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Characteristics of the structure of natural zeolites and their potential application in catalysis and adsorption processes

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Abstract

Authors present a short review of selected natural-origin zeolite materials. This article discusses the structure, classification and ability to modify natural zeolites, along with examples of their potential applications as adsorbents or catalysts.

Keywords: natural zeolites, adsorption, catalysis, clinoptilolite, mordenite, chabazite, analcime, phillipsite

1. Introduction

The decreasing availability of non-renewable energy sources contributes to greater interest in alternative, renewable energy sources. Intensive research is being conducted to limit the processing of crude oil and obtaining chemicals or fuels from them. The processing of fossil fuel generates large amounts of pollution. Chemical compounds (including sulphur compounds) are harmful to the environment and human health, and also contribute to global warming as a result of CO_2 production (Czekaj, Sobuś, 2018a).

New technologies are currently under development in which the emphasis is on factors such as the environment and economics. A new concept – biorefinery – is a promising technology for obtaining all chemical compounds, fuels and heat (Harikishore et al., 2017). One of the most promising renewable resources is biomass. Due to its chemical structure, lignocellulosic biomass has become a popular raw material for transformation into valuable compounds. While working on the raw material using various chemical, physical and biological techniques, it is possible to separate it into three fractions from which it is built (cellulose, hemicellulose and lignin) to enable the application of further processes leading to the creation of valuable chemicals and fuels (Kim, 2018; Czekaj, Sobuś, 2018b; Van Meerbeeka et al., 2019; Sun, Barta, 2018). Typically, all lignocellulosic biomass transformation processes are performed with the participation of catalysts such as liquid ions, salts or zeolites (Xiea et al., 2018; Lia at al., 2018; Ennaert et al., 2016). Zeolites, in terms of their chemical structure, have interesting sorption properties, and also have a broad range of catalytic abilities. The presence of active sites inside zeolites, or the possibility of creating such sites, enables many types of reactions to be performed: oxidation, reduction, hydrolysis and dehydration (Davis, 2003). Zeolites have a number of applications in the refining and food industry as well as in molecular sieves. Both synthesised and natural zeolites are susceptible to modification by introducing various metals, increasing the space in the pores or manipulation by increasing the specific surface in order to facilitate the diffusion and adsorption of molecules of various sizes (Yilmaz, Műller, 2009; Primo, Garcia, 2014).

The purpose of this article is to characterise natural zeolites including the presentation of their structure, their classification and their capability for modification to acquire catalytic properties that will enable the potential of obtaining a new group of natural catalysts in the transformation of biomass as well as the presentation of many applications of these interesting materials.

2. Zeolites

Zeolites belong to the group of aluminosilicates, in which free spaces and channels are present. The channel system determines the chemical and physical properties, and these conditions determine the various applications of these materials. The size of the channels varies between 3–30 Å, which allows the diffusion and adsorption of atoms, ions or small molecules (Handke, 2005; Czekaj, Sobuś, 2018c). The general pattern of zeolites is:

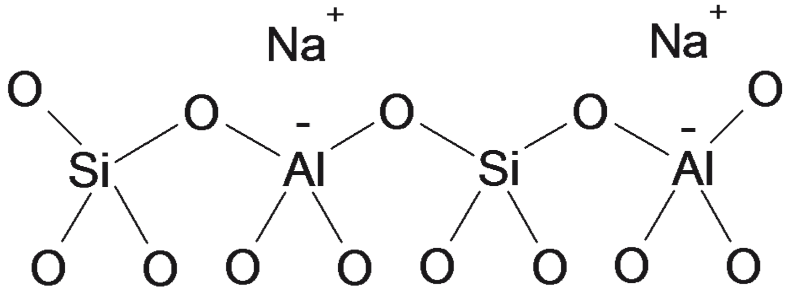

Fig. 1. Basic structure unit of zeolites (PBU) (Corma, 2003)

$$M_{x/n}\,[Al_xSi_yO_{2(x+y)}]\cdot pH_2O,$$

where:

- M - one or more divalent cations,
- n - cation charge $y / x = 1\text{-}6$ $p / x = 1\text{-}4$ (Handke, 2005)

2.1. Zeolite structure

Zeolites are crystalline materials containing atoms from group I and II in their structure, such as Na, K, Mg, Ca, Sr and Ba. The basic unit (PBU–building building unit) building a zeolite is a tetrahedral connection of silicon (SiO_4) and aluminum (AlO_4) (Kesraoui-Ouki et al., 1994).

The method of combining PBUs via oxygen causes the formation of a secondary building units (SBU). The connections of SBUs contribute to obtaining three-dimensional zeolite structures. In turn, the channel systems and free spaces observed in the zeolite materials are formed by different combinations of PBUs (Kesraoui-Ouki et al., 1994; Corma, 2003).

2.2. Mechanism of creating active centres

The specific three-dimensional structure of zeolites and the presence of free spaces can serve as “reaction channels”, where activity and selectivity can be improved by creating active sites. The introduction of aluminium atoms into the tetrahedral structure of silicon results in the formation of acidic active sites, capable of forming carbocations. The presence of a trivalent aluminium atom (or another atom of the same value) connected to four oxygen atoms forms an aluminium tetrahedron, which has a negative charge. In order to neutralise the electric charge, a cation, usually H^+, must be present in the channel. The presence of a proton leads to the formation of surface hydroxyl groups with the character of Brønsted acid active sites (adsorbing water molecules on the Al ion). The number of Brønsted acid sites is directly proportional to the concentration of these trivalent skeletal ions. Their strength depends on the type of trivalent ion and its concentration. In the case of Al, the strength of Brønsted’s active site is usually inversely proportional to the concentration of the skeleton aluminium to the silicon/aluminium module, which is equal 10 (Grzybowska-Świerkosz, 1993; Čejka et al., 2008). In cases when zeolites heat up at a temperature above 400°C, the water molecule is removed from the acidic site of Brønsted and the aluminium ion appears as an electron pair acceptor – the Lewis site is created (Dapsens at al., 2015; Dallas Swift et al., 2016).

