Study on the parameters of the microporous structure of zeolite compositions by sorption analysis methods

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Abstract. The work is devoted to the study on the influence of various factors on the microporous structure parameters of the zeolite compositions being formed. To study the parameters of the microporous structure, sorption analysis methods were used. Zeolites of the BETA type and compositions based on them were chosen as objects under study. It was found that the formation of zeolite compositions is greatly influenced by the nature of the binder (matrix) and peptizer, which determine the proportion of micropores in the zeolite composition. It is shown that in the study of the textural characteristics of zeolite compositions, preliminary sample preparation (heat treatment to remove the moisture adsorbed by them) is necessary.

1. Introduction

Currently, zeolites and materials based on them are widely used as adsorbents and catalysts for petrochemical processes. It is known that the developed system of zeolite micropores due to diffusion restrictions has a significant effect on the rate of reactions being catalyzed by zeolites [1, 2]. In this regard, an urgent task is to study the volume of micropores and the external specific surface of zeolite compositions (the surface that not includes micropores (pores smaller than 2 nm), since they are filled with liquid adsorbate during the study), including using comparative analysis methods.

In order to use the active surface of the zeolite catalyst more efficiently, an additional system of larger pores of a given size is created in it - the so-called hierarchical system of micro-mesomacropores. Zeolite materials with a developed pore system are created by forming a zeolite-binder (matrix) catalyst composition. As the latter, aluminium hydroxide is most often used. The nature of the binder, as well as the nature of the zeolite itself, have a significant effect on the porous structure of the molded material.

It is known that the conditions of post-synthetic treatment have a great influence on the characteristics of the porous and crystal structure of zeolites. So, in work [3] zeolites were leached with nitric, hydrochloric and oxalic acids. The results showed that acid leaching removed Al outside the zeolite framework resulting in an increase in mesopore volume. The authors of [4] found that it is possible to control the properties of the zeolite by changing the conditions (eg, temperature, pH, duration) of acid leaching.

The aim of this work was to study the influence of various factors (type of binder, exposure to acid or alkali) on the parameters of the microporous structure of the formed zeolite compositions.
2. Experiment
For this research, a series of BETA-type zeolites and compositions based on them were selected. For dealumination and the formation of secondary mesoporosity, the initial BETA zeolite was treated in 2M HCl at a temperature of 100°C for 1 hour with constant stirring. To desilylate and form secondary mesoporosity, the initial zeolite was treated in 2M NaOH. The samples were heat-treated at a temperature of 500 °C.

In industrial processes, catalysts are typically used in the form of molded granules. One of the ways to create zeolite materials with a developed pore system is to form a zeolite-binder catalyst composition. Aluminum hydroxide from two manufacturers, Sasol and AZK and OS Ltd, was used as a binder (matrix) in the formation of zeolite compositions.

To study the microporous structure parameters the sorption analysis methods (in particular, the de Boer method) were used. Analyzed adsorption isotherms were obtained using a Sorbi MS instrument equipped with sample preparation stations Sorbi Prep. Data processing was carried out in the LabView environment using a specially developed program [5, 6]. The following parameters were analysed: the specific surface area SBET determined by standard Brunauer – Emmett – Teller method, the external surface STSA determined by the method of statistical thicknesses of the adsorption film, and the micropore volume Vμ determined by the de Boer method.

3. Results and discussion
At the first stage of the work, it was important to determine what conditions of sample preparation should be chosen for the study. Sample preparation consisted of controlled heating of the sample in a stream of inert gas (helium). Figure 1 shows the fragments of the adsorption isotherm for BETA zeolite (without a binder) with varying sample preparation conditions (for example several processing modes are given). The obtained porous structure parameters are presented in table 1.

![Figure 1. Fragments of BETA zeolite adsorption isotherms under different sample preparation conditions.](image)

| T prep, °C | t prep, min | SBET, m²/g | Vμ (micropore volume) |
|------------|-------------|------------|-----------------------|
| -          | -           | 99         | 0                     |
| 150        | 20          | 297        | 0.092                 |
| 150        | 45-60       | 400-440    | 0.133                 |
| 300        | 20          | 434        | 0.156                 |
It should be noted that the instrumental error in measuring the specific surface area is 6%. From table 1 it can be seen that during heat treatment in the regimes of 150 °C, 60 min and 300 °C, 20 min, the specific surface values practically coincide. A further increase in the treatment temperature did not affect the value of the micropore volume. Therefore, in further measurements of the porous structure parameters, we used a sample preparation mode of 150 °C, 60 min in the cases when we studied BETA zeolite powders without a binder, and a mode of 500 °C, 60 min in cases when we studied compositions based on BETA zeolite and a hydroxide aluminum binder. The choice of the latter modes was necessary for comparing the measurement results with those of work [2].

