

Synthesis of Zeolite A: A Review

Ivan Petrov, Todor Michalev

A Synthesis of Zeolite A: *The report shows how to obtain synthetic zeolites type A, their properties and applications in modern industry. The purpose of this paper is to review the current trends in synthesis and their structure and classification. Attention is paid to how synthesis of zeolites type A, from low cost material like kaolin, natural clinker, fly ash and industrial waste, and particularly their role in solving environmental.*

Key words: *Synthetic zeolites, structure, properties, industrial and environmental applications.*

INTRODUCTION

Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals. The frameworks are composed of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, which corner-share to form different open structures. The tetrahedra are linked together to form cages connected by pore openings of defined size; depending on the structural type, the pore sizes range from approximately 0.3-1 nm [1]. The negative charge on the lattice is neutralized by the positive charge of cations located within the material's pores. In the basic zeolites, these are usually univalent and bivalent metals or a combination. The metal cations may be replaced by acidic protons via ion-exchange to ammonium and subsequent calcination. By reason of electrostatic forces it is not possible to make an Al-O-Al bond. They are made up of "T-atoms" which are tetrahedrally bonded to each other with oxygen bridges. Other "T-atoms" such as P, Ga, Ce, B and Be can also exist in the framework. Due to their exceptional properties, zeolites have been widely used in numerous technical applications as catalysts, adsorbents and ion exchangers [2,3].

The structure formula of zeolite is based on the crystallographic unit cell :

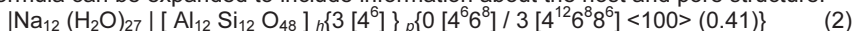
$M_{x/n} [(AlO_2)_x(SiO_2)_y] wH_2O$, where (M) is an alkali or alkaline earth cation, (n) is the valence of the cation, (w) is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can be raging from 10 to 100.

Zeolites have been well studied in terms of the relations among structure, properties and synthesis. Nowadays 180 synthetic zeolites are known. Some of the earlier synthetic zeolites include zeolites A, X, Y, L, ZSM-5 and omega. The Atlas of Zeolite Structure Types [4] , published and frequently updated by the IZA Structure Commission, assigns a three - letter code to be used for a known framework topology irrespective of composition. Illustrative codes are LTA for Linde zeolite A, FAU for molecular sieves with a faujasite topology (e.g., zeolites X, Y), MOR for the mordenite topology, MFI for the ZSM - 5 and silicalite topologies and AFI for the aluminophosphate $AlPO_4-5$ topology. The acceptance of a newly determined structure of a zeolite or molecular sieve for inclusion in the official Atlas is reviewed and must be approved by the IZA Structure Commission. The IZA Structure Commission was given authority at the Seventh International Zeolite Conference (Tokyo, 1986) to approve and/or assign the three - letter structure code for new framework topologies [4].

A typical crystal chemical formula for zeolite A (LTA) [5] would be:



This formula can be expanded to include information about the host and pore structure:



Here, the fact that the host is 3-dimensional and can be constructed by linking double 4-rings as composite building units is highlighted. The description of the pores indicates that there are sodalite cages and a 3-dimensional channel system which contains α -cavities. The channels run parallel to $\langle 100 \rangle$ (i.e., parallel to [100], [010], and [001]), and have an effective channel width of 0.41 nm (Fig.1) [5].

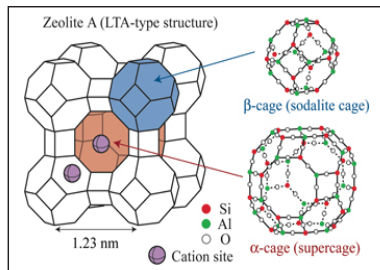


Fig.1. Features of the pores in zeolite A (IZA code LTA): the sodalite cage ($[4^66^8]$), the α -cavity ($[4^{12}6^88^6]$), the 3-dimensional channel system, and the 8-ring defining the 0.41nm effective channel width.