3. Historical outline of zeolites

The natural zeolite, stilbite, was discovered in 1756 by the Swedish mineralogist A.F. Cronstedt. During the analysis and heating of this mineral, large amounts of water vapour was released. On the basis of these observations, he called this material zeolite. In Greek, zeolite means “boiling stone” (zeo–boil, lithos–stones). However, in the first 200 years from when the first zeolite was discovered, this material had no practical applications and was classified as a group of fascinating but useless minerals. In the 1940s, a series of zeolites with a low Si/Al module was hydrothermally synthesised based on observations of the geothermal formation of natural zeolites. Successful synthesis was performed using appropriate analytical techniques and these porous materials had an impact on the rapid development of industry in the 20th and 21st centuries (Xu et al., 2007). Scientists Smith and Beck describe zeolites as crystalline and porous aluminosilicates that are capable of the adsorption and desorption of water molecules and the exchange of cations (Flanigen, 2001). In turn, Liebau (1983) defined these materials as tectosilicates containing channels in their structure, which provides the opportunity for the diffusion of adsorbed molecules.

Initially, synthetic zeolites were only inorganic materials. The breakthrough was the use in 1961 by Barrer and Denne of alkylammonium cations instead of alkaline cations in the synthesis of these materials. The presence of alkylammonium cations has proven to be beneficial for crystallisation during synthesis as they act as so-called templating agents (Cundy, Cox, 2003). Due to the use of templates of various shapes, sizes and chemical compositions, it was possible to obtain new porous crystalline structures. This allowed Mobil One to obtain in 1972, for the first time, high-silicon MFI zeolite, which played an important role in catalysis (Armor, 2011).

Natural zeolites are also formed in sedimentary environments in the process of the hydrothermal transformation of rocks. In nature, the most common minerals are analcime, chabasite, clinoptilolite, mordenite or stilbite. Their chemical compositions differ from each other and, for example, for basic rocks, zeolites with a low silicon Si/Al module are characteristic. By contrast, zeolites with a high silicon content occur in rocks with an acidic pH. Of the most common natural zeolites, clinoptilolite plays the most important role and this mineral has the most applications in various industries (Mumpton , 1977).

4. Zeolites properties

Basically, two factors determine the possibility of using zeolites in the chemical industry, namely the presence of an active site in the channel system as well as shape and geometry, which are responsible for shape selectivity, which in turn determines the possibility of performing specific reactions (Smit, Maesen, 2008).

Active sites are present in zeolites both inside the structure in the channels or pores as well as on their surfaces. The number of Brønsted acid sites determines the selectivity of catalytic reactions and in combination with the geometry of these materials also determines the shape of selective catalysts for specific types of reactions, e.g. cracking, alkylation and isomerisation (Handke, 2005; Ramachandran et al., 2005).

The presence of micropores imposes steric restrictions and the diffusion of reagents into the interior of the aluminosilicate channel system and also prevents the transport and adsorption of macromolecular compounds on active sites. The same effect is also limited by the speed of diffusion of products obtained during the reaction to the outside of the channel system. The shape and size of pores in zeolites favours specific reactions, conditioned by the sphericity of zeolites. This phenomenon was described by Friletta in 1962 and described as a form of selectivity and is dependent upon (Garcia-Martinez, Li, 2015; Dwyer, Degnan, 1993; Rinaldi, Schüth, 2009):

- pore sizes and channels that could limit the diffusion of reagents into the centre of the catalyst;
- the size of the pores and channels that prevent the diffusion of products from outside of the zeolite;
- the possible formation of various forms of transitional products in pores and zeolite channels.

The specific structure of zeolites and in particular the presence of negatively charged aluminium units, which are compensated by positive charges, called cations, gives aluminosilicate the ability to exchange ions and introduce various metal cations into the crystalline structure of these nanoporous materials (Marakatti, Halgeri, 2015).

Ion exchange is also one of the methods of modifying zeolites. The process is usually performed under hydrothermal conditions zeolites modified in such a way can be used as additives to water softeners in detergents or in the production of catalysts. Typically, ion exchange is performed by exposure of the zeolite to a solution of a salt of another cation at a specified concentration and at room temperature or higher. Ion exchange is the reaction of replacing the cation A^{a+} by B^{b+} in a zeolite. The ion exchange capacity of zeolites allows the formation of active Brønsted acid sites, the mechanism of which is described in sub-chapter 2.2. A general formula of the exchange reaction is shown below (Weitkamp, Puppe, 1999):

$$bA_s^{a+} + aB_z^{b+} \rightleftarrows bA_z^{a+} + aB_s^{b+}$$

In the 1960s, experiments were conducted by Ames to rank cations and their affinity for natural zeolite - clinoptilolite. Based on the results, the following sequence was prepared:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{2+} > Al^{2+} > Mg^{2+} > Li^+$$

The experiment was also conducted by Howery and Thomas. In this case, a number of cations and their affinity for chasuble were obtained:

$$Ti^+ > K^+ > Ag^+ > Rb^+ > NH_4^+ > Pb^{2+} > Na^+ = Ba^{2+} > Sr^{2+} > Ca^{2+} > Li^+$$

Other researchers (Semmens and Seyfarth in 1978, Sherman in 1978, Colella in 1993, and Mondale in 1995) confirmed that metals such as chromium, zinc, cadmium, copper and lead also have a high affinity for natural zeolites (chabasite, clinoptilolite, phillipsite) (Hedström, 2001).

The adsorptive properties of zeolites depends on their chemical composition, their Si/Al ratio, the presence of various metal cations and their location in the crystal structure. The adsorptive capacity can be modified through several chemical treatments – acid / base treatment, impregnation with a surfactant and also through ion exchange – additionally, the process can determine the hydrophilic-hydrophobic properties due to the presence of organic or inorganic ions (Wanga, Peng, 2010).

