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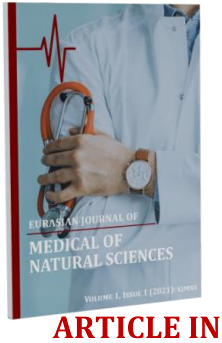

METHODS FOR SYNTHESIS OF LTA-TYPE ZEOLITES

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ABSTRACT

This article describes the structure and structure of the crystal latticye of type A zeolites and their synthesis methods. Methods for the synthesis of LTA-type zeolites using anhydrous ingrediyents ($Al_2Si_2O_7$-metakaolin, C-Al_2O_3) are presented. In addition, it was found that the synthesis of zeolites requires the synthesis of sodium aluminate of cubic and tetragonal crystal systems with crystal latticye parameters. A model for the mechanochemical synthesis of LTA-type zeolites is proposed.

МЕТОДЫ СИНТЕЗА ЦЕОЛИТОВ ТИПА LTA

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Цеолит типа LTA, $Al_2Si_2O_7$-метакаолин, кубическая и тетрагональная кристаллическая решетка NaOH, $Na_2Al_2O_4$, H_2O, Al_2O_3, SiO_2, $NaAlO_2$, $Na_2OAl_2O_3$ $NaAlSiO_4$, $Na_8Al_6Si_6O_{25}$, $4Na_2O_3Al_2O_{36}SiO_2$.

ABSTRACT

В данной статье рассмотрены структура и строение кристаллической решетки цеолитов типа А и методы их синтеза. Представлены методы синтеза цеолитов типа LTA с использованием безводных ингредиентов ($Al_2Si_2O_7$-метакаолин, C-Al_2O_3). Кроме того, установлено, что для синтеза цеолитов необходим синтез алюмината натрия кубической и тетрагональной сингоний с параметрами кристаллической решетки. Предложена модель механохимического синтеза цеолитов типа LTA.

LTA TIPIDAGI SEOLITLARNI SINTEZ QILISH USULLARI

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LTA tipidagi zeolit, $Al_2Si_2O_7$-metakaolin, , kub va tetragonal kristall panjaralar, NaOH, $Na_2Al_2O_4$, H_2O, Al_2O_3, SiO_2, $NaAlO_2$, $Na_2OAl_2O_3$ $NaAlSiO_4$, $Na_8Al_6Si_6O_{25}$, $4Na_2O_3Al_2O_36SiO_2$

ABSTRACT

Ushbu maqolada A tipidagi seolitlarni kristal panjarasi va stukturasi qanday tuzilganligi va uning sintez qilish usullarini yoritib berilgan. LTA tipidagi zeolitini sintez qilish uchun suvsiz ingrediyentlardan ($Al_2Si_2O_7$-metakaolin, C-Al_2O_3) foydalanish usullari keltirilgan. Bundan tashqari seolitlarni sintez qilish jarayonida kristal panjara parametrlari bilan kub va tetragonal kristalli tizimlarning natriy aluminati sintezini talab qilishi aniqlandi. LTA tipidagi seolitning mexanokimyoviy sintezi modeli taklif qilindi.

Introduction

In recent times, enhancing the quality of petroleum fractions through catalytic processes has become a key focus area, driven by the need to produce cleaner fuels and minimize ecological harm. Techniques such as hydrogenation, desulfurization, and dearomatization play a pivotal role in achieving environmentally compliant fuels with reduced emissions. These transformations require the use of highly efficient catalysts and sorbents that function effectively under moderate operational conditions, selectively eliminating harmful compounds like sulfur species, aromatic hydrocarbons, and nitrogen-containing substances.

Among a wide array of porous materials, synthetic zeolites—most notably those classified as Linde Type A (LTA)—are of particular interest due to their well-defined crystalline microporous frameworks, ion-exchange potential, and molecular sieving properties. LTA-type zeolites, modified through ion exchange with Na^+ or Ca^{2+} (yielding NaLTA and CaLTA forms), exhibit preferential interactions with both polar and non-polar molecules. This makes them strong candidates for the selective capture of gases such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), ammonia (NH_3), and volatile aromatic compounds like benzene and toluene.

