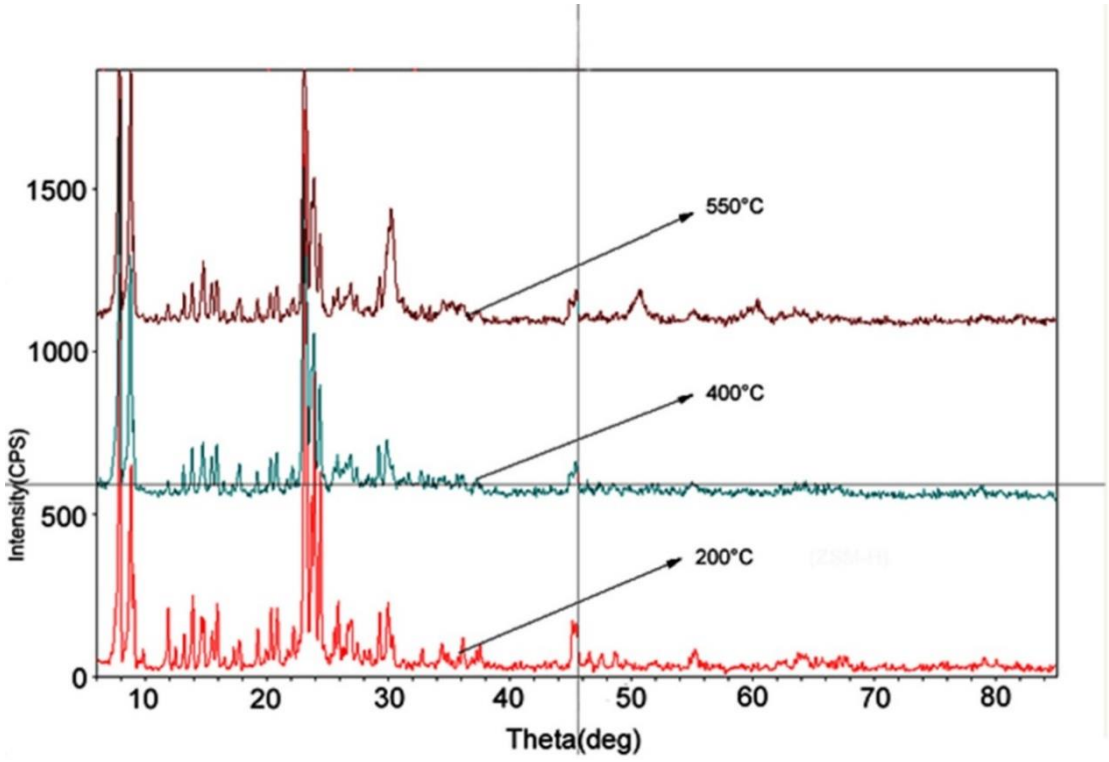


**Figure 1** Spectrum of zirconium modified zeolite ZSM-5 catalyst calcined at 200°C, 400°C and 550°C.

Figure 1 depicts the spectra of zirconium-modified zeolite ZSM-5 calcined at temperatures of 200°C, 400°C, and 550°C. As can be inferred from the spectrum of the catalyst calcined at 200°C, in addition to the ZSM-5 phase, the formation of the $ZrSi_{24}O_{50}$ phase is observed (Figure 1). The peak characteristic of the $ZrO_2$ phase is not detected.

In the spectrum of zirconium-modified zeolite ZSM-5 catalyst calcined at 400°C, the phase characteristic of $ZrO_2$ is also not visible. The observable phases are identical to those for the catalyst calcined at 200°C. As can be seen from the X-ray diffraction pattern of the ZSM-5-$ZrO_2$ catalyst calcined at a temperature of 550°C, this instance showcases the appearance of peaks corresponding to a new phase associated with $ZrO_2$ (Figure 1).

Our studies have demonstrated that the phase composition of all zirconium-modified zeolite ZSM-5 samples varies depending on the calcination temperature. Therefore, in samples calcined at temperatures of 200°C and 400°C, zirconium oxides are amorphous, and when samples are calcined at 550°C, amorphous structures transition into crystalline ones [8].

Figure 2 showcases the spectra of ZSM-5 zeolite modified with zirconium (ZSM-5-$ZrO_2$), calcined at a temperature of 550°C, with an indication of three revealed phases - $ZrSi_{24}O_{50}$, $ZrO_2$, and ZSM-5. Henceforth, we will refer to this catalyst as ZSM-5-$ZrO_2$. According to SEM-EDX, zirconium content ranged from 4.03% to 7.64% by mass. The percentage was determined across different areas of the ZSM-5-$ZrO_2$ catalyst's surface.