In the work of the Jha and Hayashi (2009), the effect of the presence and amount of ammonium ions was studied and 0.4M NaOH was used to develop the specific surface area. The natural zeolite, clinoptilolite (Akita Prefecture, Japan), was used. A high affinity of ammonium ions was observed. Their number is related to the amount of sodium ions present in the zeolite structure

Ćurković et al. (1997) investigated the possibility of removing lead and cadmium from sewage in the presence of natural zeolites. Zeolites were treated with 2M NaCl solution at different temperatures (22 and 70°C). The purpose of the modification was to remove the present K^+ and Ca^{2+} ions and leave the Na^+ ions, the presence of which significantly facilitated the ion exchange process as well as the removal of heavy metals from wastewater. The influence of temperature on the ion exchange process was also investigated, where it was observed that the increase in the rate of removal of toxic metals from the environment and their incorporation into the structure of zeolites increases as the temperature increases.

Three HEU zeolites originating from Armenia, Georgia and Greece were used in a study by Christidis (2003). The test consisted of an attempt to increase the specific surface area of zeolite by treating this material with dilute KOH and then reacting it with 6M HCl. In addition, the effect of temperature (700°C) on the zeolite stability was checked. The experiment showed an increase in both the surface area and the meso- and microporosity of the structure after treatment of the HCl sample. Similar results, although less significant, shows the effect of the KOH principle on zeolites. The increase in surface area is caused by dissolving the amorphous parts and removing silicon tetrahedral from the structure. However, heating caused the opposite effect to the above-described cases.

In the Karadag (2007) study, the adsorption of Basic Red 46 (BR46) and Reactive Yellow 176 (RY176) dyes from a water solution on natural and modified zeolites was performed. Two types of surfactants were used for modification: cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HDTMA). During the experiment, the effect of dye concentration, contact time, pH, temperature and type of surfactant used on dye adsorption were checked. Based on the obtained results, the adsorptive capacity of the dyes increased with increasing pH and temperature. It also follows that unmodified zeolites have better properties due to the neutralisation of negative ions present in zeolite by cations present in the dyes.

5. Characteristics of selected natural zeolites

The structure, properties, occurrence and possible applications of selected natural zeolites are presented below.

5.1. Analcime [ANA] $NaAlSi_2O \cdot 6H_2O$

The name analcime comes from the Greek word analkis, which means weak and powerless; this is due to the low possibility of electrification of this mineral during rubbing (Ghobarkar et al., 2003).

The cubic phase of framework type ANA (analcime) is described by the space group I a -3 d (# 230) with lattice constants a = b = c = 13.5670 Å (Iza, 2020). The crystal unit cell with alkali metals contains 448 atoms (see Fig. 2a).

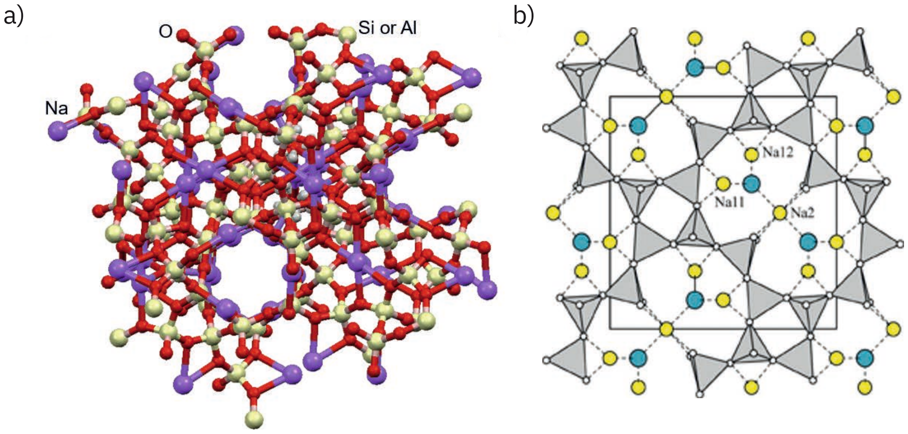

Fig. 2. The unit cell of analcime – (a) crystal unit cell, (b) crystalline structure (Iza, 2020)

The structure of ANA was determined in 1930 by Taylor. Determining the construction of analcime has become a milestone in the mineralogy of zeolites. This zeolite consists of four rings that are individually joined and are arranged in rolled up chains around the axis of the "tetrahedral" screws (Iza, 2020; Yokomori, Idaka, 1998; Coombs et al., 1959; Mintova, Barrier, 2016; Liu, 2005; Atta et al., 2012). Na^+ cations (yellow in Fig. 2b) are located in the central part of the elementary cage (there are 24 cages in the elemental cell) – most often, the amount of cation varies between 12 and 17. In turn, the water molecules occupy 16 places in the cell elementary (Iza, 2020).

Analcime occurs in rocks formed in the processes of crystallisation of magma (in basalt) and metamorphic rocks. It occurs in the following countries: USA, Russia, Tanzania, Serbia, Italy, Australia, New Zealand, Japan, Scotland (Iza, 2020; Coombs et al., 1959).

Research on the modification of ANA zeolite by incorporating specific metals into their structure is presented below along with the potential use of this material in catalytic processes.

Azizi and Tilami (2013) have developed a procedure for the production of ANA zeolite along with crystalline metals such as Co and Mn incorporated into its crystalline structure. Silicic acid, aluminium in powder form, sodium hydroxide, nickel chloride and manganese sulphate monohydrate were used for the synthesis. Silicic acid was dissolved in sodium hydroxide at 60°C for 30 minutes.

