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Natural and synthetic zeolites. Synthesis of zeolite X.

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Abstract

Structures, functions and applications of both natural and synthetic zeolites were analyzed. The project focused on zeolite X, which is a well-known natural zeolite, that can be easily synthesized in the laboratory.

Two experiments were performed in order to synthesize zeolite X, each of them had a different procedure and recipe. Only one out of two was successful as in the first one, the synthetized compound resulted in zeolite A, which we believe was due to the presence of a second unidentified phase. In the second synthesis, the one that resulted in the zeolite X production, the crystallization was able to occur at a higher temperature than the one written in the manual. The obtained products were analyzed by X-ray powder diffraction (XRD) and the results were examined with a specific program named Powdercell, as well as Excel.

The results were overall satisfying, however it would be interesting to analyze in the future the second phase which appeared in the first synthesis, in order to understand better the reason of failure.

1. Introduction

For decades, many scientists have been focusing their attention on a group of known crystalline aluminum-silicate called zeolites. Proof of this is the great number of articles, patents and books on this material. Many scientist focus their zeolite research on various aspects, such as their synthesis, structure and applications.

Zeolites are microporous crystalline solids with well-defined structures. They contain silicon, aluminum and oxygen and counter ions to maintain charge balance. Zeolites may be used for many and diverse industrial applications, from simple drying processes, water treatments, detergents and adsorbents to catalytic processes [9.]

Zeolites were considered an unknown group of minerals with one of a kind property for more than 200 years. Today, it is known about 200 different types of zeolites, of which around 40 are natural [10.] The rest has been designed and obtained in the laboratory (synthetic zeolites).
At the end of the forties of the last century, commercial demand for these materials was already very high.

Due to the very high demand, there was a shortage of raw materials to supply the industry, given the difficulty of obtaining natural zeolites to the required specifications. The main causes that hindered the use of zeolites of natural origin for such purposes were:

- Natural zeolites may contain impurities in the form of unwanted phases.
- The chemical composition varies from one to another.
- The properties of a natural zeolite do not usually present optimal results for being used in catalytic applications.

All this made the scientific interest focused on the development of synthetic zeolites.
The synthesis of zeolite involves the crystallization of a gel under hydrothermal conditions. This gel consists, mainly, of precursors of aluminum-silicate and an agent. This last can be inorganic in nature (Na^+ ions and K^+), however, organic species are more commonly used [11].
Zeolites with acidic nature have been studied for their industrial importance and environmental advantages.

The basic construction unit of the zeolite is the covalent bonded tetrahedron TO_4 (where T = Si, Al, B, Ga, Ge, P ...) whose three-dimensional union through the oxygen atoms gives rise to the typical polyhedral structure of the zeolites This three-dimensional structure has small pores and channels in which interchangeable ions are housed and where the ion exchange reaction takes place. The most common TO 4 units are SiO_4^{-4} and AlO_4^{-5} [12].

The tetrahedral, the pores where the cations are placed (which electrically compensate the structure), water and other molecules form the structure and justify the ability of zeolites to release water continuously as they are heated at relatively low temperatures, leaving the mineral structure intact. On the other hand, the dehydrated zeolite can be rehydrated easily by simply submerging it in water.

By increasing the negative charge on the framework substituting aluminum atoms, the hydrophilic character of the zeolite increases as well. Metal ions (Na, K, Ca or Mg) are normally used in order to equilibrate the overall charge [13].

Due to this fact, zeolite with its cation exchange property can be an excellent material for water purification. Zeolites can absorb the pollutants of the water purifying and filtering it, remove ammonia ions in solution by ion exchange or remove any undesired material, such as heavy metals, due to its extremely porous structure [14].

In correlation to the importance of understanding the zeolite synthesis, specifically zeolite X, and the urge of properly implementation of zeolites for future developing of alternative and more effective method for water purification, we have dedicated this semester project to the investigation of natural zeolites, leading to our research question:

Natural and synthetic zeolites. Synthesis of zeolite X

Throughout this paper, we will give an insight into two different synthesis of faujasite-type zeolites and summarize the most important applications in the industrial and environmental area.

2. Zeolites

2.1 Natural zeolites

Zeolites are aluminosilicate porous materials built in a very complex but well defined structure, consisting of tetrahedra (T) and four oxygens atoms, forming units of TO_4 where T can be silicon (Si), aluminum (Al) or occasionally Germanium (Ge) or other elements [3, 5]. They were first discovered in 1765 by Axel Fredrik Cronstedt, who found the mineral stilbite, after he heated it up with a blowpipe flame and he invented the term “zeolite” which in greek means “boiling stone”. For more than a thousand years, all over the world, volcanic rocks containing natural zeolites have been mined and used as building stones and cement. In 1862 was taken the first attempt to synthesize the first zeolite by Claire Deville [6, 7]. In the 1950s was developed the most used nowadays method for zeolite synthesis which is: reactive gel crystallization and this invention was crucial for an industrial point of view. Moreover, this innovation led to the discovery of two very important zeolites: A and X [8].

2.1.1 Structure

Zeolites have two *primary building units*(PBUs): orthosilicate and aluminate tetrahedra (one atom in the center and four atoms at the corners), which connect through oxygen ions and thus form *secondary building units*(SBUs) (Figure 1). The secondary structures are connected to form a 3D crystalline structure of the zeolite. When silicon is substituted by aluminum, the negative charge of the structure is increased and this is recompensed by alkaline metal cations [1].

Figure 1. Examples of few of the most diffused secondary building units [5].

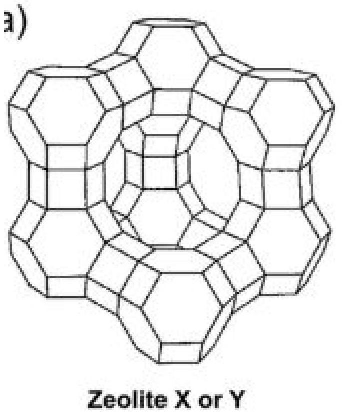


Figure 2. Structure of zeolite type X or Y [15].

The 3D crystalline structure of zeolites, which looks like a honeycomb, is very rigid and consists of a network of interconnected tunnels and cages (Figure 2). Water is able to move openly through the pores without changing the rigid structure of the zeolite. The fact that the sizes of the channels and pores are almost the same allows the crystals to act as a filter. Therefore, all heavy metals (mercury, cadmium, arsenic ...), toxins and harmful chemicals that are positively charged, are attracted and trapped by the zeolite to be discharged afterward [36].

TO_4 units are interconnected among them. In addition, when there is Si and Al, having aluminum (Al^{+3}) less charge than silicon (Si^{4+}), the charge is compensated with inclusion cations such as K^+, Na^+, Ca^{2+}, and less frequently Li^+, Mg^{2+}, Sr^{2+} and Ba^{2+}. These, although they are part of the zeolite, are external to the network, that is, they compensate the charge, but they do not build the tetrahedral units.