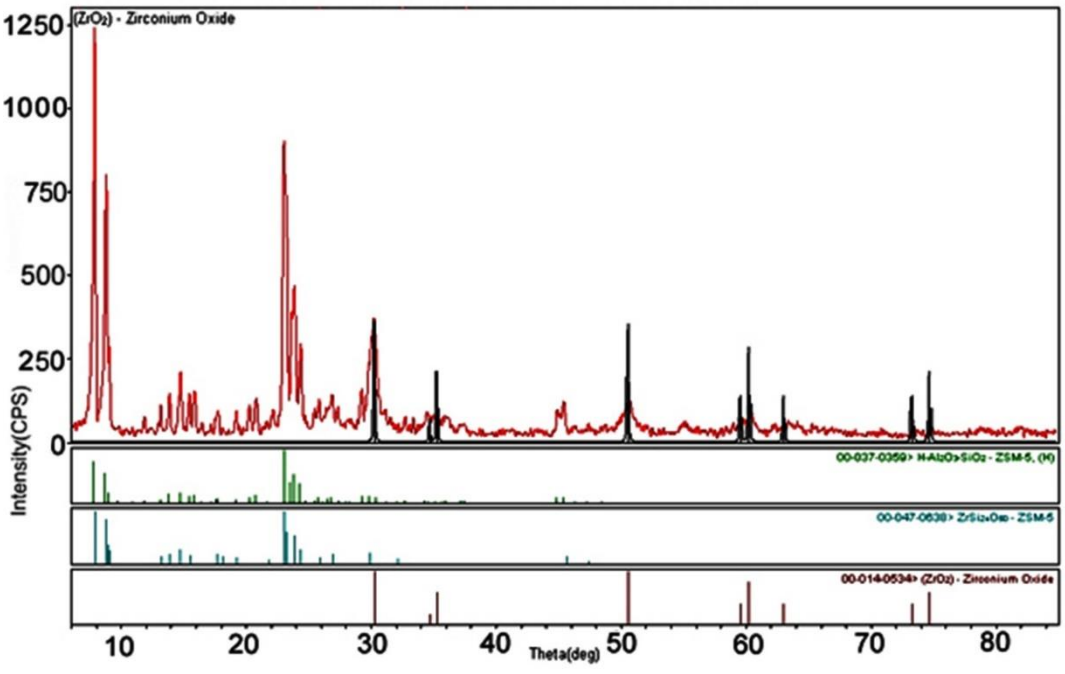


**Figure 2** Spectrum of ZSM-5-$ZrO_2$ zeolite with detailed ZSM-5, $ZrSi_{24}O_{50}$ and $ZrO_2$ phases.

Figure 3 presents the spectra of zeolite ZSM-5-$ZrO_2$ and ZSM-5, both calcined at a temperature of 550°C, as well as the spectrum of $ZrOCl_2 \cdot 6H_2O$, which served as the source of the Zr cation introduced in the form of $ZrO_2$.

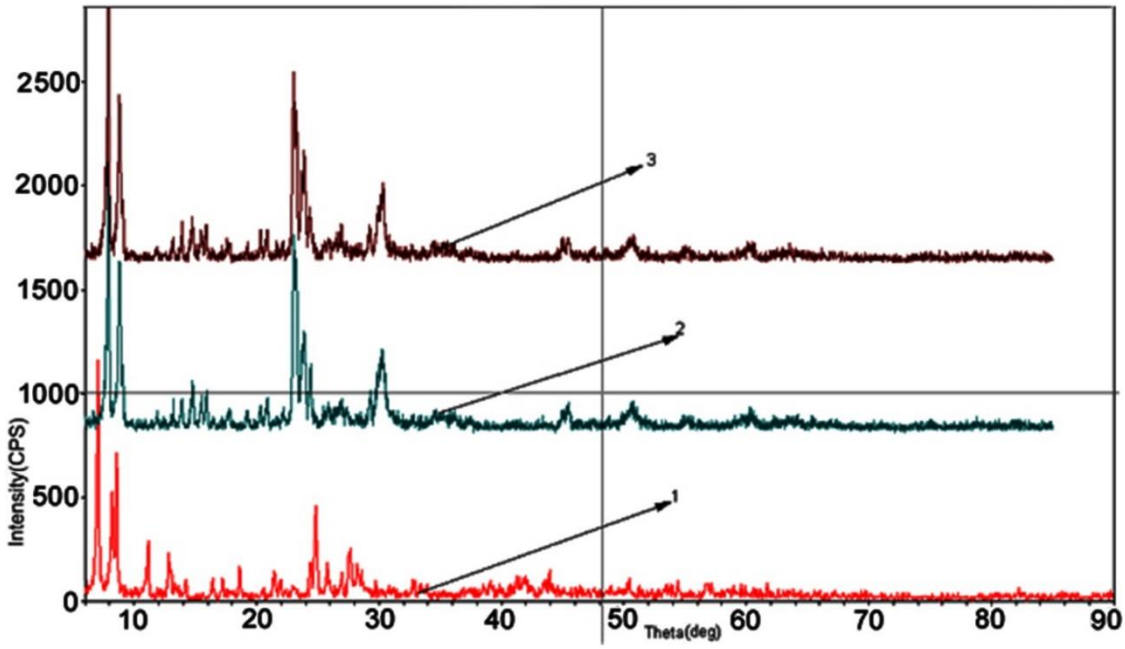


**Figure 3** Spectrum: zirconyl chloride $ZrOCl_2 \cdot 6H_2O$ (1), zeolite ZSM-5 (2) and modified zeolite ZSM-5-$ZrO_2$ (3).

