Effect of Acid Treatment on the Properties of Zeolite Catalyst for Straight-Run Gasoline Upgrading

Ludmila Velichkina *, Yakov Barbashin, Alexander Vosmerikov

Laboratory of Catalytic Conversion of Light Hydrocarbons, Institute of Petroleum Chemistry of Siberian Branch of Russian Academy of Sciences, 4, Akademichesky Ave., 634055, Tomsk, Russia; E-Mails: mps@ipc.tsc.ru; dmps@ipc.tsc.ru; pika@ipc.tsc.ru

* Correspondence: Ludmila Velichkina; E-Mail: mps@ipc.tsc.ru

Academic Editor: Md Ariful Ahsan

Special Issue: Applications of Environmental Catalysis

Catalysis Research
2021, volume 1, issue 4
doi:10.21926/cr.2104004
Received: October 10, 2021
Accepted: November 24, 2021
Published: December 01, 2021

Abstract
The objective of this research was to analyze the effect of different concentrations of nitric and hydrochloric acids on the structural, acidic, and catalytic properties of a post-synthetic treated ZSM-5 type zeolite at various temperatures. The properties of zeolite catalysts were determined using different methods, such as the Brunauer-Emmett-Teller (BET) method for specific surface area, temperature-programmed desorption (TPD) of ammonia method for acidic properties, and a flow-through unit with fixed bed catalyst (with upgrading straight-run gasoline fraction of oil) for catalytic activities of initial zeolite and acid-treated samples. The structural and acidic properties of both untreated and treated zeolites were investigated, and the effect of acid treatment on the catalytic properties of the samples in the course of upgrading the straight-run gasoline fraction of oil was determined. The post-synthetic treatment with aqueous nitric acid increased the specific surface area and volume of micropores of ZSM-5 zeolite, while the treatment with aqueous hydrochloric acid led to the formation of mesopores. Acid treatments of zeolite decreased the number of acid sites, mainly due to diminished concentration of low-temperature sites. The yield of liquid products in the conversion of straight-run gasoline fraction of oil, i.e., generation of high-

© 2021 by the author. This is an open access article distributed under the conditions of the Creative Commons by Attribution License, which permits unrestricted use, distribution, and reproduction in any medium or format, provided the original work is correctly cited.
octane gasolines with improved environmental features, was increased using acid-treated zeolites, which was due to the decrease in arene content.

**Keywords**
ZSM-5 zeolite; acid treatment; structure; acidity; catalytic activity; gasoline

---

**1. Introduction**

Synthetic zeolites are efficient catalysts owing to their increased acidity, thermal stability, and molecular sieve properties that provide higher selectivity [1]. They have a large specific surface area due to the presence of organized molecular micropores; however, several active sites located inside micropores are inaccessible to large molecules following the diffusion restrictions. Hence, much attention has been paid to the generation of zeolite-based micro-mesoporous materials, which have advantages over both microporous zeolites and mesoporous materials with its improved diffusion of reagent molecules into the crystal, decreased diffusion path of reagent and coke precursor molecules, increased acidity, and high stability under hydrothermal conditions, respectively [2-13].

Zeolite pores sized between 2-50 nm are commonly referred to as mesopores; those smaller than 2 nm are micropores, and pores larger than 50 nm are macropores [14]. Such zeolites having both micropores and mesopores, or fragments of mesopores in their intercrystalline space, are known as hierarchical zeolite systems. Micropores enable catalytic reactions, while mesopores facilitate mass transfer diffusion to active sites in the catalyst. Mesopores in a hierarchical crystal structure can either be connected with the outer surface of the zeolite, be isolated, or be interconnected with micropores.

One of the methods to obtain zeolites with a hierarchical pore system is the post-synthetic acid treatment [15-17]. Acid treatment under mild conditions removes extra-framework aluminum without releasing the aluminum from the zeolite lattice, yielding the final hierarchical structured zeolite. Further, the treatment also removes other extra-framework particles and amorphous fragments from zeolite pores for the formation of mesopores. However, highly concentrated aqueous acid solutions hydrolyzed the Si-O-Al bond not only extracted aluminum from the framework but also formed mesopores in the porous structure of zeolites efficiently.

Dealumination of zeolite alters the pore size distribution, in addition to changing its acidic properties; generally, as a result of the removal of strong Brönsted acid sites. However, under this treatment, aluminum oxide particles with intrinsically active Lewis acid characteristics remained in the interlattice space. On the other hand, an increase in the extent of dealumination increases the Si/Al ratio, pore volume, the number of silanol groups, and the number of Lewis acid sites, whereas it reduces the total number of acid sites (including extralattice hydroxyls) [18, 19]. Altering zeolites with acids causes a decrease in the aluminum content, thereby reducing the number of acid sites. In some cases, this has a positive effect on both the activity and stability of the catalytic systems [20, 21].