Because of their high adsorption capacity, excellent thermal resistance, and active surface properties, microporous zeolites are ideally suited for applications requiring both catalytic activity and adsorption efficiency. Consequently, there is increasing research interest in the development of sustainable and optimized synthesis techniques for these materials, especially those involving mechanochemical activation or hydrothermal methods. These approaches offer notable advantages over traditional synthesis routes, including shorter reaction durations, lower energy demands, and improved phase control.

Nonetheless, several scientific and technical challenges must still be addressed to fully exploit the potential of these materials in industrial contexts. Key issues include determining the ideal composition of input materials, investigating the formation of π-complexes between aromatic molecules and metal ions, analyzing the thermodynamics and kinetics of adsorption–desorption processes, and achieving consistent regulation of crystal morphology and pore architecture. Overcoming these hurdles is essential for expanding the industrial-scale use of synthetic zeolites in fuel refinement, gas purification, and catalytic processes.

A review of the literature indicates that the discovery of natural zeolites began with Kronstedt, who identified the mineral stilbite. Following this, Saint-Claire Deville achieved the first hydrothermal synthesis of a zeolite, resulting in the formation of levyne. Barrer later performed controlled synthetic experiments, ultimately producing the structure later recognized as KFI in ZK-5 zeolite within a temperature range of 170–270 °C. Milton and his research team succeeded in synthesizing A-type (LTA) and X-type (FAU) zeolites.

In 2001, Gavalas and colleagues reported the successful preparation of ZSM-5 (MFI) zeolite films using a clear, organic-free precursor solution within a 21-chamber reactor setup. This system facilitated the systematic exploration of the compositional range within the SiO_2–NaOH–Al_2O_3–H_2O reaction mixture. Two years later, in 2003, Zhang et al. investigated the combinatorial synthesis of SAPO-34 via the vapor-phase transport (VPT) technique, examining how the molar ratios of P_2O_5/Al_2O_3, SiO_2/Al_2O_3, and H_2O/Al_2O_3 influence the final CHA-type product.

Additional contributions include those of Mentzen, Boddenberg, and Bellat, who used adsorption calorimetry to assess the energetic characteristics of adsorbent materials. Meanwhile, Avgul, Kiselev, Mirskiy, and Serdobov studied the differential enthalpies of water adsorption—though their work primarily focused on conditions of average pore filling. In Uzbekistan, Prof. A.A. Azamkhojaev and his collaborators, including S.S. Khamrayev, S.Z. Muminov, and Kh.I. Akbarov, conducted notable studies on adsorption using the Magben technique.

Foundational theoretical insights into zeolitic molecular sieves were provided by Breck, whose work laid the groundwork for understanding the structural versatility and adsorption capabilities of aluminosilicate frameworks [1]. Building on this, Davis discussed the growing application of ordered porous materials—like zeolites—for selective adsorption and catalysis, underscoring the importance of pore tunability and chemical flexibility [2].

Barrer also offered a comprehensive overview of the sorptive behavior of zeolites and clays, stressing their role in separation technologies and interfacial chemistry [3]. Flanigen and co-authors investigated the synthesis and structural aspects of LTA-type zeolites, demonstrating their effectiveness in hydrocarbon processing [4].

In more recent research, Pavlov et al. developed NaLTA zeolite from kaolinite using hydrothermal treatment, highlighting the significance of precursor activation and cation exchange processes in determining adsorption performance [5]. Petrovich and colleagues analyzed the thermodynamic principles behind zeolite formation and addressed the stability of different phases under varying synthesis parameters [6].

Zones explored customizable synthesis strategies for molecular sieves, paying particular attention to the use of structure-directing agents (SDAs) and post-synthesis ion-exchange modifications to fine-tune their properties [7]. Piccione et al. introduced the idea of entropy-driven crystallization in microporous materials, showing its potential in producing zeolites with high surface area under lower energy input conditions [8].

Collectively, these studies emphasize that mechanochemical and hydrothermal methods for synthesizing NaLTA and CaLTA zeolites present an effective approach for generating materials with high selectivity, multifunctionality, and catalytic relevance.

Method.

