Original scientific papers UDK 549.67
doi: 10.7251/COMEN1402197V

INFLUENCE OF CRYSTALLIZATION TEMPERATURE ON THE ABSORPTION OF DIBUTYL PHTHALATE IN ZEOLITE A

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Abstract: In order to determine the effect of crystallization temperature on the absorption and properties of zeolite A particles, we have monitored the modified dibutyl phthalate absorption (DBP), a degree of crystalline phase, specific surface area, mean diameter of particle (D_S50 %), and performed scanning electron microscopy (SEM) of the synthesized samples of zeolites. The synthesis of samples was carried out at crystallization temperatures of 70, 75, 80, 85 and 90°C ; the raw materials (sodium aluminate and sodium silicate) were heated at 90°C. The particle size of the synthesized samples is similar in most studied systems at all temperatures of crystallization, which is in accordance with the principles of the autocatalytic nucleation and „memory effect" of the gel. An increase in the specific surface area of the synthesized samples with the increase in the crystallization temperature was observed in all the analyzed systems (3.25 to 35.31 m^2/g). It was found that the increase of crystallization temperature increases the absorption of dibutyl phthalate(0.90-1.20 cm^3/g); however, at the same time, the proportion of zeolite A in the same samples is reduced, as confirmed by SEM analysis.

Keywords : zeolite A, dibutyl phthalate absorption, crystallization temperature.

1. INTRODUCTION

Zeolites are microporous materials with voids smaller than 2 nm. The primary building blocks of the zeolite are tetrahedra of silicon $[SiO_4]^{4-}$ and aluminum $[AlO_4]^{5-}$, which are interconnected via a common oxygen atom. In this way they form a variety of structural units, the so-called secondary building blocks. Further association of secondary building blocks leads to formation of more complex three-dimensional porous structures with pores of molecular dimensions, which are called zeolitic networks [1,2].

These are special microporous materials which, thanks to their structural and sorption characteristics, are widely used in adsorption and separation processes, and as heterogeneous catalysts. The high value of the specific surface area of zeolites, which ranges up to 1000 m^2/g, gives them not only a large adsorption capacity, but also an increase in functionality due to the gas separation process. One of the properties of zeolites, particularly important for catalysis, is a highly developed internal surface with branching channels and pores that connect the cavities large enough for reactions to occur in them [3−5] .

Synthetic zeolites are usually obtained in the form of sodium cation, but can also be obtained in other cationic forms. Thus, for example, type LTA zeolite (zeolite A) $Na_{12}Al_{12}Si_{24}O_{48}$•27 H_2O, if in the sodium form, has a label NaA (zeolite 4A), in the form of calcium -CaA (zeolite 5A), in the potassium form -KA (zeolite 3A).

Although the crystallization process is quite simple in general, the process of zeolite crystallization involves a number of complex and interrelated physical and chemical processes which depend on various factors, such as temperature, pH, nature of the reactants, a source of silicate and aluminate, reaction time, concentration, etc. The type and properties of the final product of (zeolite) crystallization depends on the conditions of crystallization which are applied [6−10].

Temperature has a direct effect on the polymerization reaction of reactive silicates, aluminates and aluminosilicate species. The temperature affects a number of factors in the synthesis of zeolites: a change in the obtained phase, and the beginning of the induction period prior to crystallization. This

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induction period decreases with increasing temperature [11−12].

In order to determine the effect of temperature on the absorption properties of the particles and the zeolite A, the samples from raw materials at the temperature of 90°C were synthesized by hydrothermal („hydro-gel") method, having been crystallized at temperatures of 70, 75, 80, 85 and 90 °C. The following parameters were monitored in the synthesized samples: changes in the absorption of dibutyl phthalate (DBP), a degree of crystalline phase, specific surface area, particle size distribution (% D_S50). They were also subjected to scanning electron microscopy (SEM).

2 EXPERIMENTAL SECTION

A solution used for the process of synthesizing zeolite was aluminate solution prepared in laboratory conditions by solving hydrate $Al(OH)_3$ in 50% NaOH, in which the concentration of Al_2O_3 ranged from 100 to 120 g/l, whereas the concentration of Na_2O was between 137 and 169 g/l.