Appropriate amounts of cobalt chloride and manganese sulphate solutions were then added to the silicic acid. The whole mixture was stirred for 15 minutes. The aluminium powder was dissolved in sodium hydroxide (3.7M) to obtain sodium aluminate. The obtained aluminate was placed in a solution containing Co and Mn metals and was vigorously stirred to obtain a gel consistency. The gel was placed in an autoclave with Teflon filling. This process was performed for 5 days at 160°C. The obtained product was filtered, rinsed with deionised water and dried at 80°C. The presence of metals was confirmed by XRD and SEM-EDX.

In the work of Azizi (1, 2013), the process of oxidation of benzyl alcohol with the participation of the Cu-analcime catalyst was performed. ANA zeolite was modified by ion exchange and copper cations were incorporated into the crystal structure. The process was conducted at 25°C for 4h (0.1 g zeolite was treated with 10 ml of 1M copper(II) nitrate aqueous solution). The product was filtered, rinsed with distilled water and dried at room temperature. The oxidation reaction was performed in a round bottom flask equipped with a dropping funnel. Acetonitrile (3 ml, used as a solvent) with H_2O_2 (35%) (1.2 ml, used as an oxidant), 0.03 g catalyst, benzyl alcohol (2.8 mmol) were used. The mixture was heated under a condenser and after 4 h, the solution was filtered and the products for GC analysis were taken.

Theoretical studies were also conducted by the Azizi team (1, 2013). All calculations were made using the Gaussian 03 program. The structures were optimised using Hartree-Fock (HF) methods. Geometry optimisation was performed using the 6-31G database. Research has been conducted on the effect of solvation energy and the O-H bond length in the benzyl alcohol molecule in various solvents as well as the benzaldehyde solvation energy (continuous model - PCM) using a polarised continuous model for acetonitrile, dichloromethane, tetrahydrofuran, cyclohexane, methanol and heptane. Linear regression analysis was performed using SPSS 15.

The catalytic process was also conducted by the Bejar team (2014). The cyclohexane oxidation reaction was performed on Mn-analcime. A series of catalysts was prepared by mixing NaOH, silicic acid, manganese sources (manganese(II) carbonate, manganese(II) chloride) and aluminium nitrate nonahydrate. The whole mixture was placed in an autoclave with Teflon filling and the process was conducted in hydrothermal conditions for different times (6–72 h) and at different temperatures (120–175°C). The products after the synthesis were filtered, rinsed with distilled water and dried overnight at 60°C. Next, 50 mg of catalyst was mixed with 5 ml of solvent (dichloromethane or acetonitrile), 1 mmol of cyclohexane and 1 mmol of tert-butylhydroxide (TBHP). The mixture was stirred in the atmosphere of N_2 at 35°C for 24 hours. The products were separated and subjected to a GC analysis. The conversion of the process reached 68.2%. The products were 2-cyclohexane-1-one (46.4%), 2-cyclohexane-1-ol (30.8%), cyclohexane epoxide (2.7%) and 1,2-trans-cyclohexanediol (20.1 %).

Analcime does not have many applications (including as a catalyst or adsorption material) due to its structure and the resulting difficult diffusion of molecules. However, tuffs containing this zeolite in their structure are used as an additive in cement and concrete (usually in Bulgaria) (Iza, 2020).

5.2. Chabasite [CHA] $(Ca,Na_2)[Al_2Si_4O_{12}]\cdot 6H_2O$

The name of the chabasite comes from the Greek word khabazios, which means unknown stone from the myth of Orpheus (Ghobarkar et al., 2003).

The rhombohedral phase of framework type CHA (chabasite) is described by the space group R-3 m (# 166) with lattice constants a = b = c = 9.459 Å (Iza, 2020). The crystal unit cell with alkali metals contains 37 atoms (Fig. 3a).

The chabasite skeleton consists of 6-membered rings (Fig. 3b). Each ring, in turn, is made up of six tetrahedrons of aluminium and silicon connected by bridges (Al, Si)-O-Si with adjacent rings. Four ion channels have been

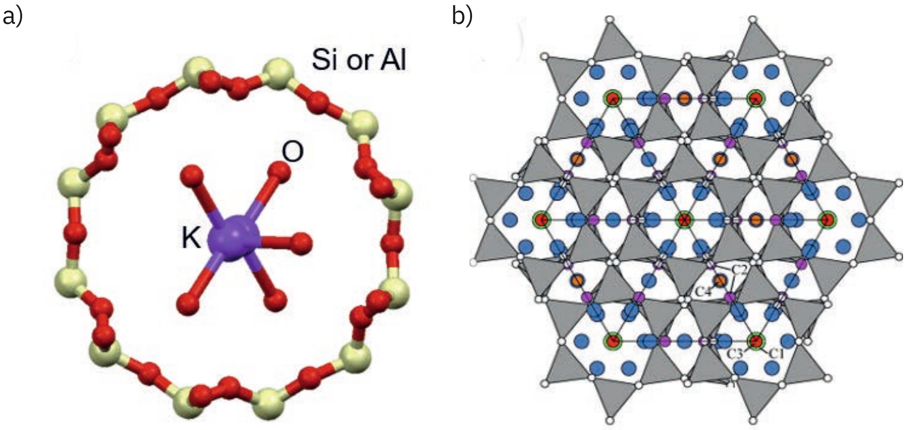

Fig. 3. Chabasite crystal structure – (a) crystal unit cell, (b) crystalline structure (Iza, 2020)

distinguished in the structure. C1 (green) bound to a double 6-membered ring and with three oxygen atoms present in the rings, C2 (pink) is present near the 8-membered ring of the chasmidite cage, connected to the three-frame oxygen atoms. C3 (red) is present near the cage but is not associated with the frame. C4 (orange) is present in the middle of an 8-membered ring. There are also water molecules in the zeolite.

In the elementary cell, there are usually 13 molecules of water and 11 of them are connected with oxygen from the skeleton (Iza, 2020; Kol'tsova, 2007; Yakubovich et al., 2005).