The main factors affecting the extent of dealumination are the nature of the acid, processing conditions, and structure of the zeolite. Therefore, the aim of this work was to study the impact of
nitric and hydrochloric acids of various concentrations on the structural, acidic, and catalytic properties of a ZSM-5 zeolite at different processing temperatures.

2. Materials and Methods

2.1 Obtaining Catalysts

A ZSM-5 zeolite with a silicate modulus of 40 (silicate module of a zeolite is characterized by the SiO₂/Al₂O₃ ratio) was obtained by hydrothermal synthesis, using hexamethylenediamine as the structure-forming additive. To obtain the H-form, the zeolite generated was decationed with a 25% aqueous solution of NH₄Cl, dried to constant weight, and calcined to remove hexamethylenediamine. Synthesis and decation procedures have been described earlier [22-24].

To meet the objectives of the present study, initial zeolite powder was treated in a water bath for 2 h with constant stirring, with 1 and 5 N aqueous nitric acid at 60 °C, and 1 and 3 N aqueous nitric acid, and 1 N hydrochloric acid solution, each at 90 °C. The choice of nitric and hydrochloric acids for the study was due to their high acidity, easy availability, and low cost of production on an industrial scale. The different conditions for the current research, such as concentration of aqueous acid solutions, and duration and temperature of treatments, were established by us analytically by carrying out a series of experiments to determine the conditions that changed the porosity and acidity of the initial ZSM-5 zeolite without destroying its crystal structure.

After the drying (6 h at 100 °C) and calcining (5 h at 550 °C) processes, the powdered samples were pressed into tablets, crushed, and only a fraction, 0.5-1.0 mm, was taken for testing. The specific bulk density of this granular zeolite catalyst was 0.713 g/cm³.

2.2 Determination of Structure and Specific Surface Area

The phase composition of the samples was determined by analyzing their X-ray patterns on a DISCOVER D8 (Bruker) diffractometer for the angles 20= 10-70°, using CuKα radiation with a Ni filter. The interplanar distances in the crystal were calculated using the centroid method [25].

Utilizing the low temperature (-196 °C) nitrogen adsorption data, the specific surface area of the catalysts (S) was determined by the Brunauer - Emmett - Teller (BET) method. The nitrogen adsorption data were obtained from an automatic gas adsorption analyzer, Sorbtometer M (ZAO “KATAKON”, Russia). To clean the surface of the samples prior to analysis, they were first dried in an oven to constant weight, followed by their final “training” in the measuring cell of a sorbtometer at 260 °C for 100 min with a stationary flow of helium at a rate of 30 mL/min before measuring them. The aforementioned conditions of "training" were selected by us, based on previous thermal analysis of zeolites, according to which, substances adsorbed on the surface of catalyst (H₂O, CO₂, etc.) were completely removed when heated to 250 °C. Currently, nitrogen has been used widely as an adsorbate for measuring the surface of materials than argon. Desorption of nitrogen was carried out at 40 °C, after which the volume and pore size of samples were calculated using the BJH model (Barett - Joyner - Halenda) from the data of adsorption and desorption isotherms.
2.3 Determination of Acidic Properties

The acidic properties of the catalysts were assessed by the process of temperature-programmed desorption (TPD) of ammonia, which helped to determine the number of acid sites and its strength distribution. In the chromatographic analysis of TPD, the sample with the molecules of the probe substance (ammonia) previously adsorbed on it, was heated at a rate of 10 °C/min in helium flow. The resulting concentration of acid sites indicated the amount of desorbed ammonia, while its strength corresponded to the temperature maxima on the desorption curve. The thermo-desorption procedure has been described earlier [26].

2.4 Determination of Catalytic Activity

The catalytic activity of the untreated (initial) zeolite and acid-treated samples was investigated in a flow-through set-up with a fixed catalyst bed in the process of upgrading the straight-run gasoline fraction of oil. The composition of feedstock for the analysis was 40.1 wt% C₃-C₁₂ n-alkanes, 26.8 wt% C₅-C₁₀ isoalkanes, 7.3 wt% C₆-C₁₂ arenes, 25.8 wt% C₅-C₁₀ cycloalkanes, with octane number 68 points.

The volume of the catalyst load in the reactor was 4 cm³. The process was carried out at a temperature of 340-400 °C with a step increase of 20 °C, and a volumetric feed rate of 2 h⁻¹ at atmospheric pressure. The sample of products obtained after 1 h of catalyst operation was taken for analysis.

2.5 Analysis of Products

Composition analysis of gaseous and liquid reaction products was carried out separately. In this process, the gaseous hydrocarbons were the by-products of the reaction. The activity and selectivity of zeolite catalysts were determined with respect to both gaseous and liquid high-octane gasoline reaction products. Catalyst yield was calculated as a percentage of the amount of the obtained catalysis (high-octane gasoline), and the volume of the feedstock (straight-run gasoline) passed through the catalyst bed, which was taken as 100%. As the coke deposit content formed on the catalysts for 4 h of their operation did not exceed 1 wt%, it was neglected while compiling the material balance of the process. Accordingly, from the known liquid yield, it was possible to calculate the amount of gas generated.

