



The Synthesis and Properties of an OFF-type Zeolite

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The technique for synthesizing powdered OFF-type zeolite of high phase purity and crystallinity has been developed. The effect of crystallization conditions on the characteristics of powdered OFF-type zeolite samples, namely, crystallinity, particle-size distribution, and adsorption of molecules has been studied. An increase in the crystallization temperature has been found to reduce the synthesis duration time; however it resulted in the formation of larger OFF-type zeolite crystals and aggregates thereof. It has been discovered that the particle size of the obtained OFF-type zeolite samples does not affect the adsorption of H₂O molecules. On the coarse-crystalline samples the slower diffusion rate of *n*-C₆H₁₄ molecules into the zeolite channels is observed; it is associated with the larger size of the adsorbed substance molecules. And for yet larger C₆H₁₂ molecules the equilibrium adsorption capacity values are decreased.

Keywords: OFF-type zeolite; crystallization; particle-size distribution; adsorption.

1. INTRODUCTION

The traps for heavy hydrocarbons in vehicle exhaust gases are made primarily of zeolite-containing materials [1]. The adsorbed hydrocarbons are retained in the trap until the engine

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temperature reaches 200-300°C; after that they are oxidized on the catalyst into carbon dioxide and water and discharged to the atmosphere.

The OFF-type zeolite is the most effective vehicle exhaust adsorbent for the removal of hydrocarbons [1]. Its synthesis was first reported in 1970 [2]. More reports by different authors appeared in subsequent years [3-9].

The difficulty of crystallizing the OFF-type zeolite of high phase purity lies in that LTL and ERI zeolites are formed from the reaction mixes close in composition [7-8]. However no due attention is paid in literature to the effect of the synthesis conditions neither on the phase purity of the OFF-type zeolite, nor on the particle size of formed crystals. In the meantime, the adsorption kinetics of different hydrocarbons may depend on the crystal size. This work is to find out the synthesis conditions for the fine dispersed OFF-type zeolite of about 100% crystallinity and to study its adsorption characteristics.

2. EXPERIMENTAL DETAILS

In literature they offer different compounds for the silicon feed to synthesize the powdered OFF-type zeolite: alkali metal silicates, silica hydrogels, etc. [3-9]. One may expect the application of silica hydrogel instead of the silicate itself would allow an increased zeolite formation rate. To confirm our assumptions, for the silicon feed we used silicic acid hydrogels prepared by settling with hydrochloric or sulfuric acid either from the sodium silicate solution (Na₂O content of 100.7 g/L, Si₂O content of 300.0 g/L) or from the mix of ortho-silicic acid oligomers (Si₂O content of 40% by mass). In a number of runs instead of hydrogels we used the solution of sodium and potassium silicate with the concentrations of 220.0, 75.0, and 14.0 g/L by SiO₂, K₂O, and Na₂O, respectively. The said solution was prepared by dissolving silica gel in sodium and potassium hydroxide solution at 140-150°C. For the aluminum feed we used sodium aluminate solution with the concentrations of 280.0 and 225.0 g/L by Na₂O and Al₂O₃, respectively; 25% aqueous tetramethylammonium hydroxide solution was used as an organic structural-forming agent (template). As shown in [2-9], the OFF-type zeolite could be crystallized within the wide range of the reaction mix concentrations: (0.7–1.6)R₂O×(3.5-5.0)Na₂O×(4.5-6.0)K₂O× Al₂O₃× (24.0-34.0)SiO₂× (400.0-500.0)H₂O. The same compositions were used in this work.

Crystallization was performed at 98 and 150°C. After the end of it the obtained suspension was filtered under vacuum. The mother liquor components were washed off the powdered zeolite until the pH of 9.0-10.0 was reached. Then the samples were thermally treated under the temperature of 500-550°C (the temperature rise rate of 150°C per hour) during 4 hours in the atmosphere of air (atmospheric pressure). During this stage the template was removed from the zeolite porous structure.