The structural formula of a zeolite is based on the crystallographic unit cell, which can be represented by:

$(Mn^+)\ 2/nO \bullet Al_2O_3 \bullet xSiO_2 \bullet pH_2O$

where n is the valence of the cation, x and y are integers.

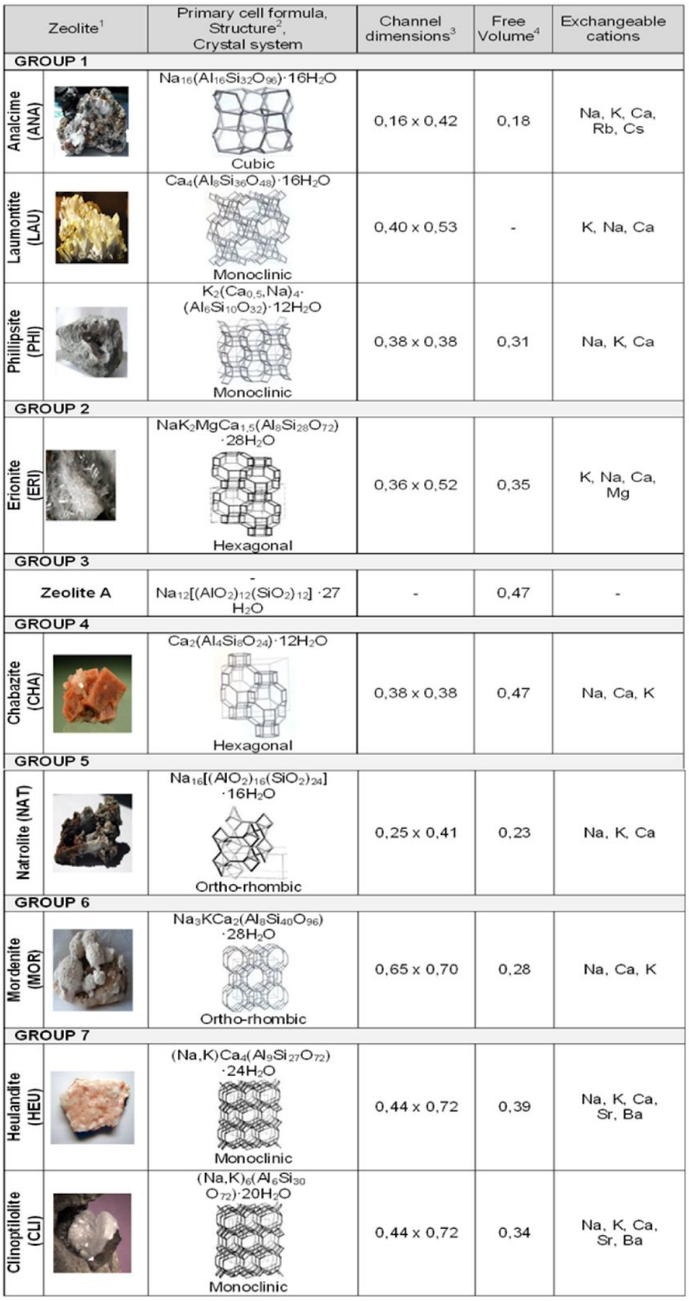
M represents an exchangeable cation of valence n. M is usually an element of group I or II, although other metal and organic cations can balance the negative charge created by the presence of Al in the structure.

x is the number of Al and Si. (Silica to alumina ratio)

p are molecules of H_2O.

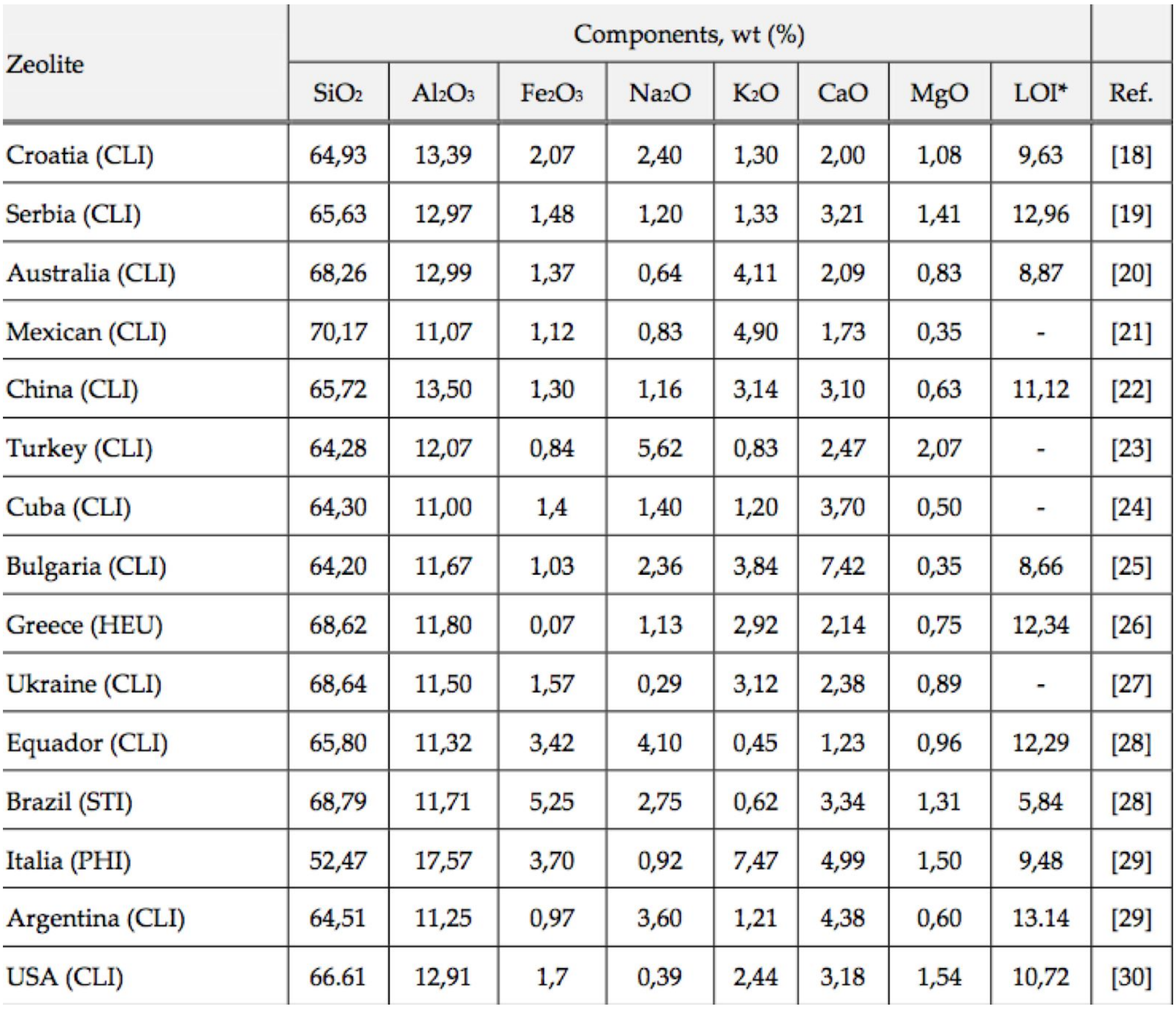
There are about 40 known natural zeolites, of which only seven have industrial applications. These seven groups of natural zeolites (Figure 3) and this division is made considering the framework of the crystal structure, its physically properties, the way in which the SBUs binds in the 3D structure, the free pore volume and kinds of exchangeable cations in the structure[4].

