ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 10
Issue 1
2025

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

THE PHYSICAL-CHEMICAL ANALYSIS OF KA ZEOLITE OBTAINED FROM LOCAL KAOLIN

MUKHAMMADJONOV MIRJALOL
PhD, Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0591) 323-9909, E-mail.: mm.muxammadjonov@gmail.com
**Corresponding author*

RAKHMATKARIEVA FIRUZA
DSc, Chief Researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan
Phone.: (0599) 819-0323, E-mail.: rakhfiruza@gmail.com

OYDINOV MUKHLIS
Assistant, Tashkent Medical Academy, Tashkent, Uzbekistan
Phone.: (0590) 337-7607, E-mail.: muxlisoydinov107@gmail.com

Abstract: In this study, AKF-78 grade Angren kaolin was used to synthesize KA zeolite. The obtained metakaolin and KCl were mixed in a 1:1 molar ratio. The prepared mixture was treated with a 2M NaOH solution and heated in an autoclave for 28 hours at 100°C. Based on the XRD data of the KA zeolite obtained through hydrothermal synthesis, it was compared with the peaks of LTA zeolite crystals. The KA zeolite synthesized from Angren kaolin through hydrothermal synthesis was found to fully correspond to the formula Al10H72K4.63Na6O91.32Si25.38 based on the XRD data. Furthermore, it was determined that the KA zeolite consists of the following elemental composition: O-51.2%, Si-25%, Al-10%, K-6.3%, Na-4.8%, and H-2.5%. The degree of crystallization and amorphicity of the zeolite was also determined. The degree of crystallization of KA zeolite was found to be 29.09%, while the degree of amorphicity was 70.91%. In the analysis of the catalytic or adsorption properties of the zeolites, crystal sizes are of significant importance. The LTA zeolite and the synthesized KA zeolite were compared using X-ray diffraction (XRD).

Keywords: Metakaolin, nanostructure, zeolite, kaolin, crystal, X-ray, hydrothermal, autoclave, diffraction, amorphous.

Introduction. Attempts to synthesize zeolites artificially were made many years ago. In 1962, Sen-Claire Devil synthesized synthetic phillipsite potassium by heating a mixture of potassium silicate and aluminate in a sealed glass tube at 200°C. Later, numerous experiments were conducted to synthesize natural analogs of zeolites under high temperatures (250-450°C) and pressure (300 MPa) conditions [1]. Zeolite synthesis is generally carried out by the hydrothermal method, which mimics natural conditions that promote zeolite crystallization. In the hydrothermal method, temperatures below 600°C and autogenous pressure conditions prevail [2]. The commercial production of Zeolite A is mainly carried out by preparing an aluminosilicate hydrogel using sodium silicate and sodium aluminate [3]. For the synthesis of Zeolite A, kaolin, a natural resource with a Si/Al ratio close to 1, is used as an alternative and inexpensive raw material.

This approach uses kaolin as a raw material similar to Zeolite A [4]. Zeolites like Zeolite A have micropore sizes ranging from 0.3 to 0.45 nm [5]. Zeolite 3A (KA) is typically obtained through cation exchange between monovalent sodium and monovalent potassium. Each unit cell, with a radius of 0.133 nm, contains 12 cations and 24 water molecules fully hydrated [6]. Zeolites are formed in hydrothermal environments and are used in various industrial and economic sectors, particularly in petroleum refining and petrochemical industries as catalysts [7].

Zeolite KA's framework structure is formed by tetrahedral units of [SiO_4] and [AlO_4] linked by common oxygen atoms. Due to its specific crystal structure, Zeolite KA has high porosity, a large specific surface area, and a high ion-exchange capacity. Zeolite KA has remarkable properties such as low toxicity, good thermal stability, environmental cleanliness, and its affinity for heavy metals, making it widely used as a detergent dryer and water softener. Zeolite KA releases potassium ions to enhance plant growth. Therefore, Zeolite KA plays a significant role in softening hard water [8].