The chemical composition of the liquid and solid phase was analyzed by means of the flame photometry and complexometric titration. The phase composition of samples was determined by the X-ray diffraction (XRD) powder pattern technique using the PHILIPS PW 1800 X-ray diffractometer with monochromatic Cu-ka radiation, at the voltage of 40KV, and the current of 40 mA. The XRD pattern readings were obtained with the increment of 2θ=0.02° and the integration time of 5 s per point. The samples were identified using a database of powder diffraction patterns –ICDD. The relative crystallinity degree (RCD, relative %) was determined by the internal reference method. According to the ASTM D 3906-03 the RCD was calculated as the ratio of the total peak area of the analyzed sample to the total peak area of the reference sample. IR-spectra were registered for the samples

press-molded with KBr using the Bruker Vertex 70V analyzer. Press molding of zeolite pellets was made under the pressure of 50kr/cm^2 to get the pellet thickness of $12\text{-}15\text{ mg/cm}^2$. Samples were dehydrated by heating under vacuum at the temperature of $400\text{-}450^\circ\text{C}$ during not less than 4 hrs in the working cell. The investigated frequency ranged from 400 through 4000 cm^{-1} .

The particle-size distribution was investigated by the laser diffraction technique. Normalized particle size measurements were made using the refraction index.

Adsorption properties of the samples were characterized by the equilibrium adsorption capacity (mg/g) with respect to the vapors of H_2O (AH_2O), cyclohexane (AC_6H_{12}), and *n*-hexane (AC_6H_{14}). The values were determined by the desiccator technique [10] based on the complete saturation of the zeolite by the vapors of the adsorbed substance, namely, water, cyclohexane, *n*-hexane under the standard test conditions ($T=20\text{-}25^\circ\text{C}$, $P/P_s=0.8$).

3. RESULTS AND DISCUSSION

Results of the XRD studies of samples obtained with different silicon feed sources are given in Fig. 1.