Chabasite was discovered by Hay in 1964 in a tuff and in tuff clays in the Olduvai gorge in Tanzania (Iza, 2020). Chabasite is one of the most widespread zeolites. It occurs in volcanic rocks (basalts, andesites), in pegmatites and in the cracks of sedimentary rocks. It is most often present in the void of metamorphic rocks. It usually co-exists with other natural zeolites such as stilbite and phillipsite. It can also be found in the sediments of hot springs (Mess et al., 2005; Montagna et al., 2010). Its distribution is as follows: Tanzania, Turkey, Italy, USA, Iceland, Japan, Australia, Canada, New Zealand, Czech Republic, Hungary (Iza, 2020).

The Majdan team (2006) used CHA zeolite as a surfactant carrier and tested the adsorption capacity of chromates. For this purpose, the sodium cations present in the zeolite structure were substituted with HDTMA (hexadecyltrimethylammonium bromide). Based on the analysis, the researchers confirmed the ability of HDTMA cations to be incorporated into the CHA zeolite structure during ion exchange due to the formation of van der Waals forces. The modified chabasite is an effective adsorbent for the removal of chromates from aqueous solutions. The adsorption capacity was compared with the modified clinoptilolite, for which it was observed that the adsorption of chromates occurs only on its surface.

Aysan et al. (2016) used chabasite in their studies to remove methylene blue (MB) from aqueous solutions. It was investigated during the experiment how the following different factors affect MB removal: contact time, adsorbent mass, pH and concentration. Natural CHA zeolite was obtained from mineral deposits in the vicinity of Ankara (Turkey). On the basis of the tests and analyses performed, it was found that the chabasite is an effective adsorbent for the purification of aqueous solutions of the methylene blue dye and can become a potential adsorbent for removing various impurities.

The natural CHA zeolite was used as an adsorber in Watson's work (2012). The experiment uses the sodium form of chabasite derived from the Bowie deposit (Arizona, USA). It was noted that admixtures of zeolites such as clinoptilolite, erionite and 32 other impurities were also present. Researchers suggested removing impurities through chemical processing (this was not decided due to increased industrial costs). For this purpose, the crude chabasite was used in the study. A sample with a grain size of 2 mm was prepared. Based on the research, conclusions have been drawn that chabasite can be a potential material for CO_2 removal, in particular from natural gas at lower temperatures.

As can be seen, chabasite has the potential to be used as an absorber of various gases and impurities from aqueous solutions due to its ion exchange capacity and the presence of an extensive structure (a system of channels and pores of various sizes).

5.3. Mordenite [MOR] $(Na_2, Ca,K_2)_4(H_2O)_{28}[Al_8Si_{40}O_{96}]$

The name of mordenite came from the name of the town in which the deposits of this natural material were discovered (Morden, Nova Scotia, Canada) (Ghobarkar et al., 2003; Kulprathipanja, 2010).

The rhombic phase of framework type MOR (mordenite) is described by the space group C mcm (# 63) with lattice constants a = 18.11, b = 20.53 and c = 7.528 Å (Iza, 2020). The crystal unit cell with alkali metals contains 97 atoms (Fig. 4a).

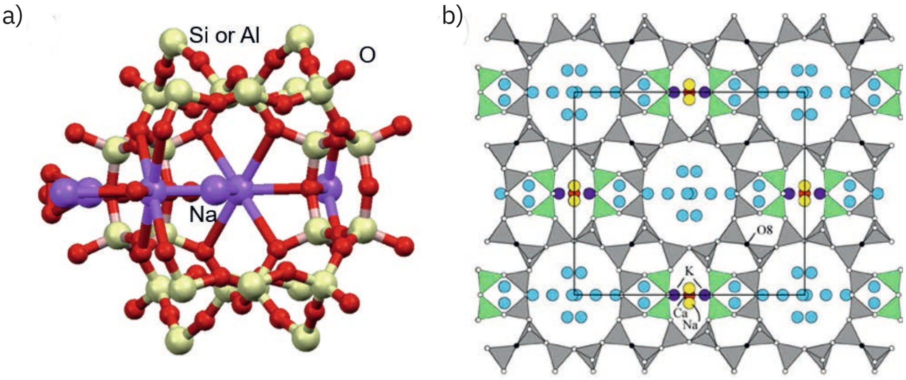

Fig. 4. Crystal structure of mordenite (MOR) – (a) crystal unit cell, (b) crystalline structure (Iza, 2020)

Natural mordenite has a high level of silicone with Si/Al ratio equal 5 while in its synthetic form, the Si/Al ratio is in ranges from 4 to 12. MOR consists of five rings, which are joined at the sides and form a three-dimensional structure. Frames are defined by a one-dimensional channel system created by 12 rings through channels consisting of 8 rings (Fig. 4 b). The diameter of 12-ring channels is 0.7 x 0.65 nm and in the case of 8-ring channels, it is 0.57 x 0.26 nm (Kulprathipanja, 2010; Masters, Maschmeyer, 2011). Cations are present in the zeolite structure in channels made of 8-membered rings; we can identify Ca^{2+} (red), Na^+ (yellow) and K^+ (purple). Water molecules are present in the 12-ring channels (Iza, 2020).

The mordenite mineral is a product of hydrothermal processes. It occurs in volcanic and granite rocks. It is also a product of silicon tuff diagenesis. It often occurs with other zeolites such as analcime, erionite, clinoptilolite or chabasite (Korkuna et al., 2006). The mordenite deposits were found along the shore of the Fundy Bay, east of the town of Morden (in King's County, Nova Scotia, Canada).

Mordenite deposits occur in USA, Greece, Japan, Chile, New Zealand, Austria, Italy, Ukraine and Bulgaria (Iza, 2020; Korkuna et al., 2006; Sanhueza et al., 2002; Hincapie et al., 2004).