The chromatographic analysis of the composition of the feedstock and conversion products was carried out by gas-liquid chromatography using a ‘Khromatek-Kristall 5000.2’ chromatographer (GK "New technologies", Russia). The composition of the liquid phase was determined using a BP-1 PONA capillary column (100 m x 0.25 mm x 0.5 µm), while a capillary GS-Gas-Pro column (60 m x 0.32 mm) and packed Carbosieve S-II column (4 m x 2 mm) were used to determine the gas phase composition. The octane numbers of the feedstock and resulting gasolines were ascertained by a calculation method based on chromatographic data [27].
3. Results and Discussions

3.1 Structural Characteristics

An X-ray pattern, containing the sets of reflections, which is a characteristic of ZSM-5 zeolites, is shown in Table 1.

Table 1 Interplanar distances (d) and relative intensities (I_{rel}) of zeolite reflections.

| Catalysts and their crystallinity, % | d, Å | I_{rel} | d, Å | I_{rel} | d, Å | I_{rel} |
|--------------------------------------|------|---------|------|---------|------|---------|
| ZSM-5 (98%)                          | 11.2 | 100     | 11.2 | 100     | 11.1 | 100     |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 10.0 | 52      | 10.1 | 66      | 10.0 | 61      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 9.98 | 50      | -    | -       | -    | -       |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 9.76 | 18      | -    | -       | -    | -       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 6.71 | 5       | -    | -       | 6.69 | 12      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 6.37 | 5       | -    | -       | 6.36 | 8       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 5.99 | 8       | -    | -       | 5.99 | 11      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 5.71 | 4       | -    | -       | 5.72 | 7       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 5.57 | 7       | -    | -       | 5.57 | 10      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 5.02 | 4       | -    | -       | 5.02 | 7       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 4.98 | 5       | -    | -       | 4.99 | 7       |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 4.61 | 3       | -    | -       | 4.61 | 7       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 4.35 | 6       | -    | -       | 4.36 | 9       |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 4.26 | 4       | -    | -       | 4.26 | 7       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 3.85 | 47      | 3.86 | 38      | 3.85 | 64      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 3.82 | 38      | 3.83 | 30      | 3.82 | 46      |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 3.75 | 11      | 3.73 | 20      | 3.76 | 18      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 3.72 | 21      | -    | -       | 3.72 | 33      |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 3.65 | 8       | 3.66 | 13      | 3.65 | 14      |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 3.05 | 5       | -    | -       | 3.05 | 8       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | 2.98 | 5       | -    | -       | 2.98 | 8       |
| ZSM-5, treated with 1 N HCl at 90°C (96%) | 2.03 | 6       | -    | -       | 2.01 | 6       |
| ZSM-5, treated with 1 N HNO_3 at 90 °C (97%) | -    | -       | -    | -       | 1.99 | 6       |

It was found that a set of characteristic bands indicating the phase purity of zeolite and corresponding to the ZSM-5 type was obtained [25]. Acid-treated samples had diffraction bands that were identical to the reflections of pure zeolites. The intensity of the diffraction bands in the region 2θ = 23-25° did not decrease during processing, which indicated that the crystalline structure of zeolite samples was preserved. Acid-treated zeolites, specifically with HNO_3, gave fewer lines than the untreated ZSM-5, depicting higher symmetry of those crystals.

Table 2 depicts the structural characteristics of the initial ZSM-5 zeolite and its acid-treated samples.
When the zeolite was treated with a hydrochloric acid solution, the removal of framework zeolite. S₅₀ and S₄₅ values of the samples differed significantly when using HNO₃ and HCl solutions due to the nature of the acids. Although both the acids were strongly monobasic and readily soluble in water, hydrochloric acid was stronger than nitric acid under similar standard conditions.

As observed from the table, in all the cases, preliminary acid treatments increased the specific surface area of the zeolite. The increase in the specific surface area of meso- and micropores was due to the increase in the specific surface area of meso- and micropores.

| Sample | S_BET, m²/g | S₅₀, m²/g | Vₚ, cm³/g | Vₘeso, cm³/g | Vₘicro, cm³/g | D, nm |
|--------|-------------|------------|-----------|-------------|--------------|-------|
| ZSM-5, treated with 1N HCl at 90°C | 372 | 199 | 169 | 197 | 0.18 | 191 |
| ZSM-5, treated with 3N HNO₃ at 90°C | 359 | 199 | 169 | 197 | 0.18 | 191 |
| ZSM-5, treated with 5N HNO₃ at 60°C | 339 | 198 | 141 | 185 | 0.09 | 199 |
| ZSM-5, treated with 5N HNO₃ at 90°C | 339 | 198 | 141 | 185 | 0.09 | 199 |
| ZSM-5, treated with 5N HNO₃ at 100°C | 339 | 198 | 141 | 185 | 0.09 | 199 |

Note: S_BET - specific surface area of the catalyst measured by the BET method; Smeso, S₅₀ - specific surface area of meso- and micropores; Vₚ, Vₘeso, Vₘicro - total specific pore volume; Vₚ, Vₘeso, Vₘicro - total specific pore volume; D - average pore diameter.