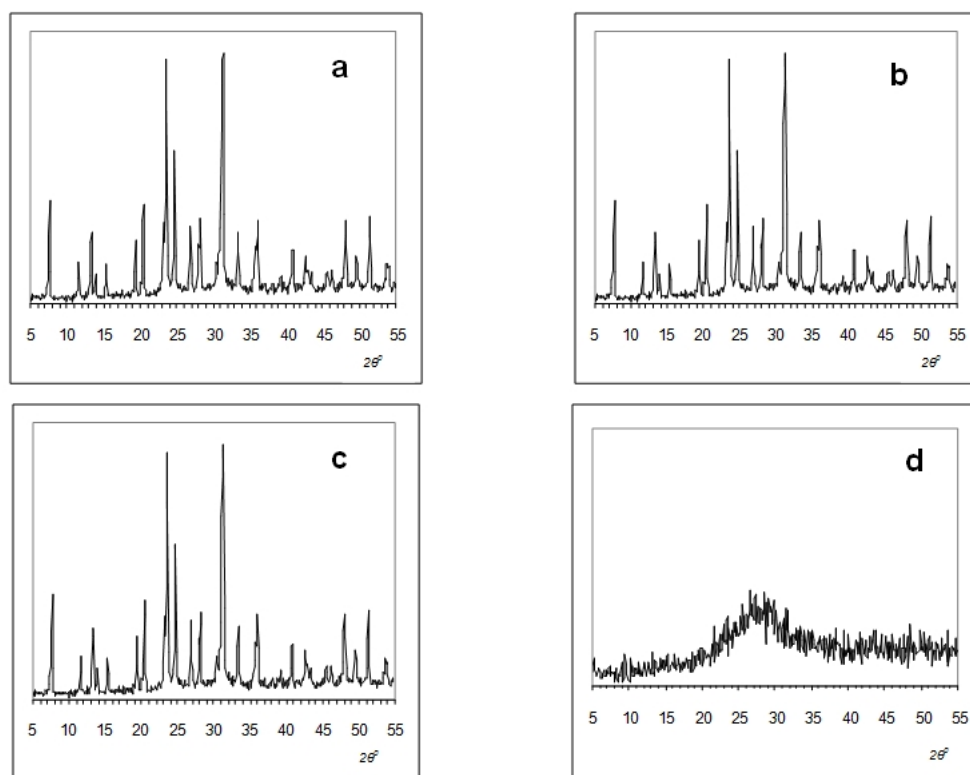


Fig. 1. XRD patterns of the reference sample and the OFF-type zeolite samples after the reaction mix crystallization with the different silicon-containing feed:
 a) the reference OFF-type zeolite sample [11]; b) the silicic acid hydrogel precipitated by hydrochloric or sulfuric acid from the solution of sodium silicate; c) the hydrogel obtained by the acidic hydrolysis of the mix of ortho-silicic acid oligomers with the SiO_2 content of 40% by mass; d) a mix of sodium and potassium silicates

It is seen that the main peaks are observed at the diffraction angles of $2\theta^{\circ}$ – 7.66, 11.65, 15.35, 19.31, 20.37, 23.53, 24.68, and 31.24. Those peaks are specific for the OFF-type zeolite only [11]. Hence, the obtained product constitutes an OFF-type zeolite of the high phase purity. The diffraction lines described above are missing on the XRD pattern of the sample synthesized using the digested silica gel (see Fig. 1, d). Hence, the product in question is amorphous. It has been found that when using hydrogels, the samples possess the crystallinity degree close to 100%.

The samples obtained with the different silicon feed were investigated by the IR-spectroscopy (see Fig. 2).

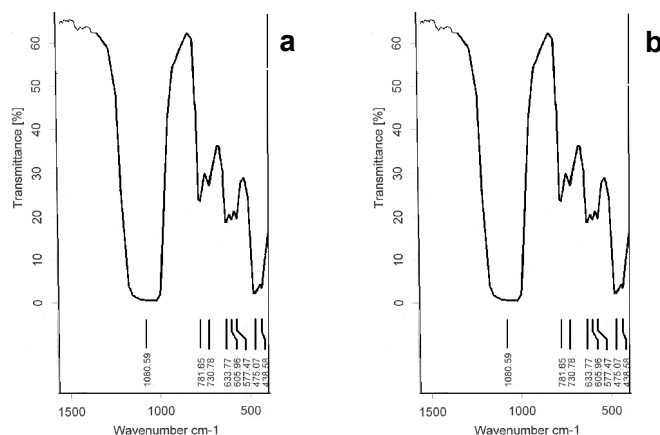


Fig. 2. IR-spectra of the offretite samples after the reaction mix crystallization using different silicon-containing feed: a) the silicic acid hydrogel precipitated by hydrochloric or sulfuric acid from the solution of sodium silicate; b) the hydrogel obtained by the acidic hydrolysis of the mix of ortho-silicic acid oligomers with the SiO₂ content of 40% by mass

The absorption bands observed in the IR-spectra could be attributed to the following two oscillation types: 1) the oscillations inside the Si(Al)O₄ tetrahedrons; 2) the oscillations of the external bonds of the tetrahedrons. The first oscillation type is responsible for the most intense absorption bands at 438, 475, 730, and 1080 cm⁻¹. The less intense absorption band at 730 cm⁻¹ is referred to the stretching vibrations of the Si(Al)-O bond. The next in the intensity absorption band at 781 cm⁻¹ is referred to the deformation oscillations of the -O-Al bond. The second type of the oscillations responsive to the nature of the bonds between the tetrahedrons in the zeolite accounts for the absorption bands at 577, 605, 633, and 1634 cm⁻¹. The absorption bands indicated above are characteristic for the OFF-type zeolite.

Thus, during the crystallization of the reaction mixes prepared with hydrogels the zeolite formation rates are close, and the resulting OFF-type zeolite samples show the high crystallinity degree and high phase purity. When the reaction mix prepared with the digested silica gel is crystallized, the zeolite formation rate is lower, and the OFF-type zeolite is not formed under these conditions. Therefore, in our further experiments we used for the silicon feed source the silicic acid hydrogel precipitated from the most accessible silicon feed – the sodium silicate solution.

