Effect of the nature of silicon source on physicochemical properties of high-silica zeolites and the activity of Zn-pentasils prepared on their basis in the course of aromatization of lower alkanes

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Abstract. The effect of the nature of the silicon source on the physicochemical properties of synthesized zeolites and the activity of Zn-containing catalysts prepared on their basis in the course of conversion of the propane-butane fraction into aromatic hydrocarbons is studied. It is shown that the silicon source plays an important role in the hydrothermal synthesis of zeolite. It has an effect on the duration of synthesis but its effect on the physicochemical characteristics of the resulting product is minor. It is established that the activity and selectivity of Zn-containing catalysts for the aromatization of lower alkanes are practically independent on the nature of the silicon source used in the synthesis of the high-silica zeolite, which is an acid carrier of these catalysts.

1. Introduction

The solution to the problem of the use of associated petroleum gas as a feedstock for the chemical and petrochemical industries is of great importance for both economy and environment. According to estimates of various sources, the amount of annually flared associated gas ranges from 15 to 35 billion m³. This leads to extremely negative economic, environmental and social consequences. Restriction on the extensive use of natural and associated petroleum gases as a feedstock for chemical processes is due to the difficult activation of the highly stable molecules of lower alkanes present in gases. Given the huge reserves of natural gas in Russia, light alkanes can be considered as an important potential source of feedstock for the chemical industry. Of particular interest is the catalytic synthesis of highly demanded aromatic compounds from low molecular weight paraffins over pentasil-containing catalysts [1-4]. Its practical implementation will predetermine a substantial increase in their production. The basis for manufacturing high-silica zeolites (HSZ) is the method of hydrothermal crystallization of alkaline alumina silica gels. The nature and type of feed reagents, the composition of the reaction mixtures, and the conditions of synthesis have a targeted effect on the crystallization process, causing changes in the structure, morphology, phase, dispersion and chemical composition of crystals, sorption capacity, strength and concentration of acid sites, and catalytic activity. The appearance of modifications of the same phase but of various stability in the course of synthesis means, that the least stable modification crystallizes first. It is then replaced by a more stable phase and so on. This continues until the product is formed that is most stable under these conditions.
However, even with due consideration of this rule, it is not possible to fully disclose the laws of synthesis. This is due to the fact that the composition of synthesis products is strongly influenced by the rate of nucleation, which depends on the conditions of preparation of the reaction mixtures, their state and structure, the size of cations, and the presence of other additives [5]. The uncertainty in the choice of synthesis conditions makes it necessary to use a wide variety of compounds as sources of aluminum and silicon cations, and also to prepare mixtures on their basis, which differ in both chemical composition and physical properties.

The purpose of this work was to study the effect of the nature of the silicon source on physicochemical properties of zeolites and the activity of Zn-pentasil prepared on their basis in the course of conversion of lower alkanes into aromatic hydrocarbons.

2. Materials and methods

The main object of the study was the synthesized high-silica zeolite of the pentasil family with a molar ratio SiO₂/Al₂O₃ = 40. Liquid glass (19% SiO₂), silicic acid (nSiO₂ • mH₂O), white carbon (86% SiO₂), and sol (40% SiO₂) were used as a source of silicon.

Zeolite K-1 based on liquid glass was prepared by adding an aqueous solution of aluminum nitrate Al(NO₃)₃ • 9H₂O and hexamethylenediamine (HMDA) as a structure-forming agent to the liquid glass (19% SiO₂, 7% Na₂O, 74% H₂O) under intensive mechanical stirring. The acidity of the reaction mixture was adjusted to pH = 10.8 by the addition of 1 N nitric acid solution.

Zeolite K-2 was prepared by mixing white carbon (WC) (86% SiO₂) with an alkali solution of NaOH under intensive mechanical stirring. Then an aqueous solution of aluminum nitrate Al(NO₃)₃ • 9H₂O and HMDA were added. The acidity of the initial reaction mixture 11.2-11.4 required no adjustment.

In the course of synthesis of K-3 zeolite, 40% sol of silicic acid was used as a source of silicon. It was added by aqueous solutions of alkali, aluminum nitrate and HMDA. The acidity of the initial reaction mixture 11.2-11.4 required no adjustment.