Depending on where the zeolites are mined, there are differences in their chemical composition (Figure 4). This is due to the fact that since they occur in nature, the composition of the material is influenced by natural phenomena [4].



Zeolite[1]	Primary cell formula, Structure[2], Crystal system	Channel dimensions[3]	Free Volume[4]	Exchangeable cations
GROUP 1				
Analcime (ANA)	$Na_{16}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$ Cubic	0,16 x 0,42	0,18	Na, K, Ca, Rb, Cs
Laumontite (LAU)	$Ca_4(Al_8Si_{36}O_{48})\cdot 16H_2O$ Monoclinic	0,40 x 0,53	-	K, Na, Ca
Phillipsite (PHI)	$K_2(Ca_{0,5},Na)_4\cdot(Al_6Si_{10}O_{32})\cdot 12H_2O$ Monoclinic	0,38 x 0,38	0,31	Na, K, Ca
GROUP 2				
Erionite (ERI)	$NaK_2MgCa_{1,5}(Al_8Si_{28}O_{72})\cdot 28H_2O$ Hexagonal	0,36 x 0,52	0,35	K, Na, Ca, Mg
GROUP 3				
Zeolite A	- $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$	-	0,47	-
GROUP 4				
Chabazite (CHA)	$Ca_2(Al_4Si_8O_{24})\cdot 12H_2O$ Hexagonal	0,38 x 0,38	0,47	Na, Ca, K
GROUP 5				
Natrolite (NAT)	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}]\cdot 16H_2O$ Ortho-rhombic	0,25 x 0,41	0,23	Na, K, Ca
GROUP 6				
Mordenite (MOR)	$Na_3KCa_2(Al_8Si_{40}O_{96})\cdot 28H_2O$ Ortho-rhombic	0,65 x 0,70	0,28	Na, Ca, K
GROUP 7				
Heulandite (HEU)	$(Na,K)Ca_4(Al_9Si_{27}O_{72})\cdot 24H_2O$ Monoclinic	0,44 x 0,72	0,39	Na, K, Ca, Sr, Ba
Clinoptilolite (CLI)	$(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$ Monoclinic	0,44 x 0,72	0,34	Na, K, Ca, Sr, Ba

Figure 3. Division of natural zeolites in seven, different groups with examples of zeolites [3].



Zeolite	Components, wt (%)								
	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI*	Ref.
Croatia (CLI)	64,93	13,39	2,07	2,40	1,30	2,00	1,08	9,63	[18]
Serbia (CLI)	65,63	12,97	1,48	1,20	1,33	3,21	1,41	12,96	[19]
Australia (CLI)	68,26	12,99	1,37	0,64	4,11	2,09	0,83	8,87	[20]
Mexican (CLI)	70,17	11,07	1,12	0,83	4,90	1,73	0,35	-	[21]
China (CLI)	65,72	13,50	1,30	1,16	3,14	3,10	0,63	11,12	[22]
Turkey (CLI)	64,28	12,07	0,84	5,62	0,83	2,47	2,07	-	[23]
Cuba (CLI)	64,30	11,00	1,4	1,40	1,20	3,70	0,50	-	[24]
Bulgaria (CLI)	64,20	11,67	1,03	2,36	3,84	7,42	0,35	8,66	[25]
Greece (HEU)	68,62	11,80	0,07	1,13	2,92	2,14	0,75	12,34	[26]
Ukraine (CLI)	68,64	11,50	1,57	0,29	3,12	2,38	0,89	-	[27]
Equador (CLI)	65,80	11,32	3,42	4,10	0,45	1,23	0,96	12,29	[28]
Brazil (STI)	68,79	11,71	5,25	2,75	0,62	3,34	1,31	5,84	[28]
Italia (PHI)	52,47	17,57	3,70	0,92	7,47	4,99	1,50	9,48	[29]
Argentina (CLI)	64,51	11,25	0,97	3,60	1,21	4,38	0,60	13.14	[29]
USA (CLI)	66.61	12,91	1,7	0,39	2,44	3,18	1,54	10,72	[30]

Figure 4. Composition of naturally occurring zeolites found in deposits in different parts of the world [3.]

2.2 Synthetic zeolites and similar materials

After the discovery of zeolites by Baron Axel Fredrick Cronstedt, many researchers have attempted to obtain in the laboratory what nature had created by itself. The facts that allowed progress in this aspect were on the one hand the development of new characterization techniques, such as X-ray diffraction that allowed a better knowledge of the crystalline structure of zeolites [17]. On the other hand, the discovery of methods for obtaining these materials on an industrial scale carried out by Union Carbide (USA) in the 40s and 50s of the last century.

There are 200 different synthetic zeolites. Numerous researchers, attracted by the potential industrial applications of zeolites, began to work on their synthesis, reaching a large number of them; some analogous to natural ones. For example, in 1948, Richard Barrer first produced a synthetic zeolite that did not have a natural counterpart, and totally new ones, such as zeolites A and X were produced by Breck et al. in 1956 and Milton in 1959 [16].

Nowadays, there are many natural and synthetic zeolites synthetized in a different way. Many natural zeolites are still being discovered by scientists. Furthermore, new synthetic zeolites are being synthesized and applied in differents industries [38].

The synthetic zeolites available on the market have a different size of pores, from around 3Å up to around 8Å.