In most zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedra, are assembled into secondary building units which may be simple polyhedra, such as cubes, hexagonal prisms or cubo - octahedra. The final framework structure consists of assemblages of the secondary units. More than 70 novel, distinct framework structures of zeolites are known. They exhibit pore sizes from 0.3 to 1.0 nm and pore volumes from about 0.10 to 0.35 cm^3/g . Typical zeolite pore sizes include: (i) small pore zeolites with eight - ring pores, free diameters of 0.30 – 0.45 nm (e.g., zeolite A), (ii) medium pore zeolites with 10 – ring pores, 0.45 – 0.60 nm in free diameter (ZSM - 5), (iii) large pore zeolites with 12 – ring pores of 0.6 – 0.8 nm (e.g., zeolites X, Y) and (iv) extra - large pore zeolites with 14 -ring pores (e.g., UTD - 1) [4, 5].

The zeolite framework should be viewed as somewhat flexible, with the size and shape of the framework and pore responding to changes in temperature and guest species. For example, ZSM - 5 with sorbed neopentane has a near - circular pore of 0.62 nm, but with substituted aromatics as the guest species the pore assumes an elliptical shape, 0.45 to 0.70 nm in diameter. Some of the more important zeolite types, most of which have been used in commercial applications, include the zeolite minerals mordenite, chabazite, erionite and clinoptilolite, the synthetic zeolite types A, X, Y, L, “Zeolon” mordenite, ZSM - 5, beta and MCM - 22 and the zeolites F and W [5].

R. M. Barrer [1] began his pioneering work in zeolite adsorption and synthesis in the mid - 1930s to 1940s. He presented the first classification of the then - known zeolites based on molecular size considerations in 1945 and in 1948 reported the first definitive synthesis of zeolites, including the synthetic analog of the zeolite mineral mordenite and a novel synthetic zeolite much later identified as the KFI framework. Barrer's work in the mid - to late 1940s inspired R. M. Milton of the Linde Division of Union Carbide Corporation to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Between 1949 and 1954 Milton and coworker D. W. Breck discovered a number of commercially significant zeolites, types A, X and Y. In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial materials for separation and purification. The earliest applications were the drying of refrigerant gas and natural gas. In 1955 T.B. Reed and D.W. Breck reported the structure of the synthetic zeolite A. In 1959 Union Carbide marketed the “ISOSIV” process for normal - isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y - based catalyst was marketed by Carbide as an isomerization catalyst [1-3].

In 1962 Mobil Oil introduced the use of synthetic zeolite X as a hydrocarbon cracking catalyst. In 1969 Grace described the first modification chemistry based on

steaming zeolite Y to form an "ultrastable" Y. In 1967 – 1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM - 5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. By 2008 industry - wide approximately 367 000 t of zeolite Y were in use in catalytic cracking. In 1977 Union Carbide introduced zeolites for ion – exchange separations [3].

ZEOLITE SYNTHESIS

The synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes. The sources for early synthesized zeolites were standard chemical reagents. Much of the study of basic zeolite science was done on natural zeolites. The main advantages of synthetic zeolites in comparison to naturally-occurring zeolites are that they can be engineered with a wide variety of chemical properties and pore sizes and that they have greater thermal stability.

The zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels (formed upon mixing an aluminate and silica solution in the presence of alkali hydroxides and/or organic bases), or solutions in a basic environment. The crystallization is in a closed hydrothermal system at increasing temperature, autogenous pressure and varying time (few hours to several days). The type of the zeolite is affected by the following factors [9-11]:

- Composition of the reaction mixture (silica to alumina ratio; OH⁻; inorganic cations). Increasing the Si/Al ratio strongly affects physical properties of the zeolites. OH⁻ modifies the nucleation time by influencing transport of silicates from the solid phase to solution. Inorganic cations act as structure directing agents and balance the framework charge. They affect the crystal purity and product yield.

- Nature of reactants and their pretreatments. The zeolite synthesis is carried out with inorganic as well as organic precursors. The inorganic precursors yielded more hydroxylated surfaces whereas the organic precursors easily incorporated the metals into the network.

- Temperature of the process. The rate of crystallization is directly proportional to temperature while the rate of nucleation is inversely proportional to temperature).

- Reaction time. Crystallization parameter must be adjusted to minimize the production of the other phases while also minimizing the time needed to obtain the desired crystalline phase.

- pH of the reaction mixture. The process of zeolitization is carried out in alkaline medium (pH>10).