The emission of carbon dioxide (CO_2) into the atmosphere contributes to environmental pollution and disrupts the climate. Additionally, carbon dioxide plays a crucial role in the chemical degradation of the ozone layer. As a result, the issue of carbon dioxide removal has become increasingly urgent. Various methods for carbon dioxide removal, including chemical adsorption, physical adsorption, chemical conversion, cryogenic separation, membrane separation, and others, are actively being researched [9-10]. Crystalline aluminosilicates synthesized by scientists are referred to as granulated zeolites without binders. Their synthesis aims at producing microporous aluminosilicates with adsorption properties comparable to those of highly dispersed zeolites [11].

Research Objects and Methods. Analytical-grade reagents and materials were used in the synthesis of synthetic KA. AKF-78 grade Angren kaolin was chosen for the synthesis of synthetic KA zeolite. Initially, the kaolin sample was ground with a HERZOG 100P mill to a particle size of up to 100 nm for the synthesis of synthetic KA zeolite. The ground sample, weighing 10 g, was treated with a 0.5 M oxalic acid ($H_2C_2O_4$) solution to remove additional iron (Fe^{+2}, Fe^{+3}) ions. The purified kaolin was washed 3-4 times with distilled water and filtered.

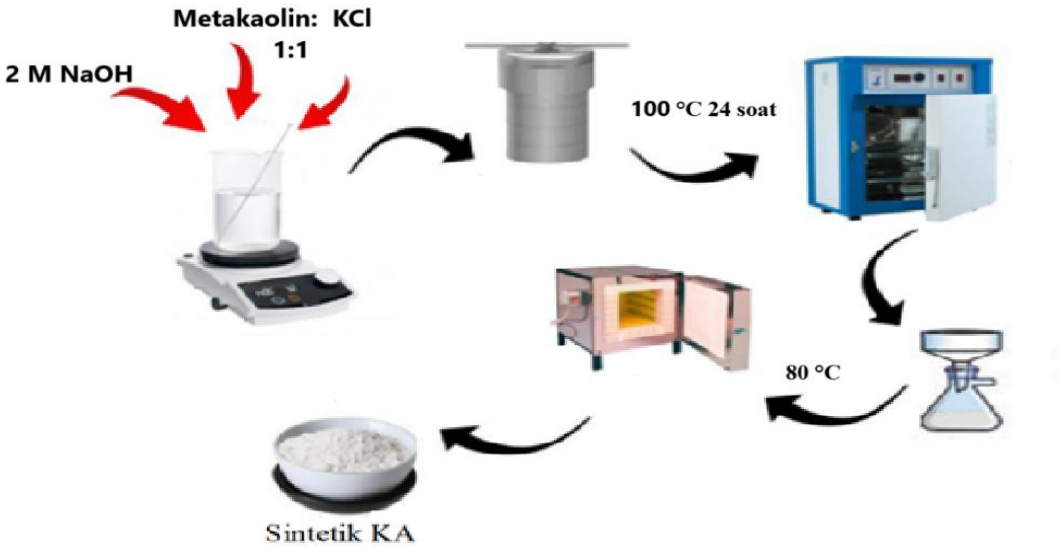

Figure 1. Synthesis diagram of KA zeolite obtained by hydrothermal method

The filtered sample was dried at 650°C in a furnace to obtain metakaolin. The obtained metakaolin and KCl salt were mixed in a 1:1 molar ratio. The prepared mixture

was stirred with a magnetic stirrer (Stable Temp Cole Palmer) for 24 hours at 60°C with a 2M NaOH solution. After that, the prepared mixture was transferred to a Teflon vessel and maintained at 100°C for 28 hours (Figure 1). To remove excess alkali from the synthesized sample, it was washed 3-4 times with distilled water until a neutral (pH 7) environment was reached, and then dried at 80°C [12].