2.2.1 Production of synthetic zeolites

Most important differences between natural and synthetic zeolites:

- Natural zeolites are extracted from a natural ore body, meanwhile the synthetic ones are produced from chemicals in processes that consume energy.
- Clino zeolites, which are a type of natural ones have a SiO_2: Al_2O_3 ratio of 5:1, synthetic ones have a ratio of 1:1, following Löwenstiens rule.
- In the structure of natural zeolites there is present more silica than in the synthetic, which contributes to the fact that they are more acid resistant. This is the cause for which synthetic ones break down in lightly acid environment, where the clino ones do not [36].
- Synthetic zeolites have a higher ion exchange capacity and a higher density than natural zeolites

2.2.2 Applications

Zeolites are able to carry out processes in a natural way and can take the place of many chemicals (dangerous for the environment).
Depending on the specific properties of a zeolite and its type, it is appropriate only for use for particular reactions [39].

a) Ion exchange:

Given natural zeolites structure we can deduct that the negative charge on the surface is due to the fact that silicon and aluminium, which are present in the basic structure, have four and three electrons respectively, which are available to form bonds with other atoms [2]. In the small pores present in the structure of zeolites, there are some exchangeable ions and it is also the place where the exchange of ions takes place [2].

b) Catalytic cracking:

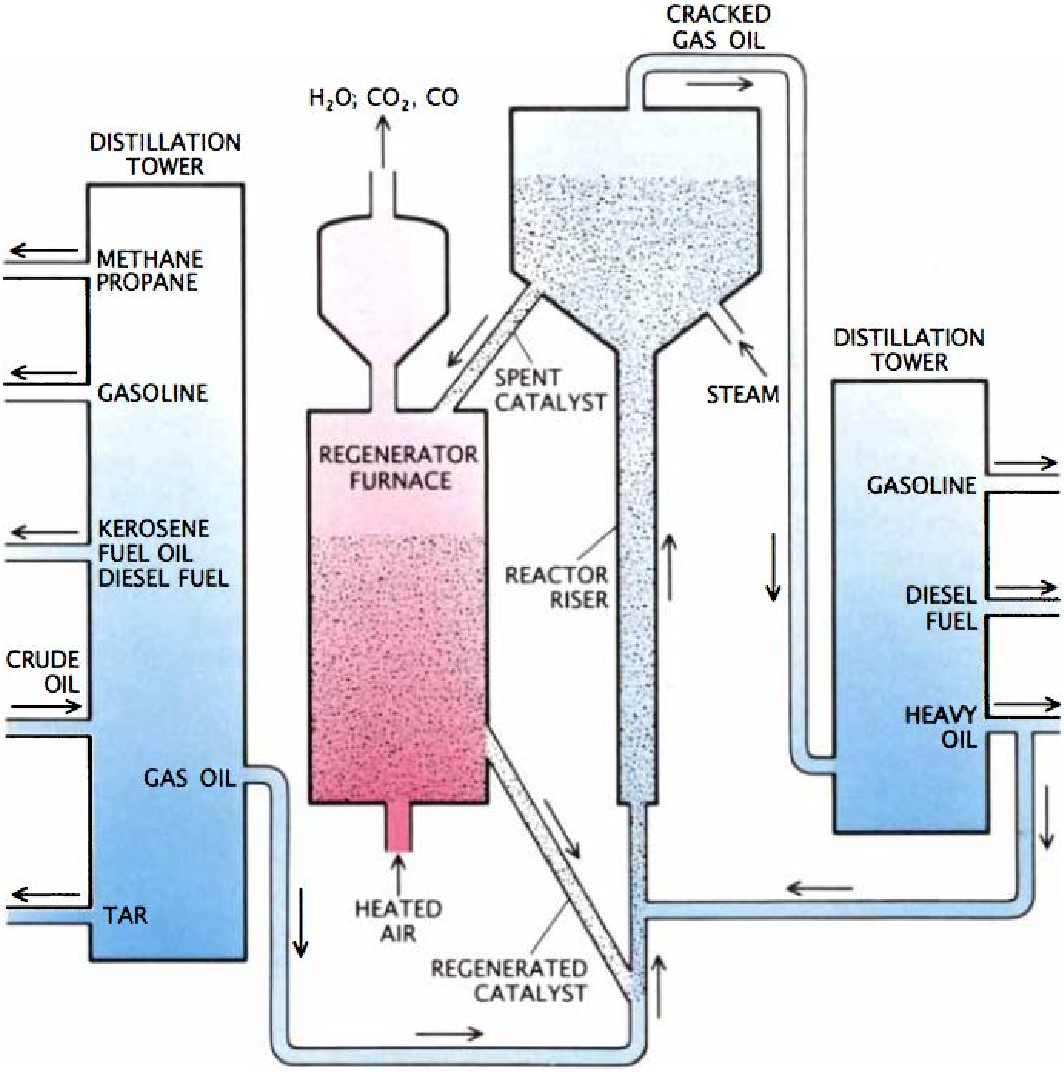


Figure 5. Catalytic cracking process [9]

It is possible to use zeolites in the production of gasoline, diesel fuel heavy oils. This process is initiated by the separation of unrefined petroleum into different products, from ones with small (methane) to ones with big (tar) molecules.

The example of such products can be found at the left of the scheme. The gas oil fragment vaporizes when getting in contact with hot particles which contain zeolite Y. The vapor is moving up the reactor riser, in which the cracking of hydrocarbon bounds takes place, after that it goes to the distillation tower where it is separated from the rest of the particles depending on the size, which are then going for the production of different compounds (ex. gasoline or diesel fuel) [9].

c) Agriculture:

The clino zeolite, which occurs in nature is used widely in agriculture for improving the soil and as a feed additive [37].
In many countries of the world, around 5% of specific zeolites are added to livestock ratios to reduce ammonia and the emission of unpleasant smell and improve feed utilization. NASA used zeolites loaded with nutrients as slow release fertilizers [38].

d) Filtration of gases:

Zeolites are a good choice in this process since they are able to remove humidity, unpleasant smells, ammonia and more toxic molecules. Zeolites eliminate humidity and other particles from the air in order to dry, separate or purify a gas [39].

e) Medical applications:

There are some countries that allow the consumption by humans of natural zeolites and they are able to eliminate diarrhea, remove toxins from the organism and even prevent cancer. When used on the skin, they are excellent moisturizers and removers of toxins [39].

f) Water purification:

Water filtration is one of the processes where the use of zeolites intervenes. The application of this substrate helps to offer a high performance compared to sand and carbon filters. The zeolite functions as ion exchanger. The zeolites are negatively charged from natural form, so they can adsorb cations, such as heavy metals and ammonia [3].

In ion exchange, they absorb the pollutants of the water purifying and filtering it. Depending on the type of zeolite used, different minerals can be extracted from water, including calcium. The pores of the zeolite with greater volume are those that benefit the retention of particles, delimiting the particle’s passage.

Zeolite works differently if it is applied in freshwater or seawater. Calcium exchange zeolites work when there is a low presence of calcium or magnesium ions. In salty waters, the zeolite

acts as a biological substrate, that is, it transforms the ammonia into nitrite and later into nitrate.
In the internal part of the zeolite the presence of oxygen is minimal due to the excess of the external consumption, which causes a settlement of the bacteria and an elimination of the nitrate converting it into nitrogen evaporated by carbon [14.]

In acid treatment, they are able to remove ammonia and humic acids depending on such factors like pH, initial concentration of the ammonia and humic acid, temperature, exposure time, etc. The results obtained showed that the most suitable material for this simultaneous removal was zeolite with a pH close to the natural waters [17].

Natural zeolite is considered an ideal means of swimming pools filtration due to its extremely porous structure. Given the ion exchange capacity, zeolite has an added advantage which is the removal of contaminants that diatomaceous earth filters cannot eliminate, such as the ammonia in solution, previously mentioned.
Zeolites need less wash cycles than sand filters and cycles are shorter, which can reduce by 30% the amount of water necessary for the maintenance of the pool.
Zeolites have a great durability and their useful life is much longer than that of sand. In short, natural zeolites offer better water quality, easier maintenance and better reduction of the amount of water needed [39].