Zeolite K-4 based on silicic acid was manufactured by adding SiO₂ • nH₂O silicic acid powder to solution of NaOH alkali under intensive mechanical stirring to obtain a 29% SiO₂, 19% Na₂O, 62% H₂O liquid glass, to which a HMDA solution and an aqueous solution of aluminum nitrate Al(NO₃)₃ • 9H₂O were sequentially added. The acidity of the reaction mixture was adjusted to pH = 10.8 by the addition of 1 N nitric acid solution.

In all cases, a high-silica zeolite in the amount of 1-1.5 wt% of SiO₂ used in the synthesis was added as seed to the reaction mixture in order to accelerate the crystallization process. The crystallization of HSZ was carried out in steel autoclaves for 1–6 days at 175 °C. At the end of the crystallization, the solid phase was separated from the liquid phase by filtration and then it was washed from excess of alkali with distilled water and dried at 100 °C in air for 8 hours. To remove the structure-forming additive, the samples were calcined at 550 °C for 16 hours.

Conversion of zeolites to the active H-form was carried out by decationization with a 25% aqueous NH₄Cl solution for 2 hours at 90 °C, followed by washing with distilled water and calcining at 550 °C for 6 hours. Based on the resulted zeolites, Zn-containing zeolite systems were prepared via the impregnation with a solution of zinc nitrate (Zn(NO₃)₂ • 6H₂O). The concentration of zinc (expressed as metal) in them was 3.0 wt%.

The quality indices of the synthesized HSZ were monitored using IR spectroscopy and X-ray phase analysis (XRF). The IR spectra of the samples under study prepared as tablets with KBr (1.2 mg of zeolite per 300 mg KBr) were recorded using a 5700 Nicolet IR Fourier spectrometer in the range of 2000-400 cm⁻¹ in air. X-ray phase analysis of zeolites was performed using a Bruker DISCOVER D8 diffractometer. The acidic properties of Zn-containing zeolite catalysts were studied by temperature-programmed desorption of ammonia. The strength of acid sites of the catalyst was estimated from the temperature maxima on the thermal desorption curve, their concentration was determined from the amount of ammonia desorbed at the moment of fixation of the desorption peaks. It was expressed in μmol per 1 g of catalyst.
To investigate the process of converting the propane-butane fraction (PBF) into aromatic hydrocarbons and to study the properties of catalysts, a bench-scale flow-type reactor was used. The catalytic conversion of PBF (propane – 77.4; isobutane – 5.8; and n-butane – 16.8 vol%) was carried out at atmospheric pressure, the reaction temperature varying from 450 to 600 °C and the feed space velocity 250 h⁻¹. The reaction products were analyzed by GLC using a Chromatec-Crystal 5000.2 chromatograph. During the experiments, the degree of conversion of the initial lower alkanes and the yield in gaseous and liquid products were determined. The selectivity towards formation of the reaction products was also calculated.

3. Results and discussion

Data on the composition and degree of crystallinity of the synthesized zeolites are given in Table 1. According to IR spectroscopy data, it was found that the crystallization rate of the catalysts under study depends on the silicon source used during the synthesis of zeolite. For example, the synthesis of zeolites on the basis of liquid glass and silicic acid lasts for 5 days. The use of WC in the course of synthesis makes it possible to reduce the synthesis time to 2 days.

Table 1. Characteristics of zeolite catalysts.

| Catalyst | Source of silicon | Synthesis time (day) | Degree of crystallinity (%) |
|----------|-------------------|----------------------|-----------------------------|
| K-1      | Liquid glass      | 5                    | 100                         |
| K-2      | White carbon-100  | 2                    | 100                         |
| K-3      | Ludox HS-40 sol   | 3                    | 93                          |
| K-4      | Silicic acid      | 5                    | 100                         |

In Figure 1 are shown X-ray diffraction patterns of zeolites synthesized with different sources of silicon. XRD data confirm that the synthesized samples belong to the zeolite of ZSM-5 structural type. They are characterized by the presence of the most intense diffraction maxima in the range 2θ = 6-50°: a triplet at 23.0, 24.0 and 24.4°, peaks at 29.3 and 29.6°, and a doublet at 45.0- 45.5° were observed. The results obtained indicate a high phase purity of the synthesized zeolites.