Results and Discussion. In this study, the KA zeolite synthesized from Angren kaolin by hydrothermal synthesis and the LTA zeolite sample were examined using X-ray diffraction (XRD) with the SHIMADZU XRD-6100. The X-ray diffractometer data revealed various X-ray diffraction peaks (Figure 2).

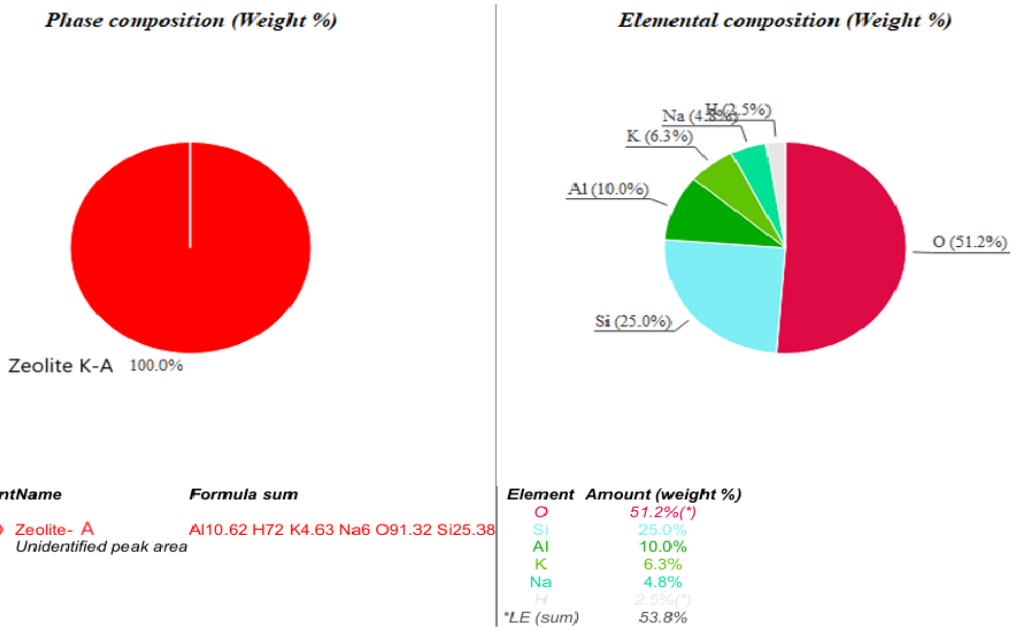

Figure 2. Elemental composition of synthetic KA zeolite

Based on the XRD data, the peaks of LTA zeolite crystals were compared with those of the synthesized KA zeolite. The KA zeolite synthesized from Angren kaolin via hydrothermal synthesis was found to fully match the formula Al10H72K4.63Na6O91.32Si25.38 based on the XRD data when compared with reference data from global crystal structure databases. Moreover, it was determined that the KA zeolite has an elemental composition of O-51.2%, Si-25%, Al-10%, K-6.3%, Na-4.8%, and H-2.5%. Analysis of the peaks in the KA zeolite crystals also revealed the degree of crystallization and amorphicity. In this case, the degree of crystallization of KA zeolite was 29.09%, and the degree of amorphicity was 70.91%.