Due to the ion exchange ability of zeolites, research was performed on the adsorption of metals, removal of heavy metals from sewage using natural mordenite. Covarrubias and others (2006) have studied the ability of zeolite ion exchange based on a synthesised zeolite based on MOR and kaolin to Cr(III). The synthesised zeolites on the basis of natural and commercially available were also compared and the natural zeolites were characterized by a higher ion exchange capacity. These materials may have potential applications in the removal of Cr(III) from wastewater.

The next article presents research on the removal of ammonium ions from wastewater with the participation of natural zeolites from the region of Dogantepe, Turkey. The mineralogical composition of this zeolite was determined to be 45% clinoptilolite, 35% mordenite, 15% feldspar and 5% quartz. This zeolite exhibits high adsorption capacity. However, this method cannot be applied to low concentrations of ammonium ions in solution (Sarioglu, 2005). Scientists Zhou and Boyd (2014) addressed a similar topic to that above, publishing a paper on ammonia removal with the participation of New Zealand mordenite in an aquaculture. However, the results were not satisfactory because only small amount (1–8%) of ammonia was removed from the water. Nevertheless, the authors suggest the use of mordenite as well as other natural zeolites for water recirculation, the removal of ammonia from small amounts of sewage or the addition of zeolite to animal feeds.

Some mordenite crystalline forms have a fibrous structure and can be life threatening, like erionite and asbestos. This was confirmed by research of the Stephenson group (1999). It is very important to analyse the crystalline composition before using this material. All fibrous zeolite forms should be used only with the use of appropriate protective measures so as not to expose people or animals to threats to health (mainly regarding respiratory tracts) while performing surface work, mining and processing.

5.4. Phillipsite [PHI] $K_2^+Na^+Ca_{0,5}^{2+}(H_2O)_{12}[Al_6Si_{10}O_{32}]$

Phillipsite was named in honour of W. Philips – English mineralogist and founder of the Geological Society in London (Gatta et al., 2009; Sani et al., 2002).

The monoclinic phase of framework type PHI (philipsite) is described by the space group P1 21/m 1’ (# 11) with lattice constants a = 9.865, b = 14.3 and c = 8.668 Å (Iza, 2020; Ghobarkar et al., 2003; Gatta et al., 2009). The crystal unit cell with alkali metals contains 140 atoms (Fig. 5 a).

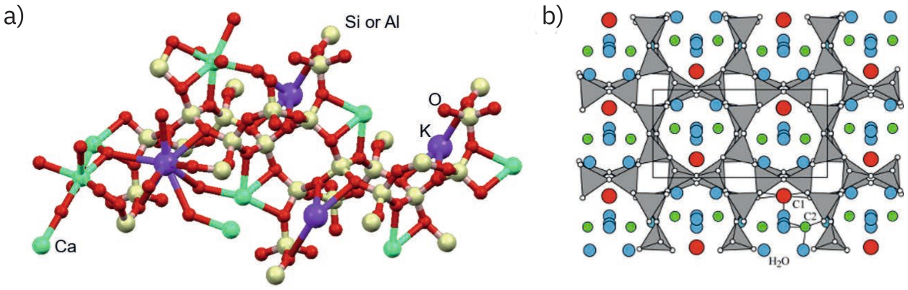

Fig. 5. Phillipsite crystal structure [PHI] – (a) crystal unit cell, (b) crystalline structure (Iza, 2020)

Phillipsite was discovered on the slopes of Mount Etna (Sicily, Italy) and described by the scientist, Lèvy in 1825 (Gatta et al., 2009). The phillipsite structure is made of double four- and eight-membered rings. There are three types of channels that make up 8-member chains (Fig. 5b). Channel parallel to the axis a has dimension 3.6 Å, parallel to the axis b has a diameter of 4.3 x 3.0 Å and parallel to the axis c has diameter 3.3 x 3.2 Å (Iza, 2020; Gatta, 2019; Sani, 2002). Na^+, K^+, Ca^{2+} cations and water molecules are present in the channels (Iza, 2020; Gualtieri et al.,2002).

Phillipsite occurs in spherical, acuminate, radial and fibrillary clusters. It is present in basalt rocks in deep sea sediments and salt lakes. It co-occurs with chalazite natrolit and analcime (Ghobarkar et al., 2003; Iza, 2020; García Hernández et al., 1994; Park, Choi, 1995; Fukui et al., 2006; Rujiwatra, 2004). Phillipsite occurs in the following countries: USA, Italy, Ireland, Germany, Australia, Japan, Czech Republic, Russia (Iza, 2020).

Possible phillipsite applications are presented below; these are due to the ion exchange capacity and the adsorption of various metals and compounds. Bampaiti et al. (2015) have performed the process of removing uranium from aqueous solutions using phillipsite modified by HDTMA (hexadecyltrimethylammonium bromide). Zeolite used for the process came from the region of Naples, Italy. The particle size of the mineral was 1 mm and 5 g of zeolite was introduced into 25 ml of 60 mmol/l HDTMA solutions.

Serri's publication (2016) focused on the possible use of phillipsite (PHI), clinoptilolite (CLI) and chabazyt (CHA) as surfactants through modification with cetylpyridine chloride (CP) to control the release of diclofenac sodium (DS). Zeolites were treated with 1M of NaCl to remove sodium cations. The whole mixture was stirred until the amount of Na^+ decreased to a level <1 ppm. The samples were then washed and air dried. Surface modification of zeolites using CP was performed during mixing in a high-speed disperser (10,000 rpm) for a strictly defined period of time and in a suitably selected amount of zeolite in a solution containing a surfactant (mass ratio 1/40). The tests were based on the assessment of the drug's kinetics of drug release in vitro in simulated intestinal fluid. The results showed that the best zeolite modified with the surfactant was clinoptilolite followed by phillipsite.