Considering the specific surface area was observed in the specific surface area of meso- and micropores, the maximum increase in the specific surface area was observed for the sample treated with 1N hydrochloric acid solution at 90°C (372 m²/g). The highest specific surface area was observed for 3N nitric acid solution at 90°C (372 m²/g) and 5N nitric acid at 60°C (370 m²/g). The lowest increase in the specific surface area was observed for the sample treated with 1N HNO₃ at 90°C (359 m²/g).

The acidity constant (pKₐ) of hydrochloric acid was 7, while the pKₐ of nitric acid was 1.4 [18].
aluminum from the zeolite was more intense than when treated with a nitric acid solution. Consequently, the channels and cavities of the zeolite were freer with an increase in its mesoporosity. The average pore diameter of zeolite ZSM-5 decreased the most for exposure to 1 N and 5 N nitric acid solutions and 1 N hydrochloric acid solution at 90 °C.

Thus, post-synthetic acid treatments of zeolite increased the value of its specific surface, which was mainly due to an increase in the specific surface area of micropores for HNO₃, and mesopores for HCl, respectively. While the total specific pore volume remained unchanged upon acid treatment of zeolite, the volume of meso- and micropores was redistributed during the usage of hydrochloric acid. Hence, compared to the initial sample, the volume of mesopores became larger. On the other hand, a decrease in the average pore diameter of the zeolite was observed during its treatment with a solution of hydrochloric acid or nitric acid under mild conditions (at 60 °C).

3.2 Acidic Characteristics

Table 3 shows the change in the acidic characteristics of zeolite samples based on the nature of the acid and conditions of post-synthetic treatments.

| Catalyst                  | $T_{max}$ of form, °C | Concentration of acid sites, μmol/g |
|---------------------------|------------------------|------------------------------------|
|                           | $T_1$ | $T_2$ | $C_1$ | $C_2$ | $C_3$ |
| ZSM-5                     | 175   | 360   | 708   | 228   | 936   |
| ZSM-5, treated with 1 N HNO₃ at 60°C | 175   | 360   | 649   | 224   | 873   |
| ZSM-5, treated with 5 N HNO₃ at 60°C | 175   | 360   | 581   | 223   | 804   |
| ZSM-5, treated with 1 N HNO₃ at 90°C | 175   | 360   | 602   | 226   | 828   |
| ZSM-5, treated with 3 N HNO₃ at 90°C | 175   | 360   | 579   | 223   | 802   |
| ZSM-5, treated with 1 N HCl at 90°C | 175   | 350   | 603   | 230   | 833   |

Note. $T_1$, $T_2$ - temperatures of the maxima of low-and high-temperature peaks on thermal desorption curves; $C_1$, $C_2$, $C_3$ - concentrations of weak and strong acid sites and their total sum, respectively.

The thermal desorption spectra of the zeolites under study demonstrated two peaks: the first was a low-temperature peak with ammonia desorption range of 100 to 300 °C, and the second was a high-temperature peak with ammonia desorption range of 300 to 600 °C. The strength of the acid sites, designated by the maxima of the peaks, was the same for all samples, except for the sample treated with hydrochloric acid. In that particular sample, the strength of acid sites of the second type decreased slightly, as evidenced by the shift of the peak maximum by 10 °C lower. While the initial ZSM-5 zeolite had the largest number of acid sites, post acid treatment samples had decreased acidity, which was principally due to the decrease in the mass of low-temperature sites. Further, the observed pattern was related to the dealumination of the zeolite with acid
solutions. In the mechanism of dealumination, the less bound extra-framework aluminum zeolite was removed initially. This increased the number of low-temperature acid sites, whereas the concentration of high-temperature acid sites stayed practically unchanged. The samples subjected to treatment with 5 N and 3 N nitric acid solutions at 60 and 90 °C, respectively, had the same acidic characteristics. Similarly, zeolite samples treated with 1 N nitric acid and 1 N hydrochloric acid at 90 °C were also characterized by equivalent acidity.