The silicon necessary for the syntheses of zeolites was taken from sodium silicate (water glass) obtained in the process of production in the alumina factory „Birač". The concentration of SiO_2 in this glass ranged from 375 to 385 g/l, whereas that of Na_2O was between 160 and 170 g/l. Distilled water was also used for the processes of synthesis apart from these raw materials.

These raw materials served for the synthesis of many samples of zeolite, in laboratory conditions, using a hydrogel method. The temperature of raw materials was 90°C, and that of crystallization 70, 75, 80, 85 and 90 °C. The process of synthesis was conducted in such a manner to satisfy the following mole ratios: $SiO_2/Al_2O_3 = 1.88$; $Na_2O / Al_2O_3 = 4.2$; $H_2O / Al_2O_3 = 90$; $H_2O / Na_2O = 25$.

The particle size and its mean diameter (D_s 50%) were determined using a laser apparatus particle analyser BA Instruments „Microsizer 201 C" in the measurement range of 0−50 μm and 30 seconds sonication at ultrasound power of 50 W. Specific surface area (SP) was determined by using low-temperature adsorption of nitrogen (BET method) at degazation temperature of 400ºC for the period of 4 hours, on the apparatus Micromeritics „FLOWSORB II 2300". Determination of the degree of crystallinity (XRD) and the identification of the samples were performed on diffractometer PHILIPS PW 1710 using Cuanticathodes (40 V, 50 mA, Kα=0,15405 μm). The samples were recorded in the area of 2θ from 5 to 40°, and the results obtained were processed using software for automatic powder diffraction (PC-APD) and ICDD/JCPDS PDF-2 database. Scanning electron microscopy (SEM) was conducted on JEOL JSM 6460LV device, and BAL-TEC, SCD 005 Sputer Coaltar was used for the preparation of samples.

3. RESULTS AND DISCUSSION

Crystallization temperature for the given mole ratio of reacting components ranged from 70 to 90 °C, with an increase of 5 °C with every following synthesis successively (Table 1). Zeolite samples synthesized at higher crystallization temperatures, (85 and 90 °C), had higher values of specific surface area (30.72 and 35.31 m^2/g), due to the fact that during nucleation at high crystallization temperatures, more nuclei are formed to continue the process of crystallization.

This fact is supported by the mean diameter of particle (D_s50%) which was 4.21 and 3.89 μm, successively for these temperatures. At the same time, larger number of smaller particles enables greater absorption of DBP (Table 1).

Table1.Physical and chemical properties of zeolite obtained in the synthesis of raw materials at the temperature of 90°C at different crystallization temperatures

Synthesis no.	Crystallization temperature [°C]	Specific surface area [m^2/g]	DBP absorption [cm^3/g]	Relative crystallinity [%]	Mean diameter of paerticleD_s50% [μm]
1	70	5,46	0,90	67,75	5,16
2	75	3,25	0,90	99,66	3,61
3	80	17,02	1,20	48,24	4,77
4	85	30,72	1,10	49,20	4,21
5	90	35,31	1,10	37,87	3,89

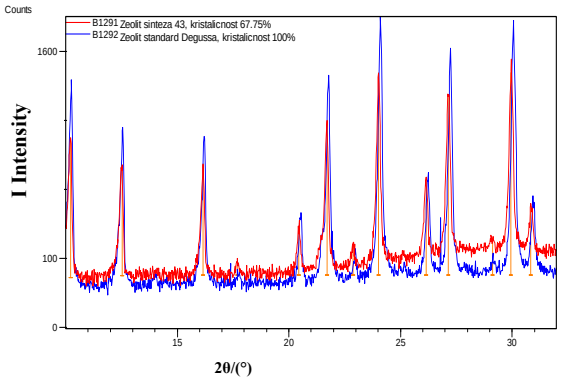


Figure1. X-ray chart of zeolite obtained at crystallization temperature of 70 °C

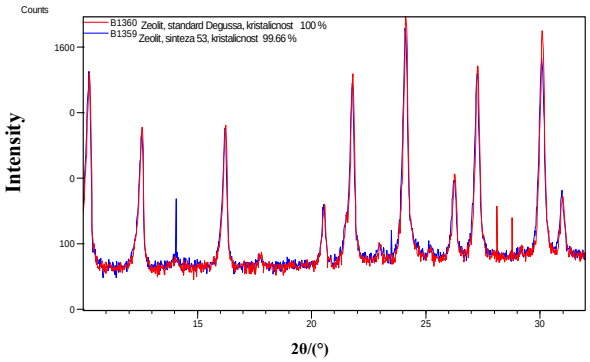


Figure 2. X-ray chart of zeolite obtained at crystallization temperature of 75 °C