Globally, intensive research continues to focus on zeolite synthesis. Particular attention is given to purifying and transforming materials rich in aluminum oxide, silicon oxide, and sodium oxide—such as kaolinite, bentonite, and illite—into crystalline forms. These transformations often involve inducing porosity and converting amorphous precursors into well-defined crystalline structures. During synthesis, aluminum oxide typically undergoes multiple reaction stages under alkaline and pressurized conditions. Mechanical approaches also enable the conversion of kaolin into zeolite. In an initial step, kaolin ($Al_2Si_2(OH)_4$) is purified and dried to approximately 1% moisture content, then calcined at 700 °C for four hours to remove structural water and initiate phase transformation into metakaolin.

$2Al_2Si_2(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4H_2O\uparrow$ (1)

The resulting metakaolin transforms into an amorphous, white powder. Sodium aluminate to be added to it must be obtained in a pure form. Therefore, thermal decomposition of 98.8% pure $2Al(OH)_3$ is required (2).

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O\uparrow$ (2)

This experiment is conducted at a temperature of 500 °C for 250 minutes. The resulting Al_2O_3 oxide must be reacted with NaOH, which has a purity of 99.9% by weight (3). This reaction is carried out at 500 °C for 60 minutes.

$Al_2O_3 + 2NaOH \rightarrow Na_2Al_2O_4 + H_2O\uparrow$ (3)

Results and discussion. As a result, sodium aluminate ($Na_2Al_2O_4$) is formed. The obtained sodium aluminate appears as a white crystalline powder. To synthesize LTA zeolite, it is necessary to mix the components in equimolar ratios. The amorphous structured metakaolin reacts with alkali (4). This process lasts for 4 hours. The remaining $Al_2Si_2O_7$ is then combined with $Na_2Al_2O_4$ (5). During stages 5–6 of the experiment, the pore structure begins transitioning from mono- to quadrupole form. A schematic representation of this process is shown in Figure 1.

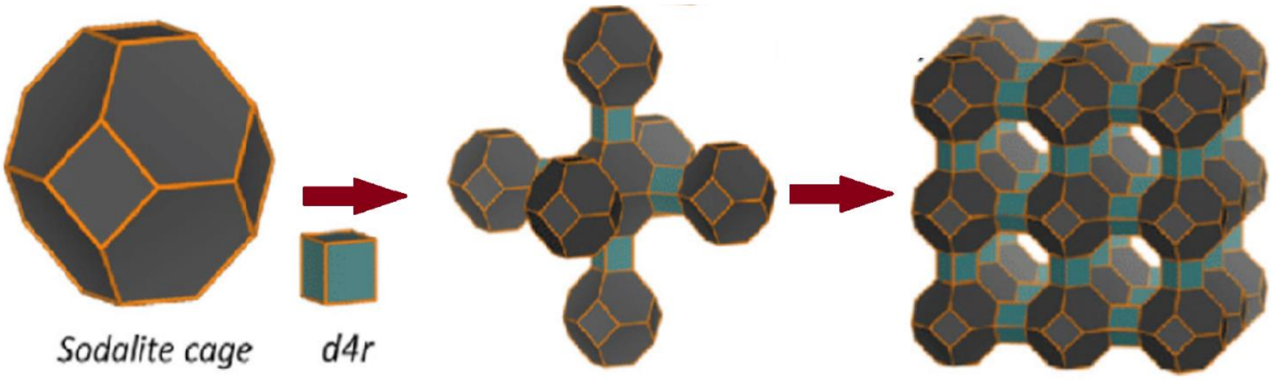


Figure 1. Formation scheme of LTA zeolite.

At the end of the experiment, the addition of aluminum oxide acts as a catalyst by interacting with the unreacted $Al_2Si_2O_7$ and NaOH (7). As a result, the formed compound $Na_{12}Al_{12}Si_{12}O_4$ further participates in the reaction.