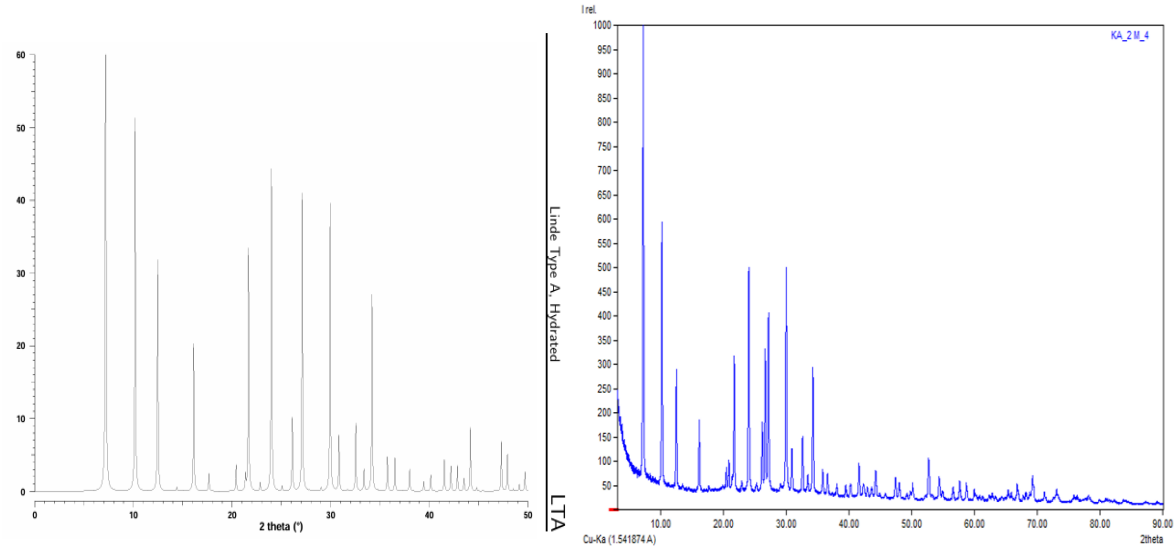

Figure 3. XRD image of synthesized KA and LTA zeolite crystals

Some zeolites often have highly isotropic or spherical morphology crystals, particularly materials like A, X, or Y zeolite, which have cubic symmetry. However, more anisotropic crystal sizes are common in other types of zeolites. For the creation of catalytic or adsorptive materials, it is preferable to have crystals with micro-pores oriented in specific directions, allowing for effective access and exit of molecules. Therefore, crystal sizes play a crucial role in the analysis of catalytic or adsorption properties of zeolites (Figure 3).

The infrared absorption and transmission of the synthesized sample were analyzed using a Bruker ALPHA II FTIR spectrometer. As shown in Figure 4, the FTIR spectrum of the synthesized KA zeolite shows a sharp absorption band at 465.84 cm^{-1} corresponding to Si-O or Al-O vibrations. Symmetric Si-O-Si vibrations were observed at 673.13 cm^{-1}, while asymmetric Si-O-Si stretching vibrations showed lower intensity. Furthermore, a sharp peak appeared at 1006.19 cm^{-1}, corresponding to the asymmetric stretching vibration of Si-O-Si. This vibration indicates that the probability of asymmetric stretching vibrations in the Si-O-Si bond is higher than that of bending vibrations. Additionally, another distinct peak is observed at 556.79 cm^{-1}, which is related to the presence of secondary four-membered rings (D4R), a secondary building unit characteristic of the LTA-type zeolite structure.

The FTIR spectrum of the synthesized KA zeolite sample also reveals two infrared regions related to the hydration water of the zeolite. In zeolite structures, water molecules are coordinated with cations, and hydrogen atoms partially bond with the oxygen ions of the framework. The interaction between the water molecules and the cations or the oxygen ions of the framework depends on the open structure of the zeolite. The broad vibration zone observed at 3488.22 cm^{-1} corresponds to the (OH) hydrogen bonded to the oxygen ions of the framework. Additionally, in the obtained spectrum, an intense absorption zone of water molecules is identified at 1660.74 cm^{-1}.