García et al. (1993) developed a phenol adsorption experiment using phillipsite. The material came from deposits from the south-east of Tenerife (Canary Islands). It was shown that a hydrogen bond formed between the surface of the zeolite (NH_4^+ group) and the phenol molecule (-OH group). Phenol adsorption is only effective when using PHI zeolite in ammonium form. However, due to limited diffusion (pore size), adsorption is only possible on the surface of the material.

5.5. Clinoptilolite [CLI] $(Na,K,Ca_{0,5})_7[Al_7Si_{29}O_{72}]\cdot 22H_2O$

The name of this zeolite comes from the Greek words klinos meaning diagonal, ptylon meaning feather and lithos which means stone (Ghobarkar et al., 2003).

The monoclinic phase of framework type CLI (clinoptilolite) is described by the space group C1 2/m 1 (#12) with lattice constants of a = 17.6620, b = 17.9110 and c = 7.4070 Å (Iza, 2020). The crystal unit cell with alkali metals contains 197 atoms (Fig. 6). The CLI framework has a three-dimensional pore structure and consists of straight internal channels along the x- and z-axes (Fig. 6 a).

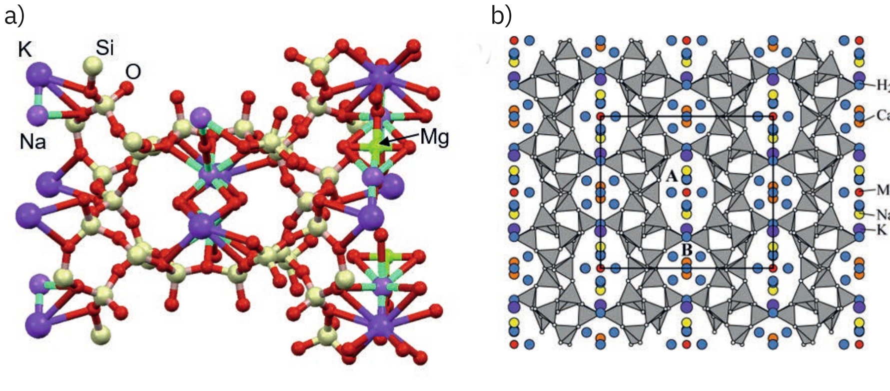

Fig. 6. Clinoptilolite – (a) crystal unit cell, (b) crystalline structure (Iza, 2020)

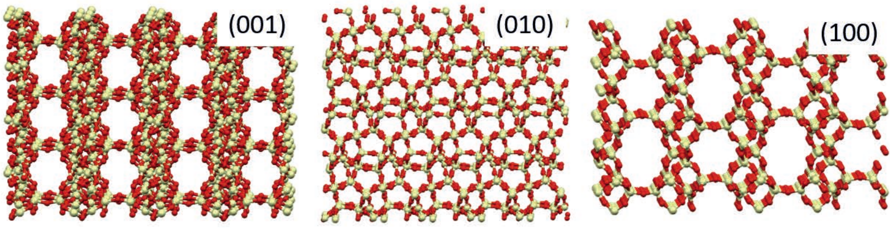

Fig. 7. Clinoptilolite structure along different surfaces

Clinoptilolite was identified for the first time by Pirsson in 1890 and misidentified as mordenite. Analysis of the deposit (location: a few kilometres north-east of Hoodoo Peak just outside the eastern border of Yellowstone National Park, Park County, Wyoming, USA, where the mineral occurs in basalt decay basins) was based only on chemical analysis. It was not until 1923 and 1932 that optical tests carried out by Schaller resulted in information that the material was a monoclinic ptilolite, and the mordenite deposits were discovered in the Table Mountains in the USA. Therefore, by deduction, the discovered mineral was defined as clinoptilolite (Schaller) although the morphology resembled heulandite. In 1934, scientists Hey and Bannister performed an XRD analysis in which the results suggested that the mineral present in Hoodoo Peak and heulandite was an isostructural material and recommended that the term clinoptilolite should not be used. Research on the determination and the division of minerals close to each other led to the definition of clinoptilolite proposed in 1960 by Manson and Sanda as a material that is present in alkaline deposits with a high Si/Al module. In turn, Mumpton stated that samples that are thermally stable above 350°C (heated for a long time) should be called clinoptilolite. Nevertheless, those responsible for the nomenclature decided to keep the use of two names – heulandite and clinoptilolite based on the silicon module (Si/Al = 4.0) (Iza, 2020; Armbruster, 2001). Clinoptilolite is a material with the Si/Al> 4 module and the heulandite form possesses Si/Al <4 (Armbruster, 2001).

Clinoptilolite belongs to the group of heulandites. The clinoptilolite frames contain three intersecting channels located in the plane [010] (Fig. 6b). The two channels are parallel to the c-axis (Fig. 7).

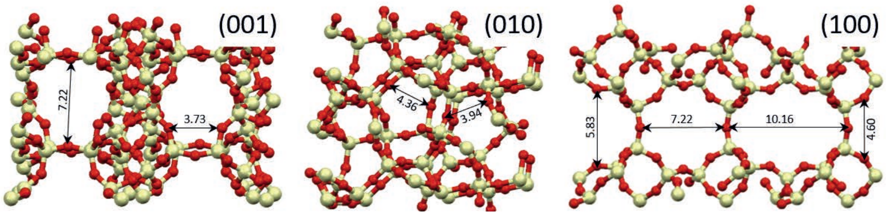

Fig. 8. Clinoptilolite – structure of pores

The A channels were created by tightly compressed ten-membered rings (3.0 x 7.6 Å). The B channels were limited by eight-membered rings (3.3 x 4.6 Å). In turn, C channels are either parallel to a-axis or are present in the plane [102]. They can also be formed by eight-membered rings (2.6 x 4.7 Å) (Fig. 8) (Iza, 2020; Hincapie et al., 2004; Covarrubias et al., 2006; Gatta, Lotti, 2019).