3.3 Catalysis

3.3.1 Gaseous Products

Table 4 describes the composition of the gaseous products of the conversion of straight-run gasoline over zeolite catalysts.

| Catalyst               | Products, %     | Process temperature, °C |          |          |          |          |
|------------------------|-----------------|-------------------------|----------|----------|----------|----------|
|                        |                 |                         | 340      | 360      | 380      | 400      |
| ZSM-5                  | C₁-C₅ n-alkanes | 64.1                    | 67.4     | 69.2     | 71.5     |          |
|                        | C₁-C₅ isoalkanes| 31.7                    | 29.6     | 27.8     | 25.5     |          |
|                        | C₂-C₄ alkenes    | 4.2                     | 3.0      | 3.0      | 3.0      |          |
| ZSM-5, treated with 1 N HNO₃ at 60°C | C₁-C₅ n-alkanes | 64.2                    | 65.1     | 65.9     | 71.8     |          |
|                        | C₁-C₅ isoalkanes| 32.2                    | 31.8     | 31.1     | 25.4     |          |
| ZSM-5, treated with 5 N HNO₃ at 60°C | C₁-C₅ n-alkanes | 65.3                    | 65.8     | 67.4     | 70.9     |          |
|                        | C₁-C₅ isoalkanes| 31.4                    | 31.0     | 29.5     | 26.2     |          |
| ZSM-5, treated with 1 N HNO₃ at 90°C | C₁-C₅ n-alkanes | 65.6                    | 66.2     | 66.3     | 70.2     |          |
|                        | C₁-C₅ isoalkanes| 30.2                    | 30.1     | 30.1     | 26.3     |          |
| ZSM-5, treated with 3 N HNO₃ at 90°C | C₁-C₅ n-alkanes | 63.0                    | 64.9     | 65.4     | 69.4     |          |
|                        | C₁-C₅ isoalkanes| 31.7                    | 31.6     | 31.2     | 27.3     |          |
| ZSM-5, treated with 1 N HCl at 90°C | C₁-C₅ n-alkanes | 63.2                    | 64.3     | 65.3     | 73.1     |          |
|                        | C₁-C₅ isoalkanes| 32.2                    | 32.0     | 31.8     | 24.2     |          |
|                        | C₂-C₄ alkenes    | 4.6                     | 3.7      | 2.9      | 2.7      |          |

From the table, it is inferred that the major part of the gaseous reaction products were normal C₁-C₅ alkanes. Out of them, more than half of them were propane and C₄-C₅ isoalkanes (about 30%), while the content of C₂-C₄ alkenes was relatively small. For all zeolite catalyst samples, the following patterns were observed with the increasing temperature: the yield of n-alkanes increased with a simultaneous decrease in the presence of isoalkanes and alkenes. Consequently, an increase in the temperature of the process promoted the escalation of cracking and proton
transfer reactions. Hence, after acid treatment, a large amount of isoalkanes and alkenes was formed on the catalyst samples due to a decrease in their acidity compared to the untreated zeolite sample.

3.3.2 Liquid Products

Table 5 depicts the group hydrocarbon composition of the feedstock and the resulting catalysts, as along with the yield and octane numbers of the resulting gasolines.

**Table 5** Effect of acid treatments of zeolites and the temperature of the process of upgrading of straight-run gasoline fraction of oil on the group hydrocarbon composition and the yield of liquid reaction products.

| Catalyst          | Products, %                  | Feedstock | Process temperature, °С |    |    |    |
|-------------------|------------------------------|-----------|--------------------------|----|----|----|
|                   |                              |           | 340                      | 360| 380| 400|
| ZSM-5             | C₃-C₁₂ n-alkanes             | 40.1      | 13.5                     | 10.5| 9.8 | 8.2|
|                   | C₄-C₁₀ isoalkanes            | 26.8      | 32.3                     | 30.6| 29.2| 28.1|
|                   | C₆-C₁₂ arenes                | 7.3       | 29.7                     | 34.8| 39.7| 48.9|
|                   | C₅-C₁₀ cycloalkanes          | 25.8      | 22.6                     | 22.2|19.5 |13.0|
|                   | C₄-C₁₀ alkenes               | -         | 1.9                      | 1.9 | 1.8 | 1.8 |
|                   | Octane number                | 68        | 90                       | 91  | 94  | 97  |
|                   | Yield in catalyze, %         | -         | 80                       | 78  | 70  | 65  |
|                   | C₃-C₁₂ n-alkanes             | 18.4      | 13.9                     | 10.7| 8.2 |
| ZSM-5, treated    | C₄-C₁₀ isoalkanes            | 32.8      | 31.3                     | 30.1| 28.4|
| 1 N HNO₃ at 60 °C | C₆-C₁₂ arenes                | 25.5      | 32.9                     | 39.6| 48.5|
|                   | C₅-C₁₀ cycloalkanes          | 21.4      | 20.1                     | 18.0|13.4 |
|                   | Yield in catalyze, %         | 87        | 90                       | 94  | 97  |
|                   | Octane number                | 86        | 81                       | 72  | 66  |
|                   | C₃-C₁₂ n-alkanes             | 16.2      | 15.2                     | 12.6| 9.4 |
| ZSM-5, treated    | C₄-C₁₀ isoalkanes            | 32.5      | 32.3                     | 31.2|29.0 |
| 5 N HNO₃ at 60 °C | C₆-C₁₂ arenes                | 26.7      | 30.6                     | 38.6|46.5 |
|                   | C₅-C₁₀ cycloalkanes          | 22.7      | 20.1                     | 15.9|13.5 |
|                   | Yield in catalyze, %         | 87        | 82                       | 73  |67  |
|                   | Octane number                | 86        | 89                       | 94  |96  |
|                   | C₃-C₁₂ n-alkanes             | 19.2      | 18.2                     | 14.8|10.9 |
| ZSM-5, treated    | C₄-C₁₀ isoalkanes            | 33.4      | 33.0                     | 32.7|30.1 |
| HNO₃ at 90 °C     | C₆-C₁₂ arenes                | 21.7      | 25.3                     | 33.6|43.3 |
|                   | C₅-C₁₀ cycloalkanes          | 23.7      | 21.5                     | 17.2|14.1 |
|                   | Yield in catalyze, %         | 89        | 86                       | 77  |68  |
The qualitative compositions of liquid products obtained from initial and acid-treated samples were very similar. Specifically, an increase in the temperature led to a decrease in the concentration of all groups of hydrocarbons, except aromatic compounds. Further, under the same conditions of increased process temperature, the decreased yield of catalyze was observed, which led to an increase in the octane number.