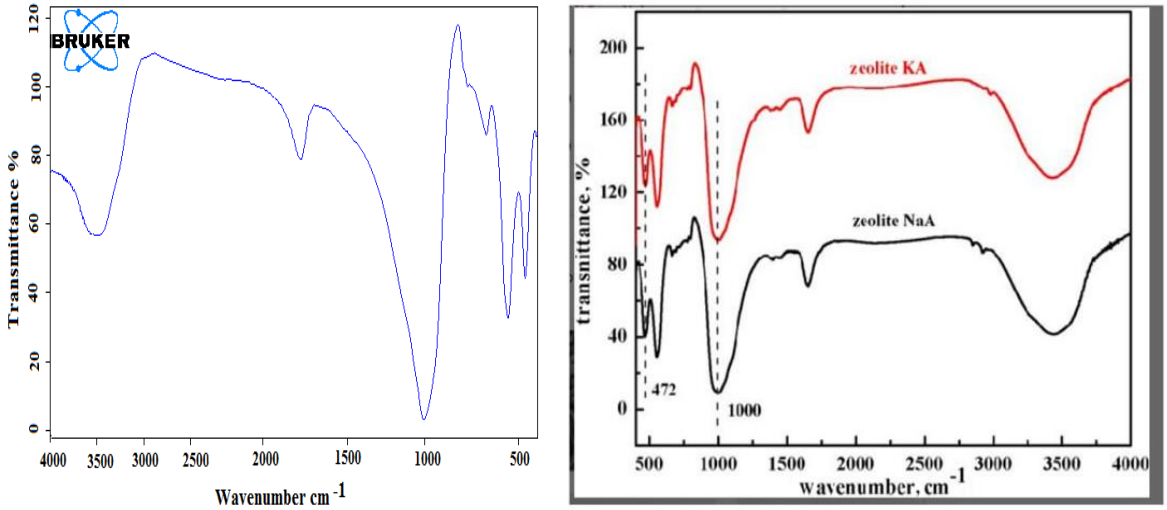

Figure 4. a) Synthesized KA zeolite; b) FTIR spectra of KA zeolite sample obtained by Peng Wang

The distinct and deep vibrational mode of the hydration water in KA zeolite indicates its hydrophilic nature and high degree of hydration. The intensity of this sensitive spectral range shows significant changes in the amorphous phase. The crystallization process of the prepared gel into KA-type zeolite material demonstrates a substantial mass conversion. Thus, the FTIR vibration spectrum of the synthesized KA zeolite confirms the formation of structurally similar units and chemically identical components.

Peng Wang and others successfully synthesized nano-sized KA zeolite particles via hydrothermal synthesis. The FTIR spectrum of the obtained KA zeolite sample is shown in Figure 4. Similar to the synthesized KA zeolite in this study, its FTIR spectrum shows a sharp peak with high intensity at 1000 cm^{-1}, which is associated with the asymmetric stretching vibration of the T-O-T bond (where T = Al or Si). Additionally, a sharp vibration zone at 472.0 cm^{-1} corresponds to the Si–O vibration, and the asymmetric Si–O–Si vibration, as well as the asymmetric stretching of the T-O-T bond, shows lower intensity compared to its asymmetric stretching mode [8].

Conclusion: In the study, AKF-78 grade Angren kaolin was used to synthesize KA zeolite. The obtained metakaolin and KCl were mixed in a 1:1 molar ratio. The prepared mixture was treated with a 2M NaOH solution and heated in an autoclave for 28 hours at 100°C. Based on the XRD data of the KA zeolite obtained through hydrothermal synthesis, it was compared with the peaks of LTA zeolite crystals. The KA zeolite obtained by hydrothermal synthesis from Angren kaolin was found to fully match the formula Al10H72K4.63Na6O91.32Si25.38, based on XRD data. It was also determined that the elemental composition of KA zeolite consists of O-51.2%, Si-25%, Al-10%, K-6.3%, Na-4.8%, and H-2.5%, and the crystallization and amorphousness levels of the zeolite were also identified. The crystallization degree of the KA zeolite was 29.09%, and the amorphousness degree was 70.91%. The crystal sizes are of great importance when

analyzing the catalytic or adsorption properties of zeolites. In the study, X-ray diffraction (XRD) was used to compare the LTA zeolite and the obtained KA zeolite. As shown in the XRD data, differences were observed at the 7, 19, 16, and 21 peaks. These changes were caused by additional crystal peaks formed due to the specific concentrations of KCl salt and NaOH used in the synthesis.