Table 2 shows the results of the study of the porous structure parameters of the initial zeolite BETA and zeolite BETA after exposure it to acid and alkali. Since the samples were already heat-treated at 550 °C during the preparation process, the measurements were carried out under the same sample preparation conditions (T = 150 °C, t = 60 min).

**Table 2.** The porous structure parameters for the series of BETA zeolites.

| Sample       | SBET, m²/g | STSA, m²/g | Vμ (micropore volume), ml/g |
|--------------|------------|------------|----------------------------|
| BETA         | 366        | 102        | 0.121                      |
| BETA + 2M NaOH | 440        | 110        | 0.133                      |
| BETA + 2M HCl | 453        | 172        | 0.130                      |

As it can be seen from the table 2, in both cases exposure to the initial zeolite with alkali and acid leads to an increase in the specific surface value, external surface value and volume of micropores. In this case, the specific surface area of the sample for BETA + 2M HCl is greater than the SBET value of BETA + 2M NaOH, with relatively identical micropore volumes (130-133 ml/g). This may be due to the formation in the latter case of a more developed mesopore system. Figure 2 shows a histogram of the size distribution of mesopores in the BETA + 2M HCl sample.

![Figure 2. The histogram of the pore distribution over sizes in the BETA + 2M HCl sample.](image)

At the next stage of the work, a series of compositions “zeolite + matrix” was investigated. All compositions were prepared in the process of kneading the catalyst mass with its subsequent molding. To prepare the composition, the quantities of zeolite and aluminum hydroxide necessary for the calculation were calculated in the mixer (corresponding to 70% and 30% by weight, calculated on the substance treated at 650 °C). In the Composition 1 aluminum hydroxide from the manufacturer Sasol...
was used as a binder (matrix), and in the Composition 2 the material from another manufacturer (AZK and OS Ltd) was taken. We believed that the porous structure parameters of the composition may be affected by the choice of a peptizer. In this series of samples, a solution of nitric acid (concentration 46% wt.) was used as a peptizing agent for compositions 1 and 2. In Composition 3, a mixture of aqueous solutions of nitric acid (concentration 46% wt.) and ammonia (concentration 12% wt.) was used as a peptizing agent in the ratio 1:1.

In all cases, the resulting mixture was stirred for 20 minutes to obtain a plastic mass and then molded into granules with a diameter of 1-1.2 mm. The zeolite - binder composition in the form of formed granules was dried in air at room temperature for 24 hours, then at a temperature of 120 °C for 2 hours. The composites were heat-treated at a temperature of 550 °C until the structure-forming component was completely annealed.

The results of the study on the porous structure parameters for zeolite compositions are presented in table 3.

**Table 3.** The porous structure parameters for the compositions.

| Sample                      | SBET, m²/g | STSA, m²/g | Vµ (micropore volume), ml/g |
|-----------------------------|------------|------------|----------------------------|
| Composition 1               | 326        | 148        | 0.083                      |
| Composition 2               | 297        | 110        | 0.087                      |
| Composition 3               | 315        | 109        | 0.094                      |

It can be seen from the measurement results that composition 3 in which another peptizer was used is the most distinguished (the value of micropore volume increased by 14% compared to sample 1). Replacing the type of binder in the composition 2 also led to an increase in the volume of micropores compared to the composition 1, while the specific surface area slightly decreased from 326 to 297 m²/g. This fact may indicate a change in the porous structure in the mesopore range, which is consistent with the results of [2].

**4. Conclusions**

In the study on the samples of zeolites without a binder (before the formation of compositions) it was found that exposure to alkali and acid leads to a change in the porous structure parameters, in particular, an increase in the volume of micropores in the zeolite. This is due to recrystallization and dealumination of the material when it is processed in an acidic medium (or with desilylation during processing in alkali). At the stage of creating zeolite compositions, the type of peptizer is of great importance for the presence of micropores. It was also established that in the study of zeolites, the sample preparation is important: the recorded micropore volume for the same material can almost double after preliminary evaporation of moisture.

**References**

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