Furthermore, new scientists are developing new researches about removal of Fe and Mn from underground water with the help of natural and synthetic zeolites and development of As removal from ground and drinking water with zeolites.

The synthetic zeolites show a high adsorption capacity, also, for organic material and anions[37].

g) Construction:

For instance, in China they replace some of portland cement with natural zeolites.
This is because as, previously mentioned, zeolites tend to accumulate water inside their structure and when the concrete is settling down they release it equally. Also the concrete that is made by mixing cement and zeolite it is very resistant and also much lighter than the traditional one [39].

h) Household:

Zeolites can be used as additives to laundry detergents

3. Zeolite X: characteristics and structure

Sodalite or cube-octahedron unit, specifically b-cavity, is a basic structure found in the most important zeolites (type A, X and Y), which is a shortened octahedron formed by Si and Al on the vertices and the oxygen atom between them [20]. The way in which the sodalites come together, gives the type of zeolite that can be obtained. If the sodalite is connected through hexagonal prisms tetrahedrally, the result is a faujasite type zeolite, to which zeolite X belongs. They are differentiated by the silica content in them.

3.1 Faujasite structure

Within the faujasite type zeolites there are two different structures, the FAU (cubic) and the EMT (hexagonal). Both structures (FAU and EMT) can be formed from sodalite. These sodalite units form the so-called b-cavities, accessible through openings of 2-2.5Å in diameter, formed by the oxygen atoms of the non-shared hexagonal faces. The set of sodalite units gives rise to the faujasite unit, for which there are three non-equivalent positions, denominated A, B and C. The FAU structure is formed by the union ABCABC, while in the EMT the union sequence it is ABABAB (Figure 6) [19]. The union of these positions gives rise to the three-dimensional structure of this type of zeolites.

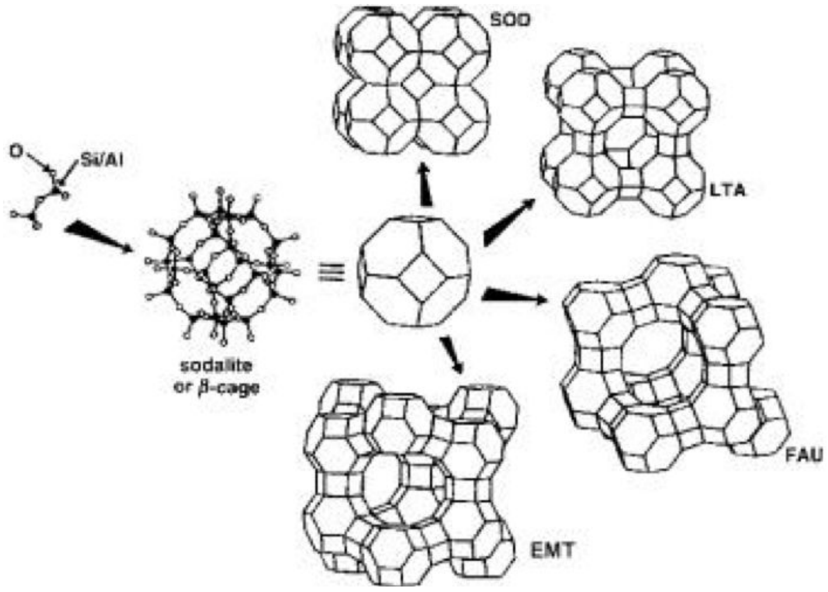


Figure 6. Structure of sodalite, EMT, LTA and EMT zeolites [40].

Depending on the opening of the pore, we find a limitation of space and properties characteristic of a molecular sieve, since molecules of equal or smaller size to these dimensions will enter only in them (Figure 6) [40]. The pore size in turn is classified by:

- Small pore: 8MR (member ring) - 3.8x3.8Å CHA type
- Average pore: 10MR (member ring) - 5.5x5.1Å type MFI
- Large pore: 12MR (member ring) - 7.4x7.4Å FAU type
- Ultra-large pore:> 12MR (member ring) - 7.5x7.2Å CFI type

In this way, a selective absorption of molecules can be carried out, discriminating according to size

According to FAU structures, the unit cell has a dimension close to 25Å and consists of 192 SiO_4 and AlO_4 tetrahedra linked through oxygen atoms. The structure is very stable with the highest space volume of the known zeolites. The unit cell contains eight large cavities, called faujasite cavities or supercavities (Figure 7). These large cavities are formed by a 12-member ring. The pore system or cavities are three-dimensional and different chemical compounds can be adsorbed on its surface, so they have a great application in adsorption, ion exchange, membrane separation and catalysis [20].

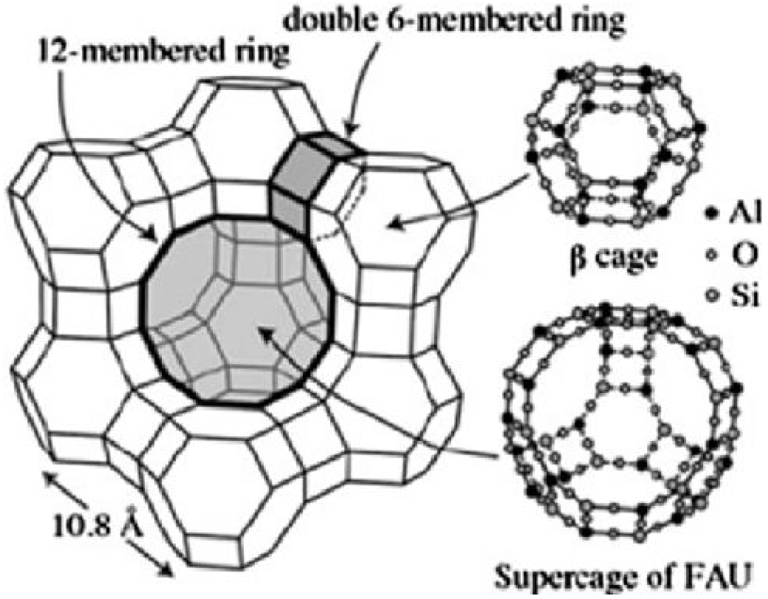


Figure 7. Structure of FAU zeolites [22].

3.2 Location of the Cations

The knowledge of the cations location and the interactions between these and the zeolite and/or the adsorbed agents is fundamental to get to understand the structures and the catalytic properties of the zeolites.