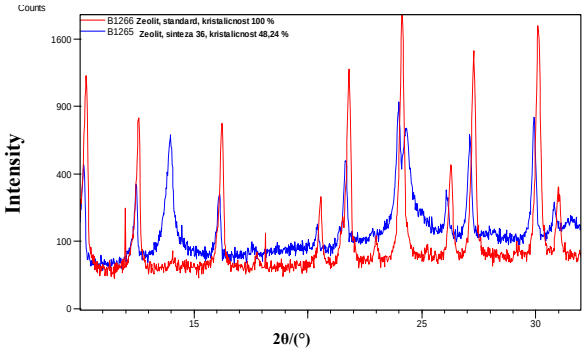


Figure 3. X-ray chart of zeolite obtained at crystallizaion temperature of 80°C

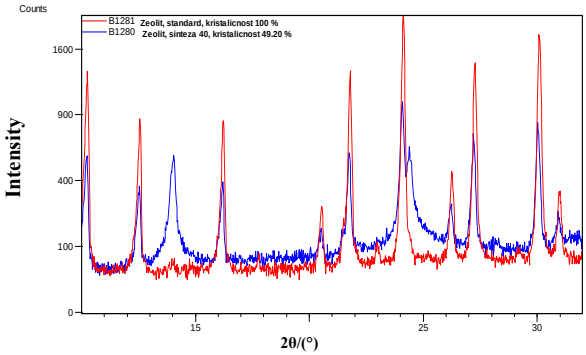


Figure 4. X-ray chart of zeolite obtained at crystallization temperature of 85°C

Relative crystallinity of synthesized samples was measured compared to the standard zeolite A „Degussa" sample. Relative crystallinity in samples synthesized at higher crystallization temperatures (85 and 90 °C) ranged from 37.87 to 49.20%. It is obvious that the samples are crystalline but the degree of crystal phase, which corresponds to zeolite A, decreases in the samples obtained by syntheses no. 3, 4 and 5. This is in accordance with the intensity of these peaks in the x-ray charts of the obtained zeolite (Figure 3, 4, 5). At the same time we can observe from the figures, that the decrease of the degree of crystal phase of zeolite A increases the intensity of peaks at 12 °θ and 22 °θ which correspond to hydro sodalite.

The x-ray chart obtained for zeolite A from synthesis no. 2 shows that the temperature of 75 °C produced zeolite of 99.66% crystallinity (Figure 2). At higher crystallization temperatures of 80, 85 and 90 °C, hydro sodalite is also produced, apart from zeolite A, and it contributes to the increase in the value of specific surface area (17.02–35.31 m^2/g) together with the value of absorption of dibutyl phthalate (1.10–1.20 cm^3/g of zeolite, Table 1).