- Other factors. The synthesis can be carried out on a continuous or semi continuous mode, which enhances the capacity, making it compatible for industrial applications.

The main problem in zeolite researchs is the availability and cost of raw material specifically the silica source. On the other hand, commercial silica (made of sand) which is available in gel, sol, fumed or amorphous solid is found to be variable in reactivity and selectivity. The preparation of synthetic zeolites from silica and alumina chemical sources is expensive. Yet, cheaper raw materials, such as clay minerals, natural zeolites, coal ashes, municipal solid waste incineration ashes and industrial slags, are utilized as starting materials for zeolite synthesis. The use of waste materials in zeolite synthesis contributes to the mitigation of environmental problems, generally in the field of water purification, removing heavy metals or ammonium, and turns them into attractive and useful products.

Kaolin based zeolites. Kaolin is clay mineral which structure represent SiO₄ tetrahedral sheets joined to Al(O,OH)₆ octahedral sheets through shared oxygens. Zeolites prepared from natural kaolin are always contaminated with trace amount of iron, titanium, calcium, magnesium, etc. which are originally present in the natural kaolin. These elements may have some influence on the zeolite properties such as brightness, hardness, catalytic activity, electrical properties, etc. Presently, many researchers are working actively in various aspects on the synthesis of zeolite from kaolin. Clay minerals,

such as kaolin, illite, smectite, interstratified illite-smectite, montmorillonite and bentonite are widely used for synthesis of zeolites. The benefits of using kaolin as an aluminosilicate source in zeolite synthesis are widely known. These authors have already studied the preparation of various zeolites from kaolin or other ashes and have made great progress in synthesis of 4A, mordenite, X, Y zeolites, etc. Kaolin is usually used after calcination at temperatures between 550-950 °C to obtain a more reactive phase metakaolin under chemical treatments, with the loss of structural water. Only a small part of AlO_6 octahedra is maintained, while the rest are transformed into much more reactive tetra- and penta-coordinated units. The conditions of the kaolin calcination strongly influence the reactivity of the obtained solids. The best conditions for obtaining a very reactive metakaolin have been discussed by several authors who reported values between 600-800 °C [6-8].

Environmental impact. Globally, millions of tones of miscellaneous solid, liquid and gaseous waste materials, such as household, commercial, industrial, agricultural, radioactive and clinical wastes, are generated annually. It follows that for efficient use of the world's resources recycling and reuse of waste is necessary. On the other hand, large daily output and the limited landfill capacity have resulted in social and environmental problems. Furthermore, the amount of these material is expected to increase dramatically in the near future and may cause major challenges and serious environmental problems.

Fly ash based zeolites. Various processes have been developed for synthesis of zeolite from fly ash, which have been reported by several patents and research articles. The processes developed include five different methodologies with variations in pretreatment steps, sodium aluminate addition, etc. as a function of structure development and exchange capacity. Fly ash is an inorganic residue resulting from the combustion of coal in electricity generating plants, consisting mostly of SiO_2 , Al_2O_3 and Fe_2O_3 . As an industrial by-product fly ash is in the process of being beneficially used in several applications. Although the Si and Al concentrations are determined by the starting fly ash composition, the type and yield of synthesized zeolite strongly depended on alkaline condition and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the starting fly ash. This ratio is important to predict whether the fly ash could successfully be converted into a specific zeolitic material by the adopted synthesis procedures. On the other hand, it is necessary to clarify the influence of the silica–alumina composition for the zeolite formation because the fly ash composition seriously changes depending on the origin of coal sources, in order to synthesize a specific zeolite from any fly ash source [8].