Gasolines obtained for the initial untreated ZSM-5 sample depicted the highest octane characteristics. After acid treatment of the samples, the accumulation of acid sites of zeolites decreased, resulting in the increase of gasoline formed while decreasing the aromatic hydrocarbons presence. According to the latest automotive fuel requirements, aromatic hydrocarbon content must be strictly limited to 35 vol%; out of which benzene should not be more than 1 vol%, olefins must not exceed 18 vol%, and octane number (which changes based on the research method) must not less be than 80 points [29]. Comparing the resultant samples of the present study with the required standards, it was found that the products of catalysis (catalyzates) obtained at 340-360 °C for untreated sample and zeolites treated with 1 and 5 N nitric acid solutions at 60 °C were in full accordance with the required index. The same held true for the catalyzates obtained at 340-380 °C for catalysts treated at 90 °C with 1 N and 3 N solutions of nitric acid and 1 N hydrochloric acid.

Along with arenes, isohydrocarbons also had high octane numbers, but their content in gasolines was not within the prescribed limit. Figure 1 illustrates the content of isoalkanes in the catalysts obtained at different processing temperatures for the initial ZSM-5 zeolite sample and over acid-treated zeolite samples.
Figure 1 Effect of the temperature of process on the yield of C₄-C₁₀ isoalkanes during the processing of straight-run gasoline fraction of oil over the initial zeolite and samples subjected to acid treatment.

The lowest amount of isoalkanes for the entire range of temperatures studied was contained in gasolines obtained for the untreated ZSM-5 zeolite. Acidic treatment of zeolite with nitric acid promoted the content of isoalkanes in the gasolines; the order in which the content increased was: 1 N HNO₃, 60 °C < 5 N HNO₃, 60 °C < 1 N HNO₃, 90 °C < 3 N HNO₃, 90 °C. This explained that the isomerizing activity of the zeolite increased under acute processing conditions. For instance, the isomerizing ability of a sample treated with 3 N HNO₃ solution at 90 °C was the highest, followed by the sample treated with 1 N HCl at 90 °C at a process temperature of 340 °C. Furthermore, an increase in the temperature of the process caused a sharper decrease in the fraction of isoalkanes in catalyzates formed for the sample treated with hydrochloric acid. However, the content of isoalkanes in the catalyzates obtained in the course of the temperature range 360-400 °C for this sample was higher than the catalyzates obtained for 1 N HNO₃ at 60 °C.

For a more comprehensive analysis of the effect of concentration and temperature of nitric acid treatment, we have presented the data on the yield of isoalkanes obtained for the untreated zeolite and acid-treated samples at various concentrations and at 60 and 90 °C (Figure 2).
**Figure 2** Effect of nitric acid concentration and temperature of zeolite pretreatment on the yield of C₄-C₁₀ isoalkanes formed in the process of conversion of straight-run gasoline fraction of oil (T = 360 °C).

It can be perceived from Figure 2 that the formation of a greater number of isostructural alkanes was directly caused by the higher acid concentrations and processing temperatures.

Figure 3 depicts the overall effect of treatment of zeolite with 1 N aqueous solutions of nitric and hydrochloric acids for 2 h at 90 °C on the yield and composition of liquid products obtained during the conversion of straight-run gasoline fraction of oil over the catalysts.

**Figure 3** Yield, composition, and octane numbers of catalyzates formed during the conversion of straight-run gasoline fraction of oil over zeolite catalysts treated with various acids (T = 360 °C).
According to the data given in Table 3, though the aforementioned samples were proximate in their acidic properties, they were moderately different in their catalytic properties. The sample treated with 1 N HCl solution exhibited higher aromatization activity during the upgradation of straight-run gasoline than the sample treated with nitric acid. Following the increase in the aromatic hydrocarbon content in the hydrochloric acid sample catalyze, its octane number increased by 3 points. On the other hand, the concentration of isoalkanes on the same zeolite sample was slightly lower than its content in the liquid product formed after treatment with HNO₃ solution. Thus, the pretreatment of the zeolite with an aqueous solution of nitric acid was more conducive to increase its isomerization activity compared to the same treatment with hydrochloric acid solution.

