The Austrian Journal of Technical and Natural Sciences, No 3–4
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-25-3.4-59-63

ANALYSIS OF THE SYNTHESIS PROCESS FOR LTA-TYPE ZEOLITE WITH ENHANCED SORPTIVE PROPERTIES DERIVED FROM METAKAOLIN

Pardayev Otabek To'khtamishovich [1,2,3], ***Abdurakhmonov Eldor Baratovich*** [3]

[1] Institute of General and Inorganic Chemistry, Academy of Sciences, Republic of Uzbekistan

[2] Termez branch of Tashkent Medical Academy

[3] Termez state pedagogical institute, st. Termez, Republic of Uzbekistan

Cite: *Pardayev O.T., Abdurakhmonov E.B. (2025). Analysis of the Synthesis Process For Lta-Type Zeolite With Enhanced Sorptive Properties Derived From Metakaolin. Austrian Journal of Technical and Natural Sciences 2025, No 3–4.* https://doi.org/10.29013/AJT-25-3.4-59-63

Absract

The synthesis of the materials in question is performed using two principal techniques. The first technique entails the production of granules composed of 65–85% mayonnaise, with an active zeolite base constituting 25–32% by weight, along with a binder material (natural clay for adsorbents and y-Al_2O_3 for catalysts). This method is primarily employed for obtaining the predominant portion of donor zeolites. The second technique involves the synthesis of donor zeolites without the use of binders. In this scenario, the granules are formed exclusively through the mutual growth of zeolite crystals, which leads to superior values in terms of adsorption capacity, concentration of catalytic active centers, and mechanical strength when compared to zeolite materials containing binders.

Keywords: *A and X zeolite, Na_2O/Al_2O_3, aluminum oxide, kaolin, aluminosilicate*

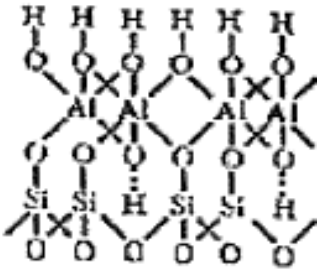
Introduction

The formation method, chemical composition, porous structure, shape, and size of amorphous aluminosilicate granules, which vary and impact the crystallization of A and X zeolites, have been thoroughly investigated in (Keltsev N. V., 1984; Pavlov M. L., 1984; Mirsky Ya. V. 1984; Hamilton K. E., 1993; Chandrasekhar S., 2008). In these investigations, the ratio of components that promote crystallization in the reaction mixtures was adjusted across a broad range to identify the optimal compositional conditions that ensure the consistent production of LTA and FAU-type zeolites with high adsorption and stability properties. In the preliminary experiments, the temperature conditions and crystallization time for each composition of the reaction mixture were selected, enabling the synthesis of zeolite granules with the highest crystalline phase content. It was observed that zeolite A formation occurred when the

Na_2O/Al_2O_3 ratio in the reaction mixture ranged from 1.0 to 2.63 and H_2O/Al_2O_3 = 50. However, it was not possible to produce granules with a high zeolite phase at Na_2O/Al_2O_3 = 1.0 (Imbert F. E., Moreno C., Montero A., Fontal B., Lujano J. 1994; Granizo M. L., Blanco-Varela M. T., Palomo A., 2000; Davies T. W. & Hooper R. M., 1985; Meinhold R. H., Atakul H., Davies T. W. & Slade R. C.T., 1992; Chandrasekhar S., 1996; Kovo A. S., 2008).

Objective: Kaolin is a crystalline natural aluminosilicate modification, with a ratio of silicon to aluminum atoms that is largely similar to zeolite A. Kaolin has a layered structure, consisting of repeating layers of silicon dioxide tetrahedra and aluminum oxide octahedra (Figure 1).

Figure 1. *Structure of kaolin*



When heated in air, kaolins undergo several stages of transformation. At about 550 °C, an endothermic dehydration process occurs, leading to the formation of a disordered metakaolin phase (aluminum disilicate).

Subjects and Methods

Metakaolin underwent crystallization in aqueous sodium hydroxide solutions with Na_2O concentrations ranging from 132 to 558 g/l. Some of the experiments were conducted using a sodium aluminate solution with Na_2O = 132 g/l and Al_2O_3 = 26 g/l. The solution composition varied within the following ranges: Na_2O (2.0–12.0), Al_2O_3, SiO_2 (2.0–2.4), and H_2O (60.0–252.0). Essentially, the same compositions were utilized in the synthesis of high-dispersity zeolite A from sodium aluminate and silicate solutions.

Results and discussion. Zeolite A with high dispersion is generally synthesized from silica-alumino-hydrogel reaction mixtures, which are formed by the reaction of sodium aluminate and sodium silicate solutions. At the same time, there is a limited body of literature on the synthesis of high-dispersity zeolite A utilizing kaolin as a source of silicon and aluminum. Therefore, this section is dedicated to the development of a method for the synthesis and analysis of the mechanisms underlying the formation of high-dispersity NaA zeolite from $Al_2Si_2O_7$.