Classical hydrothermal synthesis of zeolites from kaolin include: (i) thermally activated of kaolinite in order to get metakaolinite; (ii) hydrothermal reaction of metakaolinite with various aqueous alkali media; (iii) purification and activation of the resulting zeolite. Numerous papers have appeared on the subject of synthesized zeolites. The synthesis of zeolite Type NaA from Bulgaria kaolinite by conventional alkaline activation was investigated in [9-12]. The recommended molar composition for NaA zeolite synthesis was $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1-2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1-2. In this research, NaA zeolite was synthesized via hydrothermal method. Also, the effects of reaction time and temperature on morphology and crystalline of the synthesized zeolites were investigated. The final products were characterized by X-ray diffraction and scanning electron microscopy (SEM). It is found that the reaction time has a great effect on the crystalline of the synthesized zeolites. The low grade Kalabsha kaolin coexisting with quartz, anatase was thermally activated between 600 and 1000 °C and treated hydrothermally with 2–8 M NaOH solution with or without added water glass, using water bath or autoclave. Zeolite 4A, zeolite P, analcim and hydroxy sodalite were identified by [13]. In [14] produced zeolite NaA from the synthesis mixture which has a composition of $1\text{SiO}_2:1\text{Al}_2\text{O}_3:1.5\text{Na}_2\text{O}:6.5\text{H}_2\text{O}$ molar ratios by using a microwave oven. They characterized the products by XRD and SEM techniques. In [15] synthesized laumontite in a wide temperature range (between 30 °C and 450 °C) by hydrothermal treatment of artificial glasses of composition $1\text{CaO}-1\text{Al}_2\text{O}_3-4\text{SiO}_2$ at 1 kbar water pressure. Chandrasekhar et al. [13] synthesized zeolite NaX

from locally available natural kaolinite. First, they obtained the metakaolinite at 900 °C. Then, the metakaolinites were separately mixed with the calculated amount of NaOH solution and sodium silicate to get molar ratio $(\text{SiO}_2/\text{Al}_2\text{O}_3) = 3$; $(\text{Na}_2\text{O}/\text{SiO}_2) = 1.1$ and $(\text{H}_2\text{O}/\text{Na}_2\text{O}) = 40$ for the reaction mixture. This was aged for 24 h at room temperature and heated in air oven at 87 ± 2 °C. In [15] synthesized zeolite A and X from kaolin activated by mechanochemical treatment. They used kaolinite with a mean particle size of 1.7 μm . The process consists of grinding of kaolinite and subsequent reaction with NaOH solution at 60 °C. In [16] have achieved zeolite synthesis by hydrothermal treatment of the waste solution from selective leaching by 2 M NaOH solution of kaolinite calcined at 1000 °C for the preparation of mesoporous $\gamma\text{-Al}_2\text{O}_3$. The spent leaching solution was hydrothermally treated at 100 °C and 150 °C for 12–72 h. The initial product, hydroxy sodalite, was converted to zeolite P, after a reaction time of 72 h [17,18].

The possibility to prepare synthetic zeolites A, X from Bulgarian kaolin as the basic raw material was studied in [19-21]. The synthesis of zeolites A, X involves preliminary formation of granules granules by the method of “fluidized bed”, followed by crystallization (zeolitization). Thus, the following experimental results were obtained: using the method of “fluidized bed”, the conditions for preparation of suitable granules (“Blackberry” type) with preferred size (1-3 mm) were studied with five amorphous ceramic blends containing kaolin, amorphous SiO_2 , sodium silicate and sodium aluminate at proper quantitative ratios; five crystallizing reactive solutions containing sodium hydroxide and lithium hydroxide as additive were developed, the role of the additive in the crystallization process optimization and in the achievement of high phase purity of the zeolite synthesized was established; the conditions for hydrothermal crystallization (zeolitization) of granules were found to be: 36 h at temperature of 95°C. The structure of the synthetic product Zeolites A,X, was studied by the methods of XRD, DTA/TGA, SEM and IR spectroscopy.

In recent years there has been considerable progress made in the field of accelerating the kinetics of low-temperature inorganic synthesis. Several techniques, like sonochemical (acoustic wave stimulation), ionizing and nonionizing radiation, microwave hydrothermal, hydrothermal process with superimposed electric fields, hydrothermal process with mechanical forces, and mechanochemical, including very high uniaxial pressure and shear [22].

CONCLUSIONS

The article reviews the synthesis of zeolites, in particular zeolite type A. Shown are the structural features, nomenclature for labeling and recording of synthetic zeolites. The main methods for zeolites and their commodity and factors gets clean and efficient zeolite phases shows.

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About the authors:

Ph.D student Ivan Petrov, Department of Material Science, Bourgas Prof. Assen Zlatarov University, Tel. 359 56 858 441; Fax. + 35956880249; e-mail address: bulmarine@abv.bg

The paper is reviewed.