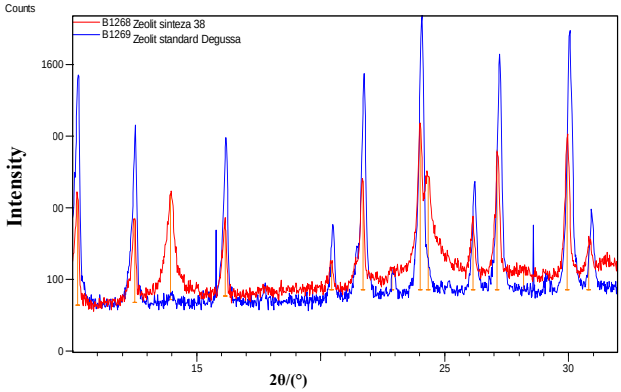
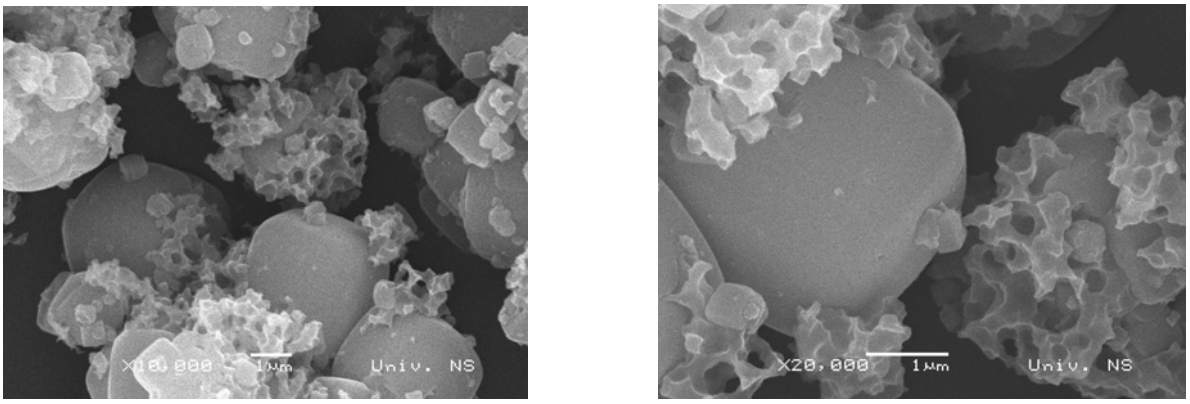


Figure5. X-ray chart of zeolite obtained at crystallization temperature of 90°C

At lower crystallization temperatures (70 and 75 °C) where the specific surface area is 5.46 and 3.25 m^2/g, absorption of dibutyl phthalate is lower and amounts to 0,90 cm^3/g of zeolite.

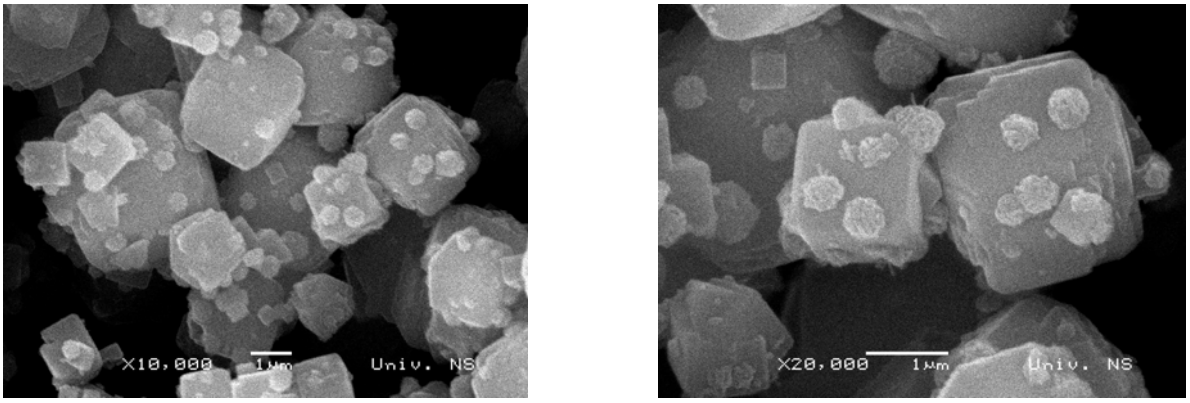
The degree of crystal phase of zeolite A cannot be brought to direct dependence on the temperature of crystallization although it ranged from 99.66 to 37.87%.(Figure 1−5).

SEM photographs of zeolite obtained at the stated conditions of synthesis, shown in Figures 6, 7, 8, 9 and 10, respectively suggest the fact that absorption of dibutyl phthalate is dependent on particle size and their mean diameter, as well as the dependence between crystallization temperature and absorption of dibutyl phthalate.