4. Conclusions

Post-synthetic treatment of zeolite ZSM-5 with aqueous solutions of nitric and hydrochloric acids caused an increase in its specific surface area from 339 to 363-373 m²/g. At the same time, while nitric acid treatment of zeolite increased the specific surface of mesopores from 198 to 199-203 m²/g, hydrochloric acid treatment increased it to 263 m²/g. In a similar manner, the specific surface of micropores during nitric acid treatment of the sample increased from 141 to 160-170 m²/g, whereas it decreased from 141 to 110 m²/g for hydrochloric acid treatment.

Considering the total specific pore volume, it remained practically unchanged between the initial (0.17 cm³/g) and treated zeolites (0.17-0.18 cm³/g). While the specific volume of the mesopores remained the same for the nitric acid treated sample (initial ZSM-5 was 0.09 cm³/g and treated sample was 0.09-0.08 cm³/g), on the contrary, hydrochloric acid increased the specific volume of the mesopores of the zeolite to 0.11 cm³/g. Similarly, the treatment of the zeolite with different concentrations of nitric acid had essentially no effect on the specific volume of micropores as it was 0.08-0.09 cm³/g for the treated samples, and 0.08 cm³/g for the initial sample. However, treatment with a solution of hydrochloric acid decreased the specific volume of micropores to 0.06 cm³/g from 0.08 cm³/g.

Analyzing the average pore diameter of the samples, under nitric acid treatment, it decreased from 1.99 to 1.97-1.85 nm, and for hydrochloric acid treatment, it decreased to 1.80 nm. Therefore, it was inferred that treatment with hydrochloric acid solution yielded a greater increase in the mesoporosity of ZSM-5 compared to treatment with nitric acid solution.

Examining the strength of the acid sites of the original and treated zeolites, it was surmised that the strength did not get altered for low-temperature sites (175 °C), but high-temperature sites decreased at 360 to 350 °C on treatment with a hydrochloric acid solution. For all the acid-treated zeolite samples considered in the study, a decrease from 936 to 873-802 µmol/g in the total number of acid sites was reported due to the decrease in the concentration of low-temperature acid sites from 708 µmol/g to 649-579 µmol/g for the treated zeolites. This was mainly ascribed to the removal of extra-framework aluminum atoms during treatment with acid solutions. In addition, the concentration of high-temperature acid sites related to the framework aluminum atoms was 228 µmol/g, which remained nearly the same even after the treatments (223-230 µmol/g), indicating the retention of the crystal structure of ZSM-5 during acid treatments.

Stringent conditions of preliminary acid treatment increased the isomerizing ability of zeolite catalysts (the yield of C₄-C₁₀ isoalkanes on treated zeolites increased to 2.7 wt% at 400 °C from
initial ZSM-5 value of 1.3 wt% at 340 °C and yield of liquid products of the process of conversion of straight-run gasoline fraction oil (up to 9% at 340 °C and up to 5% at 400 °C), which were 3 N concentration of nitric acid solution or 1 N hydrochloric acid solution at a processing temperature of 90 °C. In conclusion, to increase the amount of catalyzate with a higher content of isostructural hydrocarbons, it is recommended to use a nitric acid solution. In addition, the results obtained can be used to further enhance the methods and technology utilized for modifying zeolite catalysts and producing high-octane gasolines.

Author Contributions

Ludmila Velichkina planned and conducted all experimental studies (except BET). After processing of experimental data, she wrote the manuscript. Yakov Barbashin conducted analytical research using the BET method. Alexander Vosmerikov supervised and revised the final version of the manuscript.

Funding

The work was performed within the state assignment of the Institute of Petroleum Chemistry of the SB RAS funded by the Ministry of Science and Higher Education of the Russian Federation.

Competing Interests

The authors have declared that no competing interests exist.

Additional Materials

The following additional materials are uploaded at the page of this paper.