Previous studies have shown that a preliminary thermochemical treatment at low temperatures (~30 °C) is crucial for the formation of X-ray amorphous sodium aluminate in the granules during the production of granulated zeolite A from synthetic X-ray amorphous aluminosilicate granules. High phase purity and crystallinity of zeolite granules were achieved solely under these conditions during the subsequent crystallization process conducted at temperatures between 55 and 78 °C. This research further explores the influence of the duration of the initial exposure of highly dispersed metakaolin at 30 °C for periods of 1 to 6 hours. Crystallization was performed thereafter at temperatures between 60 and 80 °C for a period of 6 to 24 hours.

The results of the investigation, as shown in Table 1, examine the impact of the initial activation time of metakaolin in a sodium hydroxide solution at 30 °C on both the crystallization degree and the water adsorption capacity of the resulting crystallization products.

Table 1. *Examined the influence of the duration of pre-treatment at 30 °C on the properties of crystallization products formed in a hydroxide solution at 60 °C over a 20-hour period*

№	Duration, h	Zeolite A content according to X-ray phase analysis, %	AE_{water} sm^3/g
1	0	91.5	0,23
2	1	96.1	0,25
3	4	96.1	0,25
4	6	96.1	0,25

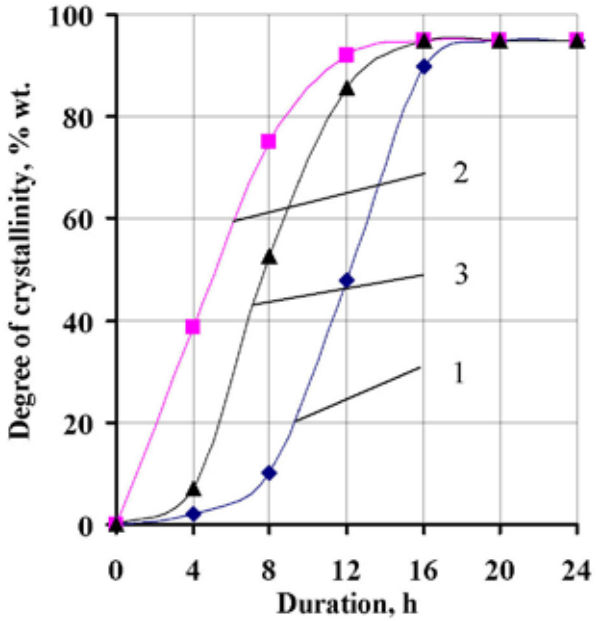
It is clear that a one-hour low-temperature treatment is adequate to yield zeolite A with a high degree of crystallinity during the subsequent crystallization. Prolonging the duration of this process does not influence either the crystallinity or the adsorption characteristics of the resulting product.

The presence of foreign chemical elements, constituting 2.0–3.0% by weight in the Al2Si2O7 composition, prevents the attainment of complete zeolite A formation.

Figure 2 illustrates the kinetic curves for the crystallization of metakaolin in sodium hydroxide and aluminate solutions at temperatures of 60 °C and 80 °C.

It is recognized that, during the crystallization of X-ray amorphous granules into zeolites of types A and X, the diffusion of crystallizing components from the solution to the surface and within the granules could represent the rate-limiting step.

Figure 2. *Depicts the crystallization kinetics of metakaolin: curve 1 represents the sodium hydroxide solution at 60 °C, curve 2 corresponds to the sodium hydroxide solution at 80 °C, and curve 3 shows the sodium aluminate solution at 60 °C*



In our case, it appears that the diffusion stage is not limiting during the crystallization of zeolite A due to the high dispersion of the metakaolin powder particles, and therefore, the effect of low-temperature treatment is not significant (Figure 2., Curve 2).

Table 2. *Kinetics of crystallization of metakaolin at 60 °C in hydroxide* and aluminate** solutions.*

Name of indicators	Duration of crystallization							
	Aluminate solution				Alkaline solution			
	4h	8h	16h	24h	4h	8h	16h	24h
Zeolite A content according to XRD data, % wt.	3	48	92	96	2	8	88	96
Cation exchange capacity of the solid phase, mgCaO/g zeolite	31	82	137	138	8	15	131	138
AE_{water} sm^3/g	0,01	0,12	0.23	0.25	0.01	0.02	0.22	0.25

** PC: 2,4 Na_2O • Al_2O_3 • 2,4 SiO_2 • 60 H_2O; C(Na_2O) = 132,0 g/l*

*** PC: 2,4 Na_2O • Al_2O • 3–2,0 SiO_2 • 60 H_2O; C(Na_2O) = 132,0 g/l; C(Al_2O_3) = 26,0 г/л;*

It is apparent that with the rise in temperature from 60 °C to 80 °C, the crystallization time reduces from 20 to 16 hours, and the synthesis in the aluminate solution leads to a notable enhancement in the crystallization rate.

Table 2 provides information on the crystallization kinetics of Prosyanovskiy metakaolin in both alkaline and aluminate solutions.