The FT-IR analysis of KA zeolite was carried out using a Bruker ALPHA II FT-IR spectrometer. The FTIR spectrum showed a sharp vibration zone at 465.84 cm^{-1}, corresponding to Si-O or Al-O vibrations. The symmetric Si–O–Si vibration was observed at 673.13 cm^{-1} and showed lower intensity compared to the asymmetric Si–O–Si stretching vibration. The asymmetric Si–O–Si vibration appeared at 1006.19 cm^{-1}. This vibration indicates that the probability of asymmetric stretching vibrations in the Si-O-Si bond is higher than that of bending vibrations. The FTIR spectrum of the KA zeolite particles obtained by hydrothermal synthesis by Peng Wang and others was found to fully match the spectra of synthetic KA zeolite.

References:

1. Goronovsky, I. T. **A Brief Chemistry Handbook** / I. T. Goronovsky, Yu. P. Nazarenko, E. F. Nekryach. − Kyiv: Naukova Dumka, 1987. – 820-829 p.

2. Eduardo Pérez-Botella, Susana Valencia, and Fernando Rey. **Zeolites in Adsorption Processes: State of the Art and Future Prospects**. *Chemical Reviews*, 2022, 17647-17695 p.

3. I. H. Farag, J. Zhang. **Simulation of Synthetic Zeolites-S4A and 5A Manufacturing for Green Processing**. *Engineering Science and Technology*, 2 (2012) 188-195 p.

4. Q. Miao, Z. Zhou, J. Yang, J. Lu, S. Yan, J. Wang. **Synthesis of NaA Zeolite from Kaolin Source**. *Front. Chem. Eng. China*, 3 (2009) 8–11 p.

5. M.X. Oydinov, E.B. Abduraxmonov, F.D. Dimetova. **Synthesis of Synthetic Zeolites from Kaolin and Their Nanostructures**. *Yosh Olimlar Axborotnomasi*, No. 4(2), 2023. *Scientific Journal*, ISSN 2181-5186.

6. Almudena García-Sánchez, Elena García-Pérez, David Dubbeldam, Rajamani Krishna, and Sofía Calero. **A Simulation Study of Alkanes in Linde Type A Zeolites**. *Adsorption Science & Technology*, Vol. 25, No. 6.

7. V.S. Radomsky, E.S. Astapova, A.V. Filimonov. **UDC 538.9**. *Scientific and Technical Proceedings of SPbGPU. Physics and Mathematics Sciences*, 4, 2011.

8. Peng Wang, Qi Sun, Yujiao Zhang, Jun Cao. **One-Step Hydrothermal Synthesis of Zeolite KA from Kaolin**. *Micro & Nano Letters*, 2019, Vol. 14, Iss. 13, pp. 1298–1302. doi:10.1049/mnl.2019.0190.

9. Gomes, V.G.; Yee, K.W.K. **Pressure Swing Adsorption for Carbon Dioxide Sequestration from Exhaust Gases**. *Separation and Purification Technology*, 2002, 28, 161–171. [CrossRef]

10. Pires, J.Saini, V.K, Pinto, M.L. **Studies on Selective Adsorption of Biogas Components on Pillared Clays: Approach for Biogas Improvement**. *Environmental Science & Technology*, 2008, 42, 8727–8732.

11. High Purity, Low Silica. X-Type Zeolite Binderless Shaped Product and Gas Separation Method Employing It / Kotagiri, Yasuki Harada, Atsushi Nakamoto, Yoshiyuki Yoshida, Satoshi Hirano, 2002. Pat. 6478854 (USA). *IPC B01J 20/18 (20060101)*.

12. Oydinov Muxlis, Abduraxmonov Eldor, Rakhmatkariyeva Firuza. **Synthesis of NaA Zeolite from Local Kaolin and Its Physicochemical Analysis**. *Academy of Educational Research Publishing*, International Scientific Journal of Chemistry and Technology. DOI: 10.5281/zenodo.10045868.

CONTENTS

CHEMICAL SCIENCES

TECHNICAL SCIENCES: MECHANICS AND MECHANICAL ENGINEERING