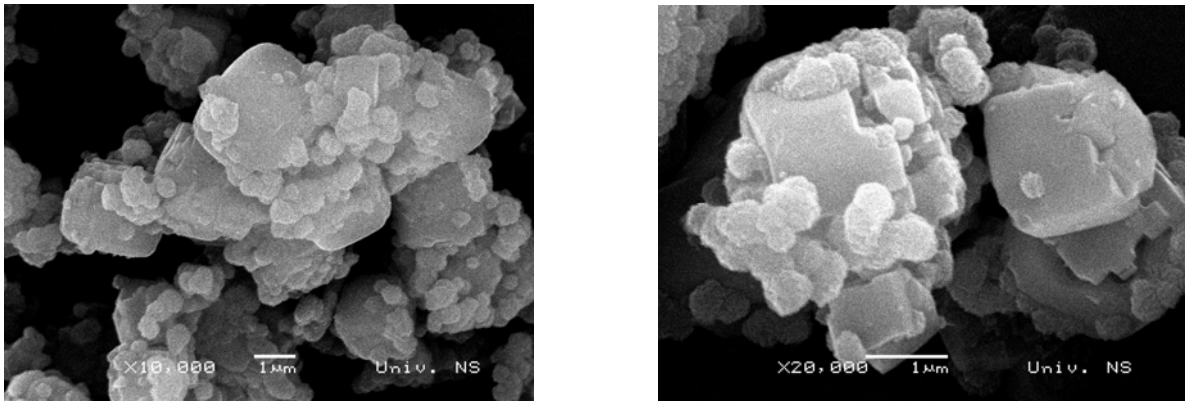
a) b)

Figure 6. SEM photograph of zeolite obtained by synthesis at crystallization temperature of 70°C, a) enlargement 10 000, b) enlargement 20 000



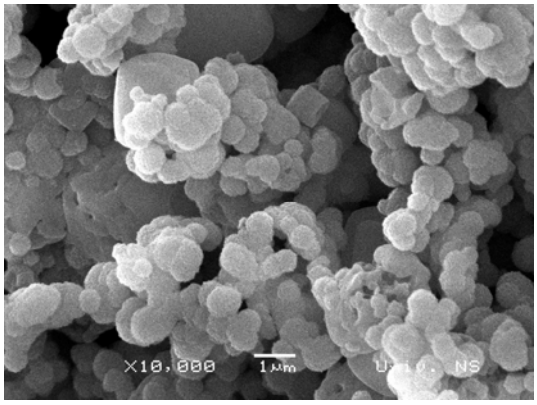
a) b)

Figure 7. SEM photograph of zeolite obtained by synthesis at crystallization temperature of 75°C, a) enlargement 10 000, b) enlargement 20 000



a) b)

Figure8. SEM photograph of zeolite obtained by synthesis at crystallization temperature of 80°C, a) enlargement 10 000, b) enlargement 20 000



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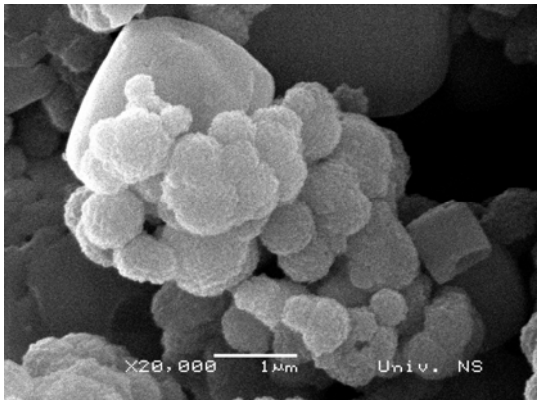
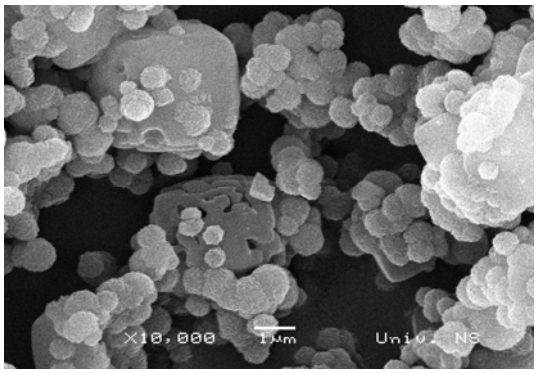


b)

Figure 9. SEM photograph of zeolite obtained by synthesis at crystallization temperature of 85°C, a) enlargement 10 000, b) enlargement 20 000)