It is clear that the crystallization of metakaolin in the aluminate solution takes 16 hours. The formation stages of X-ray amorphous sodium aluminosilicate and crystal nuclei proceed more quickly in the aluminate solution compared to the alkaline solution, with zeolite A achieving 48% of its weight after just 8 hours. This is further corroborated by data on the adsorption capacity of condensed water vapor and the cation-exchange properties of zeolites, particularly the substitution of Na^{+} cations with Ca^{+2}.

Table 3 provides details on the composition of the reaction mixture and the influence of sodium hydroxide concentration in the solution on the characteristics of the metakaolin crystallization products.

It is clear that zeolite A, exhibiting varying crystallinity levels, can be synthesized from the reaction mixtures of all the compositions analyzed. Additionally, a critical factor for achieving phase-pure zeolite is maintaining a Na_2O/H_2O ratio between 0.03 and 0.04. This corresponds to NaOH concentrations ranging from 135 to 160 g/l in the crystallization solution. During crystallization in an alkaline environment, the formation of zeolite A is accompanied by the partial formation of a hydrosodalite phase mixture.

Thus, the most favorable compositions of the reaction mixtures examined are as follows:

$$(2{,}0–2{,}4)\ Na_2O{*}Al_2O_3{*}2{,}0SiO_2(60{,}0–100{,}0)\ H_2O$$

Upon crystallization of these reaction mixtures, zeolite A demonstrates a high level of crystallinity and AEVOD. Additionally, both the NaOH consumption and the quantity of mother liquor requiring disposal are minimal.

Table 4 presents a comparison of the properties of crystallization products derived from metakaolins synthesized from clays under identical conditions. The data indicate that, in both instances, zeolite A is formed with a high degree of crystallinity.

Table 4. *Characteristics of crystallization products obtained from metakaolins derived from deposits in an alkaline solution*

№	Name of kaolins	Zeolite A content according to X-ray phase analysis, % by weight	AE_{water}, sm^3/g
1	Angren kaolin	95,5	0,24
2	Pakhtachi kaolin	95,5	0,24

** CR: 2,4 Na_2O • Al_2O_3 • 2,4 SiO_2 • 60 H_2O; C(Na_2O) = 132,0 g/l, 30 °C (1 h) (20 h)*

Conclusion

In our view, one of the contributing factors to the identified limitations is the relatively low reactivity of metakaolin in comparison to gels, leading to a slower crystallization process. Additionally, granules derived from kaolin, with a diameter of merely 2–4 mm, experience either excessive or inadequate conversion of hydroxide into the solution after calcination at temperatures between 5 and 65 °C. As a result, the crystallization of these granules occurs exclusively on the surface, leaving the internal layers unaffected.

References

Keltsev N. V. Fundamentals of adsorption technology / N. V. Keltsev – Moscow: Chemistry, 1984. – 592 p.

Pavlov M. L. Study of the crystallization region of NaA zeolite in the form of polycrystalline intergrowths/ M. L. Pavlov, Ya. V. Mirsky, V. V. Pirozhkov // ZhP H. 1984. – № 8. – P. 1857–1859. – 115 p.

Mirsky Ya. V. Kinetics of crystallization of aluminosilicate granules into polycrystalline intergrowths of type A zeolite/ Ya. V. Mirsky, V. V. Pirozhkov, M. L. Pavlov // Kinetics and catalysis. 1984. – Vol. 25. – Issue. 1. – P. 22–25.
Hamilton K. E. The effects of the silica source on the crystallization of zeolite NaX/ K. E. Hamilton, E. N. Coker, A. G. Dixon, R. W. Thomson // Zeolites – 1993. – Vol. 13. – P. 645–653.
Chandrasekhar S. Microwave assisted synthesis of zeolite A from metakaolin / S. Chandrasekhar, P. N. Pramada // Microporous and Mesoporous Materials. 2008. – Vol. 108. – P. 152–161.
Imbert F. E., Moreno C., Montero A., Fontal B., Lujano J. Venezuelan natural aluminosilicates as a feedstock in the synthesis of zeolite A // Zeolites- 1994. – Vol. 14. – P. 374–378.
Granizo M. L., Blanco-Varela M. T., Palomo A. Influence of the starting kaolin on alkali activated materials based on metakaolin. Study of the reaction parameters by isothermal conduction calorimetry // Journal of Materials Science, –2000. – Vol. 35. – P. 6309–6315.
Davies T. W. & Hooper R. M. Structural changes i Kaolinite caused by rapid dehy droxylation // Journal of Material science Letters, 1985. – Vol. 4. – P. 39–42.
Meinhold R. H., Atakul H., Davies T. W. & Slade R. C.T. Flash calcination of kaolinite studied by DSC, TG and MAS NMR // Journal of Thermal Analysis, – 1992. – Vol. 38. – P. 2053–2065.
Chandrasekhar S. Influence of metakaolinization temperature on the forma tion of zeolite 4A from kaolin // Clay Minerals, 1996. – Vol. 31. – P. 253–261.
Kovo A. S. Development of Zeolite X and Y from Ahoko Nigerian Kaolin // Chemical Engineering: First Year Ph.D Report Manchester The University of Man chester, 2008. – 119 p.

submitted 20.04.2025;
accepted for publication 04.05.2025;
published 29.05.2025

Contact: eldor8501@gmail.com