The study of the effect of the reaction mix composition showed that the OFF-type zeolite of the high phase purity is formed exclusively in the following reaction mix composition range: $(0.7-0.8)R_2O \times (4.5-4.7)Na_2O \times (5.6-5.7)K_2O \times Al_2O_3 \times (25.0-26.0)SiO_2 \times (448.0-460.0)H_2O$. In the other instances the zeolite is either not formed or a mixture of OFF, ERI, and LTL phases is obtained.

The addition of seed crystals (the crystals of a zeolite of the necessary structural type) into the reaction mix is known to considerably affect the crystallization rate [12,13]. Therefore, to reduce the duration time of the crystallization we have performed the experiments with the crystalline "seed" that constituted the powdered OFF-type zeolite in the amount of 5-10% by mass. The effect of the crystalline "seed" additive quantity on the duration time of the crystallization and the properties of the obtained samples has been studied; the results are given in Table 1.

Table 1. Effect of the crystalline "seed" quantity on the crystallization duration time, RCD, and adsorption characteristics of the samples obtained

"Seed" quantity, % by mass	Duration time, days	RCD	AH ₂ O	AC ₆ H ₁₄	AC ₆ H ₁₂
0	8	100	170	257	303
5	6	40	70	103	121
5	7	70	120	180	212
5	8	100	170	257	303
10	5	70	120	180	212
10	6	100	170	257	303
10	7	100	170	257	303
10	8	100	170	257	303

The reaction mix composition: $(0.7-0.8)R_2O \times (4.5-4.7)Na_2O \times (5.6-5.7)K_2O \times Al_2O_3 \times (25.0-26.0)SiO_2 \times (448.0-460.0)H_2O$; the temperature of 98°C; the crystalline seed – powdered OFF-type zeolite

Obviously, the addition of 5 % of the crystalline "seed" by mass does not bring a substantial impact on the synthesis duration time. Only the addition of 10 % of the "seed" by mass results in the reduction of the crystallization duration time from 8 to 6 days. In this procedure the properties of the obtained products do not differ from those of the samples obtained without the crystalline seed additives.

The temperature of the synthesis [12,13] is the primary kinetic factor of the zeolite crystallization. As the temperature rises, both the induction period and the entire crystallization process are cut down. However, each zeolite type is formed within a specific temperature range, and the composition of the synthesized products is very responsive to the temperature variations.

In [14,15] the results of synthesis of the powdered OFF-type zeolite at 150°C are reported. The rise of the crystallization temperature from 98°C to 150°C has been found to cause the cut in the crystallization duration time down to 69 hrs. However, the data on the crystal size and adsorption characteristics of the obtained samples are not given. Therefore we have performed the crystallization of an OFF-type zeolite at 150°C in the presence of 10% of the crystalline "seed" by mass. The results obtained during the study of the effect of the crystallization duration time on the properties of the obtained products are shown in Table 2.

Table 2. Effect of the crystallization duration time on the RCD and adsorption characteristics of the samples obtained

Duration time, days	RCD	AH ₂ O	AC ₆ H ₁₄	AC ₆ H ₁₂
0,5	50	80	136	116
1	100	170	257	303
2	100	170	257	303
3	100	170	257	303

The reaction mix composition: (0.7-0.8)R₂O×(4.5-4.7)Na₂O×(5.6-5.7)K₂O×Al₂O₃×(25.0-26.0)SiO₂×(448.0-460.0)H₂O; the temperature of 150°C; 10% by mass of the crystalline seed – powdered OFF-type zeolite

It is seen that 24 hours at 150°C is the sufficient crystallization time for the OFF-type zeolite with the crystallinity degree close to 100%. An increase in the crystallization time up to 72 hours does not bring a substantial impact on the crystallinity degree and adsorption characteristics of the OFF-type zeolite sample.

Hence, in this work the powdered OFF-type zeolite was synthesized at the temperature of 98°C during 144 hours (the OFF-1 zeolite sample) and during 24 hours (the OFF-2 zeolite sample). The particle size distribution and the adsorption characteristics of those samples have been investigated.