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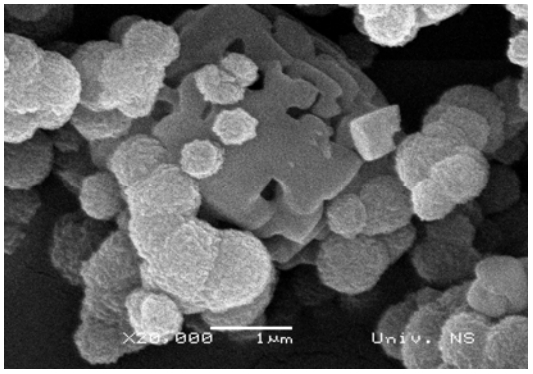

b)

Figure10. SEM photograph of zeolite obtained by synthesis at crystallization temperature of 90°C, a) enlargement 10 000, b) enlargement20 000

The fact that the temperature of 75°C produced zeolite of 99.66% crystallinity suggest that the dominant phase is zeolite A, which is confirmed by SEM analyses of the samples. (Figure 7).

The particle size in the synthesized samples is similar in most systems investigated at all crystallization temperatures, which is in accordance with the principles of autocatalytic nucleation and „memory effect" of the gel.

The dependences of the analyzed systems obtained by „hydro-gel" method were confirmed by researches performed using „dry-gel" method by a group of authors in China. Relative crystallinity in these systems as well shows a direct dependence on temperature which is confirmed by SEM photographs [12].

4. CONCLUSION

The amount of the absorbed dibutyl phthalate depends on crystallization temperature of zeolite. Higher crystallization temperatures of 80, 85 and 90 °C produce, apart from zeolite A, hydro sodalite which contributes to an increase in the value of specific surface area ranging from 17.02 to 35.31 m^2/g. The increase of absorption of dibutyl phthalate occurred in the synthesized samples at the same time (1.10−1.20 cm^3/g of zeolite), for samples synthesized at stated crystallization temperatures (Table 1).

At lower crystallization temperatures of 70 and 75 °C the value of the specific surface area of synthesized samples was 5.46 and 3.25 m^2/g respectively, and the absorption of dibutyl phthalate was lower and amounts to 0.90 cm^3/g of zeolite.

Relative crystallinity of zeolite A cannot be observed as directly dependent on crystallization temperature and was in the interval of 99.66 to 37.87% (Figures 1−5).

However, the fact that the temperature of 75 °C produced a sample whose crystallinity is 99.66%, indicates that the dominant phase is zeolite A, which is confirmed by SEM analyses of the sample (Figure 2).

The mean diameter of the particle (D_s50%) in the synthesized samples is similar in the majority of analysed systems at all crystallization temperatures and this is in accordance with the principles of auto-

catalytic nucleation and the „memory effect" of the gel.

Having in mind the conclusions of these researches, the future task should focus on determining the pore size, chemical composition of the powders formed, moisture and other parameters regarding the quality of the zeolite produced (JIK or similar) with the aim to achieve the optimal temperature of synthesis.

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УТИЦАЈ ТЕМПЕРАТУРЕ КРИСТАЛИЗАЦИЈЕ НА АПСОРПЦИЈУ ДИБУТИЛФТАЛАТА ЗЕОЛИТА А

Сажетак: У циљу одређивања утицаја температуре кристализације на апсорпцију и особине честица зеолита А, праћена је промјена апсорпције дибутилфталата (DBF), удјела кристалне фазе, специфичне површине, величине средњег пречника честица (D_s50%) а урађена је и скенирајућа електронска микроскопија (SEM) синтетисаних узорака зеолита. Синтеза узорака одвијала се на температури кристализације 70, 75, 80, 85 и 90 °C, док су сировине (натријум-алумината и натријум-силиката) биле загријане на температури од 90 °C. Величина честица синтетизованих узорака сличне су у већини испитиваних система при свим температурама кристализације, што је у складу са принципима аутокаталитичке нуклеације и „ефекта памћења" гела. Повећање специфичне површине синтетизованих узорака са повећањем температуре кристализације уочено је у свим анализираним системима (3,25−35,31 m^2/g). Нађено је, да са повећањем температуре кристализације расте апсорпција дибутилфталата (0,90−1,20 cm^3/g), али се истовремено у истим узорцима удио зеолита А смањује, што је потврђено SEM анализом.

Кључне ријечи: зеолит А, апсорпција дибутилфталата, температура кристализације.

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