![Figure 1](image_url)

Figure 1. X-ray patterns of zeolites synthesized with different sources of silicon.

From a comparison of the intensity of characteristic peaks shown on X-ray patterns with the intensity of the peaks on the X-ray pattern of the reference sample, it follows that the degree of
crystallinity of zeolites obtained with liquid glass, silicic acid and white carbon is 100%, while with sol – 94% (Table 1).

Acidic characteristics of Zn-containing zeolite catalysts are presented in Table 1. The presence of two peaks on the thermal desorption curves of the synthesized samples suggests the presence of two types of acid sites – weak and strong ones. The highest concentration of acid sites of both types is characteristic of Zn-pentasil, obtained on the basis of a zeolite synthesized from a sol. Their total concentration is 1327 µmol/g. The use of silicic acid as a silicon source in the course of zeolite synthesis results in a manufacture of Zn/K-4 catalyst with similar acid characteristics. The Zn/K-1 catalyst is characterized by the lowest concentration and strength of weak acid sites, while the Zn/K-2 sample – by the lowest concentration of strong acid sites.

Table 2. Acid characteristics of Zn-containing zeolites.

| Catalyst | $T_{\text{max}}$ (°C) | $T_{\text{I}}$ | $T_{\text{II}}$ | $C_I$ | $C_{II}$ | $C_S$ |
|----------|---------------------|----------------|----------------|-------|----------|-------|
| Zn/K-1   | 210                 | 405            | 980            | 125   | 1105     |
| Zn/K-2   | 215                 | 405            | 1002           | 107   | 1109     |
| Zn/K-3   | 215                 | 410            | 1161           | 166   | 1327     |
| Zn/K-4   | 220                 | 400            | 1074           | 170   | 1244     |

Note. $T_I$, $T_{II}$ are the temperatures of peak maxima for form I and II; $C_I$, $C_{II}$ and $C_S$ are the concentrations of acid sites in form I, II, and total concentration, respectively.

Thus, investigation of the acidic properties of Zn-containing catalysts obtained on the basis of zeolites synthesized with different sources of silicon showed that the catalysts slightly differ from each other by the distribution and ratio of acidic sites of different nature.

The results of studies of catalytic properties of Zn-containing zeolites prepared using various sources of silicon are presented in Table 3.

Table 3. Composition of the products of PBF conversion over Zn-containing catalysts.

| Catalyst | T (°C) | X (%) | $Y_{ar}$ (%) | $S_{ar}$ (%) | $S_{cr}$ (%) | $S_{\text{hydr}}$ (%) | $S_{\text{H}_{2}}$ (%) |
|----------|--------|-------|--------------|--------------|--------------|-----------------------|----------------------|
| Zn/K-1   | 450    | 39    | 2.9          | 7.4          | 83.7         | 3.2                   | 5.5                  |
|          | 500    | 86    | 37.2         | 43.4         | 52.7         | 1.2                   | 2.7                  |
|          | 550    | 100   | 37.7         | 37.7         | 58.5         | 0.8                   | 2.9                  |
|          | 600    | 100   | 44.2         | 44.2         | 51.3         | 1.1                   | 3.3                  |
| Zn/K-2   | 450    | 38    | 2.8          | 7.2          | 82.9         | 4.0                   | 5.6                  |
|          | 500    | 95    | 33.6         | 35.5         | 61.1         | 0.8                   | 2.6                  |
|          | 550    | 100   | 37.9         | 37.9         | 58.3         | 0.8                   | 2.9                  |
|          | 600    | 100   | 45.5         | 45.5         | 50.1         | 0.9                   | 3.5                  |
| Zn/K-3   | 450    | 25    | 1.4          | 5.5          | 81.8         | 5.6                   | 6.5                  |
|          | 500    | 76    | 34.2         | 45.1         | 50.1         | 1.9                   | 2.9                  |
|          | 550    | 99    | 37.6         | 38.1         | 58.0         | 1.0                   | 2.9                  |
|          | 600    | 100   | 43.2         | 43.2         | 52.1         | 1.4                   | 3.2                  |
| Zn/K-4   | 450    | 21    | 1.7          | 7.8          | 75.8         | 8.2                   | 7.4                  |
|          | 500    | 73    | 32.7         | 44.8         | 49.8         | 2.2                   | 2.9                  |
|          | 550    | 99    | 36.4         | 36.9         | 59.5         | 0.9                   | 2.7                  |
|          | 600    | 100   | 43.0         | 43.0         | 52.6         | 1.2                   | 3.1                  |