The catalysts under investigation, ZSM-5 and ZSM-5-$ZrO_2$, were utilized in the process of oil fraction alkylation with catalytic cracking gases.

Table 3 presents the main physicochemical properties of the alkylates obtained on samples of the ZSM-5 and ZSM-5-$ZrO_2$ catalysts calcined at temperatures of 200°C, 400°C, and 550°C.

**Table 3** Basic physicochemical properties of alkylates obtained on the ZSM-5 and ZSM-5-$ZrO_2$.

| Name | Physicochemical properties | | | | |
|---|---|---|---|---|---|
| | $\rho_4^{20}$, kg/m$^3$ | $n_D^{20}$ | Kinematic viscosity, mm$^2$/s | | Viscosity index |
| | | | 40°C | 100°C | |
| Initial distillate fraction of turbine oil (T-30) | 910.8 | 1.5004 | 49.87 | 6.1284 | 49.9 |
| Alkylate (ZSM-5 + $ZrOCl_2 \cdot 6H_2O$, 200°C) | 896.2 | 1.4984 | 43.918 | 5.7816 | 56.5 |
| Alkylate (ZSM-5 + $ZrOCl_2 \cdot 6H_2O$, 400°C) | 897.5 | 1.4994 | 45.565 | 6.2733 | 78.6 |
| Alkylate (ZSM-5-$ZrO_2$, 550°C) | 898.0 | 1.4954 | 37.986 | 7.0715 | 137 |
| Alkylate (ZSM-5, 550°C) | 897.8 | 1.4987 | 45.40 | 6.30 | 80.7 |

v determined that the phase composition of modified zeolite ZSM-5-$ZrO_2$ samples undergoes changes depending on the calcination temperature. Increasing the temperature from 200°C to 550°C results in the transition of the amorphous phase to the crystalline phase. The crystalline structure of the catalyst contributes to an augmentation in its activity, leading to significant improvements in the viscosity-temperature properties of the distillate fraction of T-30 turbine oil during the alkylation process (with the viscosity index increasing from 49.9 to 137).

The research further revealed that the alkylate obtained on a sample of the ZSM-5-$ZrO_2$ catalyst demonstrated superior viscosity-temperature properties compared to the alkylate produced on

ZSM-5. Concurrently, the viscosity index of the original T-30 turbine oil increased from 49.9 to 80.7 during alkylation.

Simultaneously, all alkylates exhibited lower kinematic viscosity values at 40°C and higher viscosity index values than the original oil.

## 4. Conclusion

Our research indicates that the calcination temperature of catalyst samples also impacts their activity in the alkylation of distillate oil fractions with catalytic cracking gases. In the modified ZSM-5 catalyst calcined at a temperature of 550°C, the presence of $ZrSi_{24}O_{50}$ and $ZrO_2$ phases was confirmed via the X-ray diffraction. However, the calcination of the catalyst at temperatures of 200°C and 400°C did not result in the emergence of a phase corresponding to $ZrO_2$.

Therefore, introducing $ZrO_2$, specifically zirconium metal, into the composition of ZSM-5 zeolite altered the catalyst's activity about the alkylation reaction. The presence of the $ZrO_2$ phase in the catalyst composition enabled the production of an alkylate with superior viscosity-temperature characteristics (viscosity index of 137). On the other hand, alkylation of the distillate fraction of the turbine oil with catalytic cracking gases on the ZSM-5 catalyst resulted in a viscosity index increase of up to 80.7. Thus, including a modifier such as $ZrO_2$ in the ZSM-5 zeolite facilitated an even greater enhancement in the viscosity-temperature characteristics of T-30 oil, especially noteworthy when compared to the initial index of the oil – 49.9.

These results affirm the presence of Zr in the composition of the catalyst, which altered the ratio of the Lewis and Bronsted acid sites of the ZSM-5 zeolite. This shift corresponded to an increase in the Lewis acid sites and a decrease in the Bronsted acid sites. As such, in the alkylation reaction of the distillate fraction of T-30 oil with catalytic cracking gases, both Bronsted and Lewis acid sites participate, but Lewis acid sites to a greater extent. This is corroborated by studies examining changes in the ratio of acid sites in zeolites upon the introduction of metals during various reactions [9, 10].

## Author Contributions

Galina Huseynova general project management, participated in the discussion of the results, carrying out the alkylation process, article preparation. Nushaba Aliyeva conducted X-Ray diffraction, experimental data processing. Gular Gasimova received modified catalysts, carrying out the alkylation process, conducted data collection.

## Competing Interests

The authors have declared that no competing interests exist.

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