Results of the crystal size distribution studies for the obtained OFF-1 and OFF-2 samples are given in Fig. 3. It is seen that at 98°C the zeolite (OFF-1 sample) with the narrow crystal size distribution is formed, the crystal size not exceeding 3.0-4.0 μm. With the temperature rise up to 150°C the zeolite with much wider crystal size distribution is produced; more so, some amount of particles within the range of 30.0-45.0 μm can be seen. One might assume that the latter consist of the aggregates of the smaller crystals.

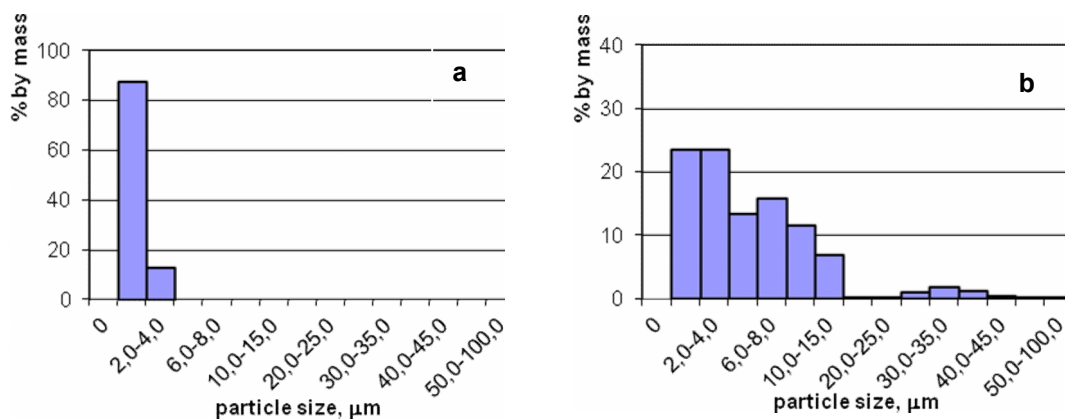


Fig. 3. The crystal size distribution in the OFF-type zeolite samples: a) OFF-1; b) OFF-2

The results obtained may be attributed to the fact that at 98°C the crystal nucleus formation rate is higher than the crystal growth rate. Therefore, a large quantity of the crystal nuclei is simultaneously crystallized into the particles of similar size. When the temperature rises, the ratio of the crystal nucleus formation to the crystal growth varies, and the newly formed nuclei are involved into the growth of the already existing crystals [16].

Thus, the temperature rise has been shown to cut down the synthesis duration time, yet in this case the larger OFF-type zeolite crystals and aggregates thereof are formed.

The zeolite crystal size distribution is known to affect the diffusion rate of the adsorbed substance molecules [16]. On this reason in this work we studied the adsorption kinetics of C_6H_{12} , $n-C_6H_{14}$, and H_2O molecules on the OFF-1 and OFF-2 samples. In Fig. 4 the results of the adsorption kinetic studies for H_2O (see Fig. 4, a), $n-C_6H_{14}$ (see Fig. 4, b) and C_6H_{12} (see Fig. 4, c) vapors on the OFF-1 and OFF-2 samples are shown.

From the presented data one can see that the differences in the OFF-1 and OFF-2 crystal size distribution do not present a visible effect both on the kinetics and on the equilibrium adsorption capacity values of rather small-sized H_2O molecules. For the larger $n-C_6H_{14}$ molecules the equilibrium adsorption capacity values for both samples are also close, but the time to attain them is less on the OFF-1 sample as compared to the OFF-2 sample (see Fig. 4, b). Hence, in the latter sample the diffusion rate of the $n-C_6H_{14}$ molecules is lower.

For yet larger C_6H_{12} molecules the equilibrium adsorption capacity values are higher for the OFF-1 sample than for the OFF-2 sample (see 4, c). It is likely the formation of the crystal aggregates denies C_6H_{12} molecules a certain part of the intracrystal area somehow making it inaccessible.