$6Al_2Si_2O_7 + 12NaOH \rightarrow Na_{12}Al_{12}Si_{12}O_{48} + 6H_2O$ (4)

$6Al_2Si_2O_7 + 6Na_2Al_2O_4 \rightarrow Na_{12}Al_{12}Si_{12}O_{48} + 6H_2O$ (5)

$6Al_2Si_2O_7 + 12NaOH + 3Al_2O_3 \rightarrow Na_{12}Al_{12}Si_{12}O_{48} + 3Al_2O_3$ (7)

The formation of pores in LTA zeolite ($Na_{12}Al_{12}Si_{12}O_{48}$) depends on the arrangement of silicon and aluminum atoms. The molecular structures of these compounds are shown in Figure 2. These pores, along with sodium aluminate and sodalite cages, are formed as a result of mechanical activation in a vibrational mill.

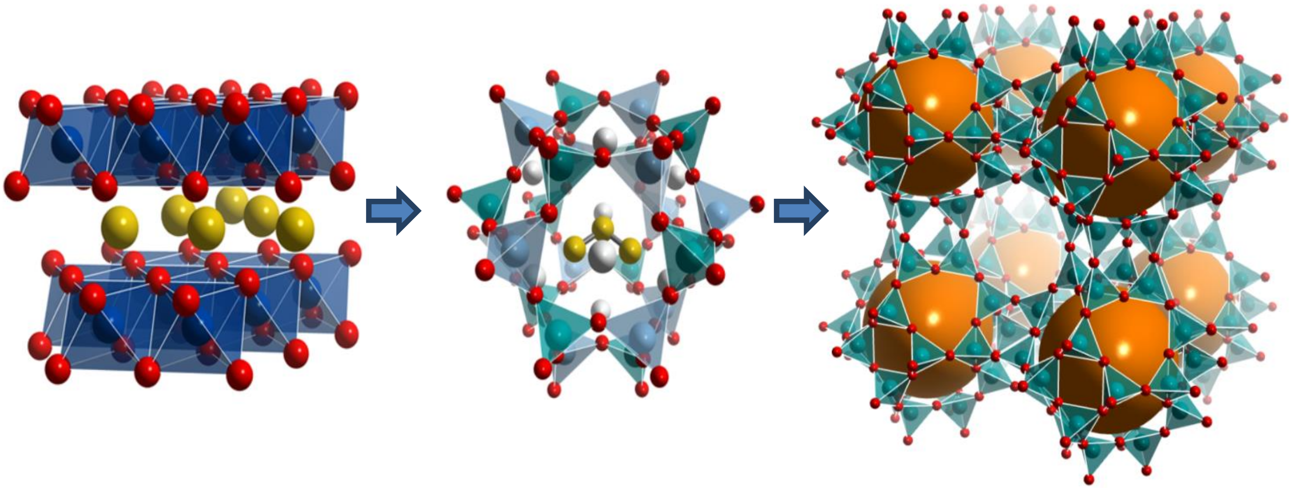
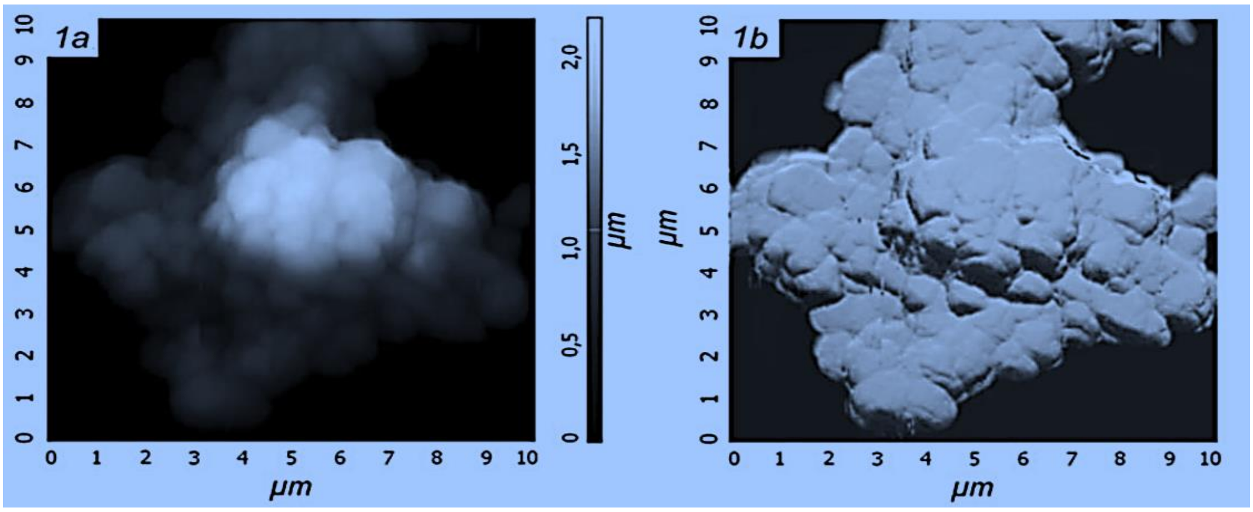