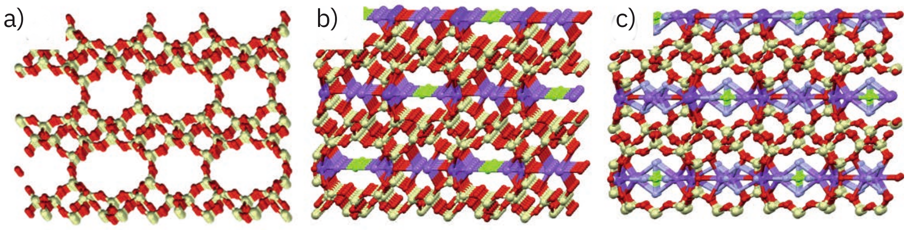

Fig. 9. Clinoptilolite along (100) surface – locations of alkali metals and water

There are two main channels in the zeolite structure in which cations such as Na^+, Ca^{2+}, K^+ and Mg^{2+} are present (Fig. 9). Sodium and potassium cations are usually located at the intersection of channels A and C. By contrast, calcium cations are present in channel B and may also be present in channel A. Na^+, Ca^{2+} and K^+ ions are present in the plane [010] and are coordinated with four frame oxygen and four molecules of water. Mg^{2+} cations are usually found in channel A and are coordinated with six disordered water molecules (Favvas et al., 2016; Garcia-Basabe et al., 2010; Ragnarsdóttir, 1993; Ackley, Yang, 1991).

Clinoptilolite can be found in sedimentary rocks (a component of bentonites and some claystones). It also occurs in plutonic masses (granite, pegmatite), in volcanic rocks (basalt, andesite, porphyry) and in metamorphic rocks. Clinoptilolite is often associated with other zeolites such as mordenite, erionite, analcime, chabazite or phillipsite. Clinoptilolite also co-occurs with montmorillonite (Iza, 2020). It occurs in the following countries: USA, Greece, Mexico, Turkey, Serbia, Japan, Hungary, Bulgaria, India, New Zealand and Slovakia (Iza, 2020; Inglezakis et al., 2001; Chmielewská-Horváthová, 1992).

Due to its structure, adsorption capacity and ion exchange properties, clinoptilolite is used in many industries. Some applications of this zeolite in various fields are presented below (Grce, Pavelić, 2005; Kulprathipanja, 2010; Masters, Maschmeyer, 2011).

The clinoptilolite is used in various fields. The team of Malekian (2011) determined the effect of modified clinoptilolite surfactant on nitrate leaching and plant growth in their research. For this purpose, zeolite which came from the deposits in Semnan (Iraq) was used.

An article by the Reháková team (2004) presents possibilities of using zeolite (from the Hrabovec deposit in eastern Slovakia) in agriculture. The research was conducted with regard to the use of clinoptilolite as an additive to fodder and soils and the removal of stench and gases (including ammonia). The experiment shows that due to its physico-chemical and non-toxic properties, this material can be used in agriculture and agrochemistry. For example, fertiliser with the addition of zeolite has many advantages. The experiment conducted by Eprikashvili et al. (2016) also confirms the positive use of zeolite as a fertiliser. In this case, barley growth was checked. The presence of the mineral improves the growth of this grain.

Figueroa-Torres et al. (2016) conducted an experiment to check the sorption capacity of clinoptilolite. The obtained results indicate the ability of zeolite to remove iron and copper from the solution. This material may prove to be a promising and cheap biosorbent for the removal of various metals during wastewater treatment.

There were also attempts to use clinoptiololite as a catalyst. In their work, Mahdi et al. (2016) focused on the conversion of glycerol from biodiesel production. The process was conducted in a 500 ml batch reactor for 30-60 minutes. During the experiment, it was checked how the change in the ratio of reagents, the ratio of glycerol to the catalyst, the diameter of zeolite particles and temperature affect the conversion of glycerol. The best results were obtained with the use of clinoptilolite with a particle diameter of 0.46 mm and performing the process at 100°C for 30 minutes. In the publication of the Pavlovic team (2019), the reaction of the esterification of levulinic acid was performed in which the catalyst was a modified clinoptilolite (Zeolite tuffs from the deposits of Slanci, Serbia). SnO_2 and SO_4/SnO_2 were introduced into the zeolite structure. The conversion of levulinic acid to ethyl levulinate and octyl levulinate were conducted in a batch reactor with a magnetic stirrer. The catalysts before the process were activated in an oven at 200°C for 1 hour. The reaction was performed for 5 hours. Catalysts based on natural zeolite and modified by SnO_2 and SO_4/SnO_2 showed high catalytic activity in the levulinic acid esterification process.

6. Summary

Natural zeolites have a very large potential for application due to their porous structure and their natural occurrence in the environment. Most natural zeolites have smaller pores than synthetic materials. However, the natural zeolites presented above (clinoptilolite, mordenite, chabazite, analcime, phillipsite) have, after non-exclusive modifications, pores and channels that could guarantee similar or even better catalytic and adsoptive properties than in the case of synthetic zeolites. Therefore, future research on the potential applications of natural zeolites is essential. As shown above, certain groups all over the world are trying such modifications of natural zeolites at the laboratory scale, which will increase in the near future.

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Charakterystyka struktury zeolitów naturalnych oraz ich zastosowań w katalizie i procesach adsorpcji

Streszczenie

Autorzy przedstawili krótki przegląd wybranych materiałów zeolitowych pochodzenia naturalnego. W artykule omówiono strukturę, klasyfikację i możliwości modyfikacji naturalnych zeolitów, wraz z przykładami ich potencjalnych zastosowań jako adsorbentów lub katalizatorów.

Słowa kluczowe: naturalne zeolity, adsorpcja, kataliza, klinoptylolit, mordenit, chabazyt, analcime, filipsit