For zeolites with FAU structure there are, in principle, five available positions where the cations equilibrate the negative charge (Figure 8). Position I is located in the center of the hexagonal prisms that join two sodalite units. The cations in positions II and III are located in the faujasite cavity (supercavity) on the non-shared hexagonal faces and on the square faces, respectively, and those interact directly with the adsorbates in the faujasite cavity. The positions I 'and II' are located inside the sodalite unit and correspond to a displacement of positions I and II along the axis perpendicular to the face. It has also been reported a position III 'that would be located in the faujasite cavity and that is occupied by larger cations [21, 22].
The cations in position I are coordinated octahedrally with 6 oxygen atoms in the chain. In positions I ', II' and II the coordination is with 3 oxygen atoms of the chain, but due to the location of these positions (inside the sodalite unit and in the faujasite cavity) they are somewhat different in terms of symmetry and gradients of electric field [23]. Centers III are the most asymmetric and the most catalytically important. However, they present difficulties to be observed due to the smaller population and greater mobility [21, 22].

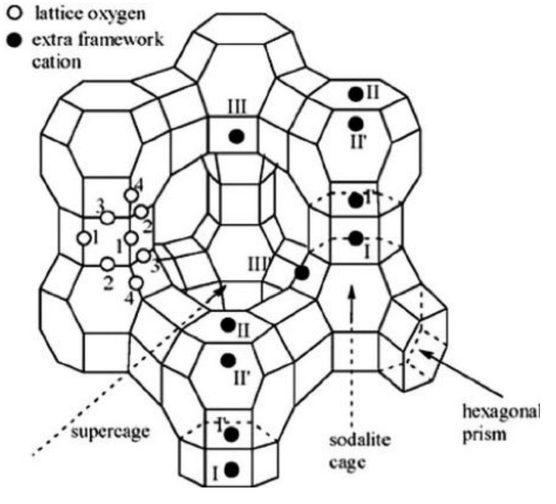


Figure 8. Faujasite zeolite structure and position of the cations [22].

The EMT cations structure are placed in positions similar to those of the FAU structure, but due to the different union of the faujasite units, they have two types of hexagonal prisms and two faujasite cavities, being two positions I different, as well as two positions I 'and II in the sodalite unit and in the faujasite cavities [24].

3.3 Synthesis of zeolite X

The synthesis of zeolite X is a crystallization process that develops from an amorphous gel, which is depolymerized and solubilized by releasing silicate and aluminate components that must be reorganized to form the crystalline structure of the zeolite.

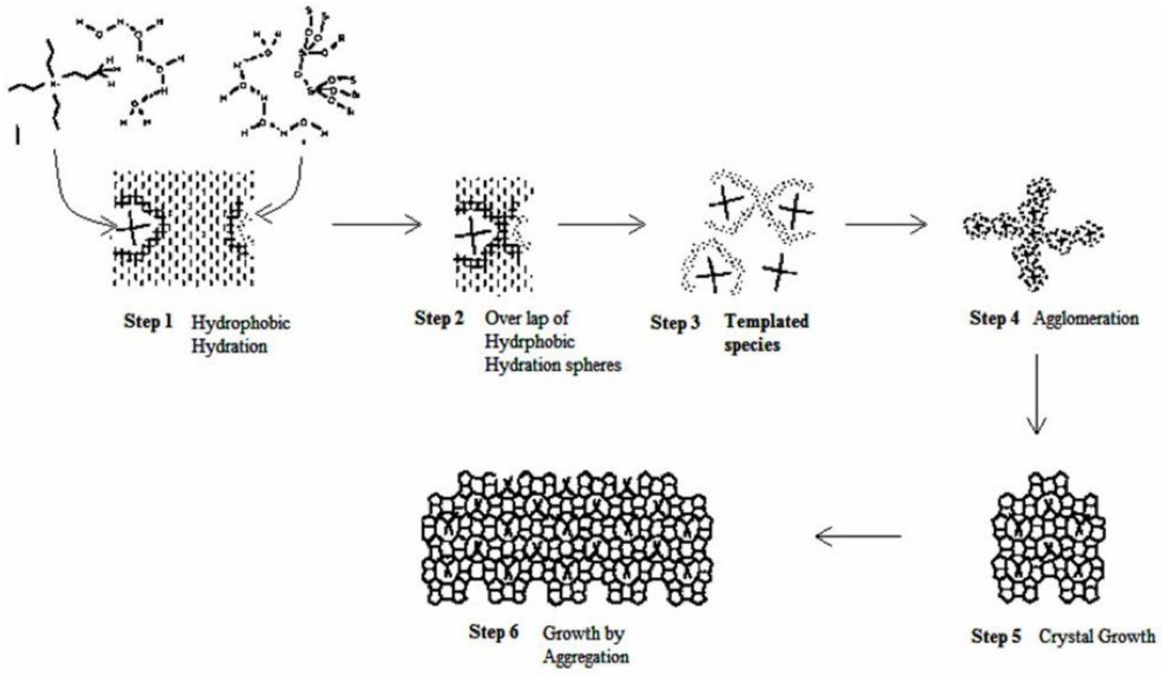


Figure 9. Zeolite formation [39].

The most interesting feature of zeolites is the possibility of controlling, in certain media, the chemical composition of the walls as well as the pore diameter and its topology. Zeolite X is hydrothermally synthesized using a wide range of raw materials, being mainly different sources of silica and alumina, which are usually composed by sodium silicates, sodium aluminate, aluminum salts or colloidal silica.

The hydrothermal synthesis of zeolite X involves the transformation of a mixture of Si and Al compounds, metal cations, organic molecules and water into crystalline aluminum-silicates.

As an agent, inorganic cations such as Li^+, Na^+, K^+, and / or soluble organic species such as quaternary ammoniums are used.

The process of converting the amorphous gel into zeolites is thermally activated and takes place in a temperature range from 60°C to 100°C, except in zeolites with higher silicon content where higher temperatures are needed, and autoclave synthesis is carried out. In the synthesized material the organic agent fills the interior of the pores stabilizing the structure. During the synthesis process, self-assembly takes place between the inorganic and organic components, through weak Van der Waals interactions. It is evident that the nature of the starting species, the composition and structure of the agent, as well as the synthesis conditions, will determine whether a crystalline or amorphous material is obtained and what type of crystalline material is finally synthesized.

The elimination of these organic molecules by combustion or extraction leaves the microporous system of the material free [25].

The syntheses are generally made with silicon and aluminum sources. However, there are other potential sources of silicon and aluminum for the synthesis of zeolites. Until now, there have been many studies on synthesizing zeolites from natural minerals such as kaolinite, bentonite, feldspar and others, due to the effective crystallinity results and a high capacity of cation exchange [25].

4. Comparison of the synthesis of zeolite X, Y and A. Transformation from zeolite X to zeolite A

The synthesis of zeolites took place around 1950 by its industrial application of ion exchangers. The obtaining of these solids was based on a method from saturated aqueous solutions of appropriate composition. For around 1968, Barrer and Milton incorporate to the method, the use of very reactive alkaline gels, with lower conditions of pressure and temperature, with an efficient reduction of time of synthesis.
Over the years, all zeolites have been obtained by simple modification of this method, for example, replicating the conditions of their formation in nature, using high pressures and temperatures higher than 200°C.