1. List of Symbols and Abbreviations.

References

1. Velichkina LM. Hydrogen-free domestic technologies for conversion of low-octane gasoline distillates on zeolite catalysts. Theor Found Chem Eng. 2009; 43: 486-493.
2. Serrano DP, Escola JM, Pizarro P. Synthesis strategies in the search for hierarchical zeolites. Chem Soc Rev. 2013; 42: 4004-4035.
3. Na K, Choi M, Ryoo R. Recent advances in the synthesis of hierarchically nanoporous zeolites. Microporous Mesoporous Mater. 2013; 166: 3-19.
4. Koohsaryan E, Anbia M. Nanosized and hierarchical zeolites: A short review. Chinese J Catal. 2016; 37: 447-467.
5. Parkhomchuk EV, Sashkina KA, Parmon VN. New heterogeneous catalysts based on zeolites with hierarchical pore system. Pet Chem. 2016; 56: 197-204.
6. Ponomareva OA, Kasyanov IA, Knayzeva EE, Konnov SV, Ivanova II. Effect of the degree of zeolite recrystallization into micro–mesoporous materials on their catalytic properties in petroleum refining and petroleum chemistry processes. Pet Chem. 2016; 56: 819-826.
7. Shvets OV, Konyshева KM, Kurmach MM. Morphology and catalytic properties of hierarchical zeolites with MOR, BEA, MFI, and MTW topology. Theor Exp Chem. 2018; 54: 138-145.
8. Bai R, Song Y, Li Y, Yu J. Creating hierarchical pores in zeolite catalysts. Trends Chem. 2019; 1: 601-611.
9. Peng P, Gao XH, Yan ZF, Mintova S. Diffusion and catalyst efficiency in hierarchical zeolite catalysts. Natl Sci Rev. 2020; 7: 1726-1742.
10. Qu H, Ma Y, Li B, Wang L. Hierarchical zeolites: Synthesis, structural control, and catalytic applications. Emergent Mater. 2020; 3: 225-245.
11. Chen LH, Sun MH, Wang Z, Yang W, Xie Z, Su BL. Hierarchically structured zeolites: From design to application. Chem Rev. 2020; 12: 11194-11294.
12. Talebian-Kiakalaieh A, Tarighi S. Synthesis of hierarchical Y and ZSM-5 zeolites using post-treatment approach to maximize catalytic cracking performance. J Ind Eng Chem. 2020; 88: 167-177.
13. Zou R, Dong X, Jiao Y, D'agostino C, Yan W, Fan X. Controllable synthesis, diffusion study and catalysis of hierarchical zeolites. Chem J Chinese U. 2021; 42: 74-100.
14. Tao Y, Kanoh H, Abrams L, Kaneko K. Mesopore-modified zeolites: Preparation, characterization, and applications. Chem Rev. 2006; 106: 896-910.
15. Müller M, Harvey G, Prins R. Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl4 by 1H, 29Si and 27Al MAS NMR. Microporous Mesoporous Mater. 2000; 34: 135-147.
16. Giudici R, Kouwenhoven HW, Prins R. Comparison of nitric and oxalic acid in the dealumination of mordenite. Appl Catal A-gen. 2000; 203: 101-110.
17. Kuvatova RZ, Travkina OS, Kutepov BI. Synthesis of micro/mesoporous ZSM-5 zeolite using natural aluminosilicate. Catal Ind. 2021; 13: 99-104.
18. van Donk S, Janssen AH, Bitter JH, de Jong KP. Generation, characterization, and impact of mesopores in zeolite catalysts. Catal Rev Sci Eng. 2003; 45: 297-319.
19. Rieg C, Li Z, Kurtz A, Schmidt M, Dittmann D, Benz M et al. A method for the selective quantification of Bronsted acid sites on external surfaces and in mesopores of hierarchical zeolites. J Phys Chem C. 2021; 125: 515-525.
20. Kim J, Choi M, Ryoo R. Effect of mesoporosity against the deactivation of MFI zeolite catalyst during the methanol-to-hydrocarbon conversion process. J Catal. 2010; 269: 219-228.
21. Feng R, Yan X, Hu X, Yan Z, Lin J, Li Z, et al. Surface dealumination of micro-sized ZSM-5 for improving propylene selectivity and catalyst lifetime in methanol to propylene (MTP) reaction. Catal Commun. 2018; 109: 1-5.
22. Velichkina LM, Korobitsyna LL, Vosmerikov AV, Radomskaya VI. The synthesis and physicochemical and catalytic properties of SHS zeolites. Russ J Phys Chem. 2007; 81: 1618-1622.
23. Korobitsyna LL, Velichkina LM, Vosmerikov AV, Radomskaya VI, Astapova ES, Ryabova NV, et al. Ultra-high-silica ZSM-5 zeolites: Synthesis and properties. Russ J Inorg Chem. 2008; 53: 169-173.
24. Korobitsyna LL, Kapokova LG, Vosmerikov AV, Velichkina LM, Ryabova NV. Synthesis and properties of high-modulus zeolites. Theor Found Chem Eng. 2011; 45: 500-504.
25. Treacy MM, Higgins JB. Collection of simulated XRD powder patterns for zeolites fifth (5th) revised edition. Elsevier; 2007. p.586.
26. Hidalgo CV, Itoh H, Hattori T, Niwa M, Murakami Y. Measurement of the acidity of various zeolites by temperature-programmed desorption of ammonia. J Catal. 1984; 85: 362-369.
27. Dettmer-Wilde K, Engewald W. Practical gas chromatography. 1st ed. Berlin: Springer; 2014. p.1-902.
28. Rumble J. CRC handbook of chemistry and physics. 102nd ed. Boca Raton: CRC Press; 2021. p.1-1624.
29. European Parliament, Council of the European Union. Regulation (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information [Internet]. Luxembourg: Official Journal of the European Union; 2007. Available from: http://data.europa.eu/eli/reg/2007/715/oj.