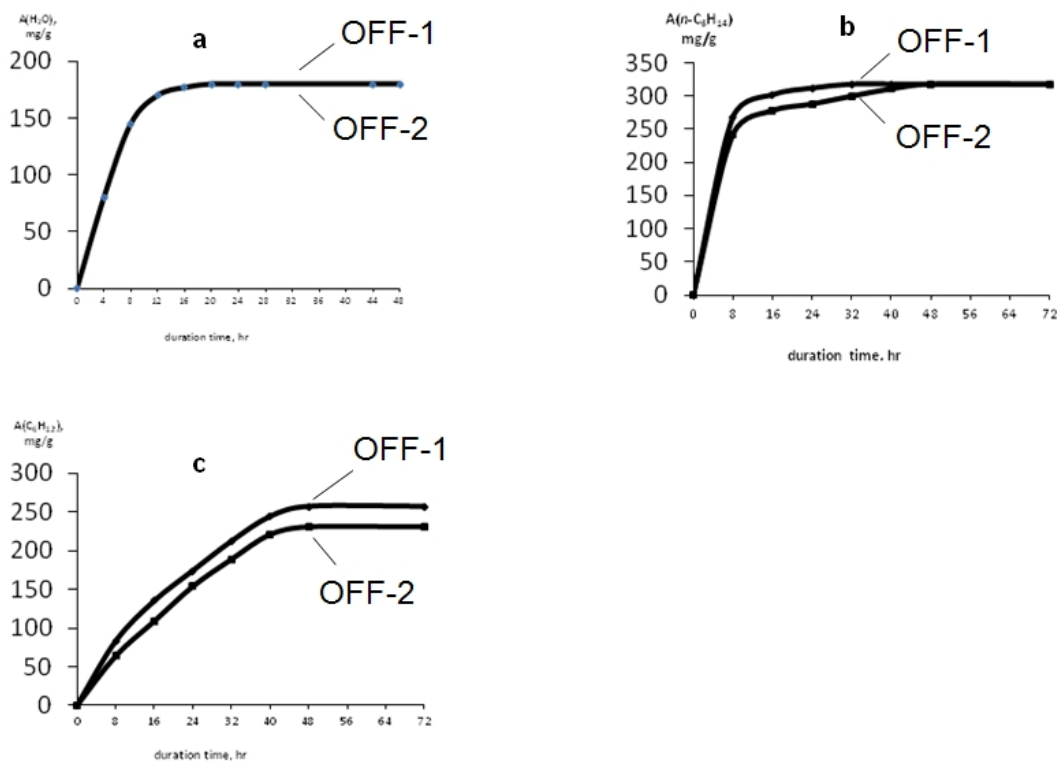


Fig. 4. Effect of the adsorption duration time on the quantity of the adsorbed substance: a) H_2O (A_{H_2O} , mg/g); b) $n-C_6H_{14}$ ($A_{C_6H_{14}}$, mg/g), c) C_6H_{12} ($A_{C_6H_{12}}$, mg/g), on the OFF-1 and OFF-2 samples

4. CONCLUSION

The hydrothermal crystallization during 144 hr at 96-98°C of the reaction mixes of the following composition: $0.7-0.8R_2O \times (4.5-4.7)Na_2O \times (5.6-5.7)K_2O \times Al_2O_3 \times (25.0-26.0)SiO_2 \times (448.0-460.0)H_2O$ prepared with the silicon-containing feed of the hydrogels precipitated from the solution of sodium silicate and 10% of the crystalline "seed" by mass has been shown to yield the powdered OFF-type zeolite of high crystallinity degree ($\approx 100\%$) and the crystal size within the range of 2.0 thru 4.0 μm .

The temperature rise up to 150°C has been found to reduce the crystallization duration time from 144 down to 24 hours. However a considerable amount of crystals within the size range of 4.0 – 15.0 mm appears in the meantime.

It has been found that the impact of the crystal size distribution in the OFF-type zeolite on the adsorption of different molecules depends on the size of the latter. There is no impact for H₂O molecules; the diffusion rate for the larger *n*-C₆H₁₄ molecules into the zeolite channels is lower for the coarse-crystalline sample; and for yet larger C₆H₁₂ molecules the equilibrium adsorption capacity values are decreased.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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