The synthesis of zeolite A, X and Y follow the same parameters but under different Si/Al ratio, temperature and pressure, according to their structure and properties.

4.1 Zeolite A

The zeolite type A has a Si / Al ratio of 1. It is made up of two types of polyhedra, a simple cube (D4R), C4-C4 and a truncated octahedron formed by 24 tetrahedra, also called " β cage" or "sodalite cage". These two coupled polyhedrons integrate the characteristic structure of type A zeolite, which encloses the so-called "super cage", which gives it an internal diameter of 11.4 Å and a pore opening of 4.2 Å [27] (Figure 10).

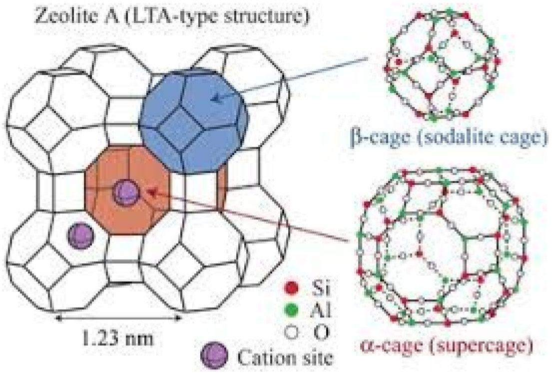


Figure 10. Structure of zeolite A [27].

4.1.1 Characteristics of Zeolites A used as adsorbents [45]

Type of zeolite A	Cation (equilibrate the overall charge)	Pore diameter	Uses as a molecular sieve in industry
3A	K^+	3Å	Adsorbs NH_3, H_2O, used to dry gases, polar and organic liquids, does not adsorb C_2H_6. Also used in water removal in the cleaning of fluids by means of ultrasonic baths.
4A	Na^+	4Å	Adsorbs H_2O, CO_2 (excellent), SO_2, H_2S, C_2H_4, C_2H_6, C_3H_6 and ethanol. It does not adsorb C_3H_8 or longer chain hydrocarbons. It is used to dry non-polar liquids and gases.
5A	Ca^{2+}	5Å	Adsorbs linear hydrocarbons to n-C_4H_{10}, alcohols to C_4H_9OH, mercaptans to C_4H_9SH. Does not adsorb Isocomponents or ring structures with more than 4 carbon atoms. Also for oxygen purification and regeneration.

4.2 Zeolites with FAU structure

The zeolites with FAU structure are represented by the zeolite X and the zeolite Y. Both have topologically the same crystalline structure but different Si / Al ratio. The Si / Al ratio of zeolite X is in the range of 1 to 1.5 and 1.5 to 3 in the case of zeolite Y. Both zeolites belong to the cubic system, just as zeolite A is made up of two types of units. However, for the X and Y zeolites the polyhedra cage type β by double rings of six tetrahedra (D6R), C6-C6, coupled to the " β cage" or "sodalite cage" by four of their hexagonal faces, the union of both structures form the "super cage" [26].

For these zeolites the supercage α has an internal diameter of 12.4 Å, access to this chamber is formed by 12 oxygen atoms generating a close opening of 8 Å. Like zeolite A, these zeolites have two interconnected three-dimensional channel systems. The main channels are formed by the system of the super cage, already mentioned that measure 7.8 Å in terms of diameter. The second system originated by the alternating connection of the sodalite cages and super cages , which is entered by 6 oxygen atoms, has a diameter of 2.2 Å [26] (Figure 11).

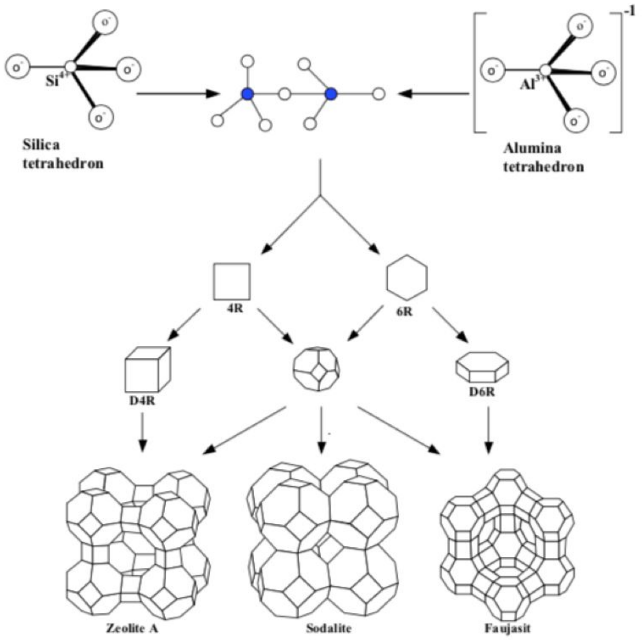


Figure 11. Structural unit of zeolite A, sodalite and faujasite [30].

4.2.1 Characteristics of Zeolites A used as adsorbents [45]

Y	Cation (equilibrate the overall charge)	Pore diameter	Uses as a molecular sieve in industry
10 X	Na^+	8Å	Adsorbs aromatic hydrocarbons. Used for gas drying.
13 x (10 A)	Ca^{2+}	10Å	Adsorbs di-n-butylamine. Used to dry hexamethylphosphoramide. Used to pre-purify water due to its high affinity to water and carbon dioxide.
NaY	Na^+		Adsorption of metaxylene. Drying of gases.
KY	K^+		Adsorption of paraxylene. Drying of gases.

Zeolite X and Y have been hydrothermally synthesized in a wide range of composition. Zeolites Y with higher silicon / aluminum ratio can be obtained by dealuminization with chemical treatments or by treatments with steam streams to hydrolyze the aluminum of the structure and replace it with silicon [29].

The defined pore diameter, as in zeolite A, gives zeolite X and Y the property of molecular sieve. The main channels are of sufficient size for access to most of the organic molecules commonly used as reagents. Like zeolite A, zeolites X and Y can have different compensation cations that give different capacities at the adsorbent level.

Zeolites X and Y, have important roles at the catalytic level, is special in the petroleum and petrochemical industry in catalytic cracking and hydrocracking processes [28].

The synthesis of zeolite X has the difficulty of easily produce zeolite A in heating systems at elevated temperature. Zeolite A (~ 4Å) and hydroxisodalite (~ 2.5Å) are more closed structures and therefore, more stable than zeolite X, so they are impurities that are difficult to eliminate.

Previous experiments showed that, in general, zeolite X with a low silicon / pure aluminum molar ratio cannot be obtained, since it seems to not be pure with hydroxisodalite.

By decreasing the silicon/aluminum ratio, the area where the crystallization of zeolites A and X takes places, is overlapped.

From these experiments, it has been highlighted the importance of an earlier aging stage to favor the formation of zeolite X without impurities from other phases (hydroxisodalite or zeolite A) and reduce the time of synthesis.