Figure 2. Molecular structure of LTA zeolite formation.



Mechanical milling in a vibrational ring mill influences the shape and size of materials through mechanical vibration. This type of mechanical impact facilitates bonding between solid-phase particles. Accordingly, it leads to interactions between the crystals of sodium aluminate and sodalite pores.

Figure 3. Scanning analysis of $Al_2Si_2O_7$ formation.

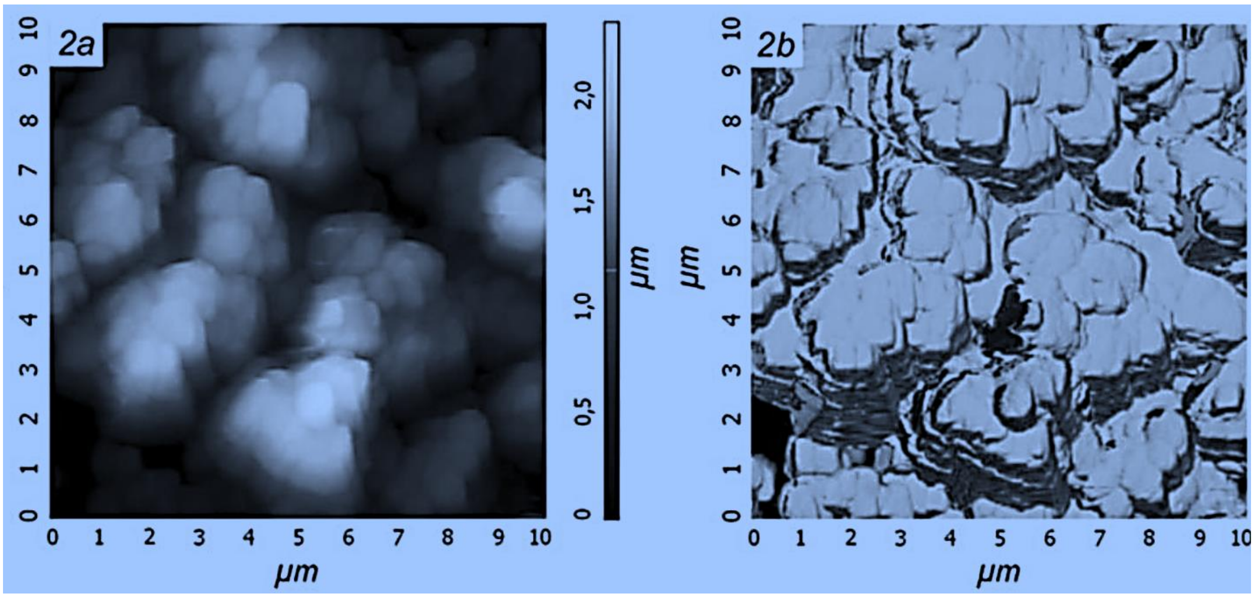


Figure 4. Scanning analysis of $Na_2Al_2O_4$ formation from Al_2O_3 + 2NaOH.