Note. X is the propane conversion; $Y_{ar}$ is the yield in aromatic hydrocarbons; $S_{ar}$, $S_{cr}$ and $S_{\text{hydr}}$ are the selectivities towards the formation of products of aromatization, cracking and dehydrogenation; $S_{\text{H}_{2}}$ is the selectivity towards hydrogen formation.
As can be seen from the presented data, Zn-containing zeolites are characterized by almost the same total catalytic (measured by the degree of conversion of PBF) and aromatization activity. Some differences are observed only at the initial temperatures of the process. The catalysts are practically similar in their catalytic properties at 550 °C and above. In the presence of all the catalytic systems under study, a noticeable conversion of PBF begins already at 450 °C and at 500 °C and above the desired product (aromatic hydrocarbons) are formed. With an increase in the process temperature for all samples, an increase in the conversion of PBF is observed, and at a reaction temperature of 550 °C and above, the feedstock converts almost completely.

Studies of the composition of the resulted liquid and gaseous products of the conversion of PBF over Zn-containing zeolites prepared using various sources of silicon showed that they do not differ from each other in their qualitative compositions, but differ in their quantitative contents. In Table 4 are given the data on the composition of the gaseous products of PBF conversion over Zn-pentasil. The contents of hydrogen, ethylene and propylene in gaseous products obtained over Zn-containing samples under study differ slightly, while the differences in the content of methane and ethane are significant. Hence, the conversion over Zn/K-1, Zn/K-3 and Zn/K-4 results in a lower content of methane and higher of ethane, while the content of methane and ethane obtained over the Zn/K-2 sample is almost the same. It is possible to note a rather low content of olefins in the reaction products, which indicates that they are intermediate products that actively enter into further interactions leading to the production of aromatic hydrocarbons.

Table 4. Composition of the gaseous products of PBF conversion over Zn-containing zeolite catalysts (T = 550 °C).

| Catalyst | H₂ | methane | ethane | ethylene | propane | propylene |
|----------|----|---------|--------|----------|---------|-----------|
| Zn/K-1   | 4.6| 39.4    | 54.2   | 1.2      | 0.5     | 0.1       |
| Zn/K-2   | 4.7| 45.4    | 48.3   | 1.2      | 0.3     | 0.1       |
| Zn/K-3   | 4.6| 33.8    | 57.9   | 1.2      | 2.1     | 0.4       |
| Zn/K-4   | 4.2| 34.6    | 57.5   | 1.1      | 2.3     | 0.3       |

In Figure 2 are presented the data on the composition of liquid products of the PBF conversion over Zn-containing zeolites synthesized with different sources of silicon. It is evident that the quantitative compositions of aromatic hydrocarbons produced over these catalysts vary notably. The highest amount of benzene, toluene and xylene (BTX fraction) was formed over Zn/K-4 catalyst, obtained on the basis of zeolite synthesized with silicic acid, while the BTX fraction of the lowest concentration was obtained over Zn/K-2 catalyst, prepared on the basis of zeolite with WC. The compositions of products formed over Zn-containing zeolites synthesized with liquid glass and sol differs slightly, but the amount of alkyl naphthalenes formed over the latter catalyst is lower. Differences in the compositions of gaseous and liquid reaction products formed over the catalysts under study containing the same amount of modifying additive, are due to the different flow rates at particular stages of the process, i.e. the nature of the zeolitic carrier affects the catalytic properties of the catalytic system.
4. Conclusion
As a result of the study, it was found out that Zn-containing catalysts prepared on the basis of zeolites synthesized from alkaline alumina silica gels using different silicon sources differ slightly in their physicochemical and catalytic properties in the course of PBF aromatization. This suggests the possibility of using different in their nature sources of silicon for the synthesis of zeolites. In this case, the different durations of hydrothermal synthesis is the only significant factor that must be considered. The availability and price of the reagent should also be taken into account. Therefore, in the production of an effective catalyst for aromatization of gaseous hydrocarbons the quality indices of a zeolite carrier are critical, whose characteristics are not essentially affected by the silicon source.

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