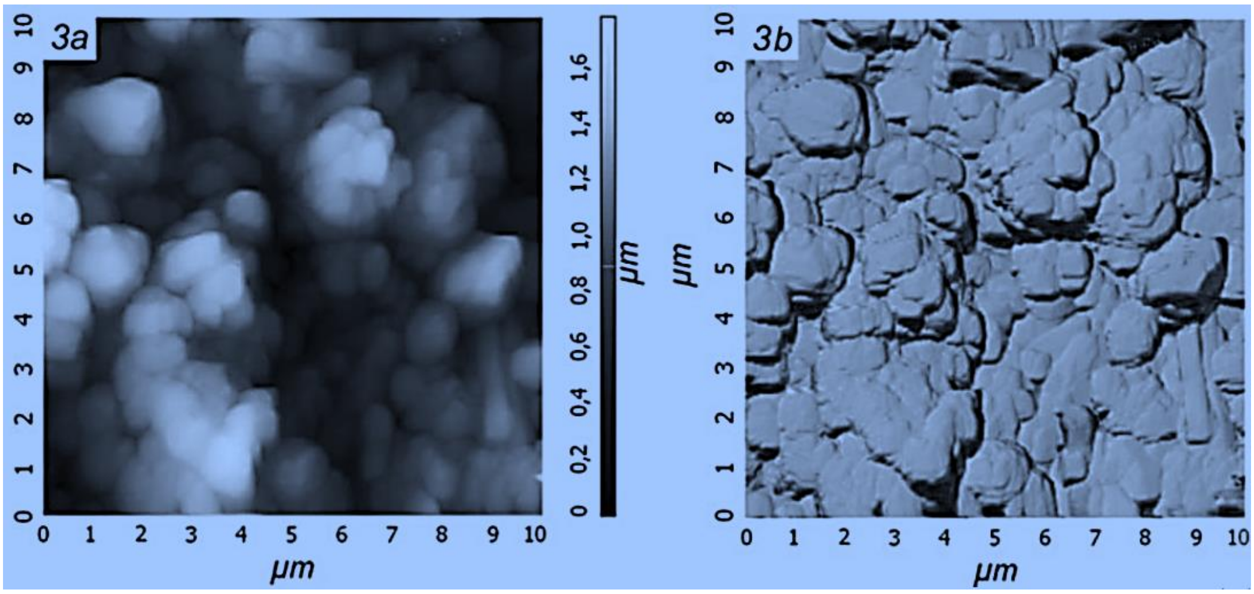


Figure 5. Scanning analysis of $Na_{12}Al_{12}Si_{12}O_{48}$ formation.

The final product of the synthesis is formed at the $Na_{12}Al_{12}Si_{12}O_{48}$ stage. The product obtained after the fourth stage depends on the type of sodium aluminate that has interacted with the sodalite cages. The formation of cubic or tetragonal crystal structures of sodalite pores is influenced by their interaction with sodium aluminate. Therefore, there is a possibility of pore formation in LTA zeolite, as clearly shown in Figure 2b. Thus, sodium aluminate with cubic or tetragonal crystal structures may function as an SDA (structure-directing agent). As mentioned above, cubic and tetragonal sodium aluminate frameworks can form within a few minutes in a vibrational device.

Conclusion

The proposed initial mechanisms of zeolite synthesis described above, as well as recent mechanistic insights into zeolite formation, are based on experimental evidence observed in various reaction systems. Different mechanisms have been suggested for the nucleation and crystallization of zeolites. It is evident that most of these proposals are associated with the location of key processes—such as whether nucleation and crystal growth occur in the solid phase or in solution—especially concerning the formation of zeolite nuclei. It has been shown that the synthesis of LTA zeolite requires anhydrous ingredients (metakaolin, alumina, and sodium aluminate). The presence of structural water in the raw materials (kaolin, aluminum hydroxide, and sodium hydroaluminate) leads to the formation of unwanted sodalite or nepheline phases.

It has been concluded that sodium aluminates with cubic or tetragonal structures—whose lattice parameters are close to those of zeolites—are favorable for the synthesis of LTA zeolite. These aluminates act as structure-directing agents (SDAs). Sodium aluminates with other crystal structures and different lattice parameters tend to form sodalite and lead to the presence of crystalline sodium aluminate phases. There exists an optimal synthesis time determined by the formation of crystalline sodium aluminate: either with cubic or tetragonal symmetry, or in the absence of other structures (such as orthorhombic symmetry). These two factors define the optimal time for synthesis.

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