5. Structure determination of zeolites

5.1 Structure analysis by X-ray Powder Diffraction

In order to determine a zeolite structure and verify if this synthesized catalyst does not contain a large amount of impurities, all samples are analyzed by this technique.

X-ray diffraction is one of the most widely techniques used for the determination of solid matter. Its origins go back to the beginning of the 20th century (Laue, 1912, W.H. Bragg and W.L. Bragg, 1915), who designed a tool for diffraction and reflection of X-rays by crystalline matter that allowed to show the electromagnetic nature of this radiation.

X-ray are diffracted by the electrons that are around the atoms, being these atoms grouped in a periodic and orderly manner, so when receiving X-ray, they disperse in all directions, producing interference phenomena, both constructive and destructive. Most of the dispersions are destructive type, canceling each other. However, since the crystals are dispersed in a periodic repetition, it can happen that the scattered waves are in phase, spreading in certain directions and amplified by constructive interference, thus originating a diffraction pattern characteristic of the sample [30].

This is true when the X-rays diffracted by parallel planes separated by a distance "d", have a path difference equal to an integer of the wavelength of the incident beam. The x-rays used in diffraction are in the interval 0.5-2.5 A.

Bragg's law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample, described by a simple equation [40]:

$n\lambda = 2d \cdot \sin(\theta)$

Where n is an integer

λ is the wavelength
d is the distance between successive parallel planes
θ is the angle of incidence

Powder diffraction data can be collected using either transmission or reflection.

- Reflection: it is used for solid samples. It takes short time to get results, it acts directly over the surface desired and it gets better signal to noise ratio.
- Transmission: it used for flat surfaces. It takes longer time than reflection, it measures through the sample, it gets a dataset of both desired and undesired containing in the sample.

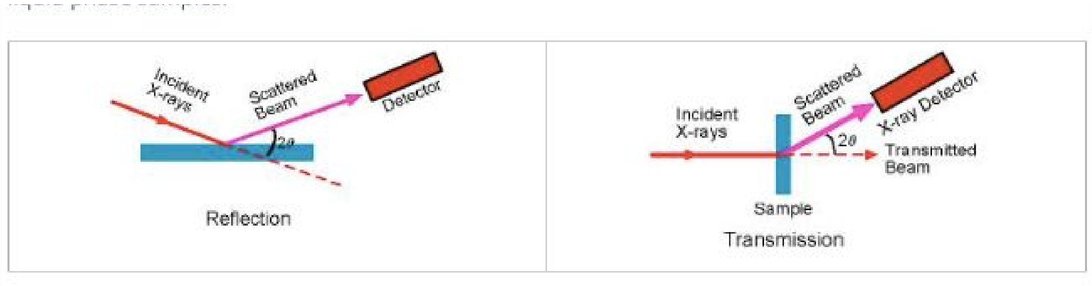


Figure 12. Reflection and transmission geometry in XRD [42].

XRD in a crystalline sample allows us to identify crystalline phases (since all crystalline solids have their characteristic diffractogram) both in their qualitative and quantitative aspects, from single crystal, a few grains in beam or a full power average. Studies of polymorphism, phase transitions, measurement of particle size, determination of phase diagrams, determination of the ratio between two or more crystalline phases etc., are usually performed by this analytical technique. This technique is used after each synthesis, ion exchange and, if necessary, calcination, to ensure that the catalyst structure has not undergone changes [31].

The X-ray diffractometer is an instrument that uses a beam of chromatic radiation. When this beam impacts on a powder (a crystalline aggregate), it produces diffracted beams that follows the Bragg's law. These beams are detected by high sensitivity tubes, allowing a graphical evaluation. It is also possible the use of a microprocessor or a standard data processing system, to evaluate the interatomic distances and relative intensities, allowing a structural and analytical determination [31].

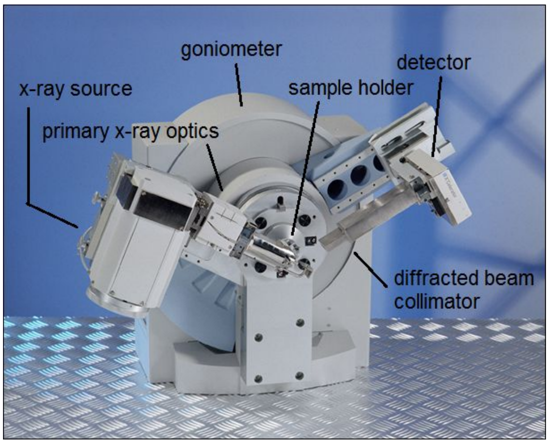


Figure 13. Components of a X-ray powder diffractometer [43].

5.2 Structure analysis by Neutron-Diffraction

The majority of crystalline structures are determined X-ray diffraction, although in special circumstances it is very useful to use the neutron diffraction. Unlike X-rays that are diffracted by electrons, neutrons are diffracted by the nuclei. The neutron scattering is isotropic and does not decay with sin Θ / λ. Also it does not vary with Z as the X-rays and different isotopes of the same element diffract from neutrons differently [47].

Broglie's law is described by a simple equation [46]:

λ = h/mv, de Broglie
where λ is wavelength
h is Planck's constant
m is the mass of a particle
v is the velocity

It is important to note that the electrons also have an associated wave, which allows adequate speeds and therefore, perform any diffraction experiment. It is useful for compounds identification since it is possible to select specific crystallites and obtain diffractograms that depend on the relative orientation of the microcrystal with respect to the electron beam. Furthermore, in multiphase samples, you can obtain the diffractograms isolated from each phase while that in neutron and x-ray diffraction obtains the superposition of the diffractograms of all phases. However, due to the intensities of the diffraction peaks, it is very difficult to obtain crystalline structures.
Neutron diffraction require a lot of material and machines since it is used, specially for heavy samples with a high absorption property. On this way, it detects any molecule of

water. It is also used for magnetic structures. However, it takes longer time to measure, comparing to X-ray powder diffraction and some samples decompose [47].
The most famous technique for this kind of experiments it is the one called “Synchrotron”, a particle accelerator with variable wavelength and it is characterized by fast measurements.

6. Kaolin: Activation and other uses

Traditionally, kaolin is the basic raw material used to obtain zeolites with low content of silicon dioxide containing (like NaX and NaY). Kaolin is a rock formed by mineral type kaolinite, halloyzite, nacrite, dickite, and by other components such as quartz, feldspars, micas, ferrites, among others. Its structure is built of silicon layers (Si_2O_5) bonded to similar aluminium hydroxide layers ($Al(OH)_4$), called Gibbsite layers. Gibbsite is an aluminium hydroxide mineral which is bonded to the silicate layer (Silicate/Gibbsite) in a common layer called S/G layer [31].

Metakaolin is a highly reactive amorphous phase from kaolin, which possesses a suitable reactivity for the synthesis of zeolites, including those with low Si / Al ratio [1] It contains a high content of aluminosilicates and inestable under highly alkaline conditions. The zeolite’s synthesis from metakaolin is followed by Two steps: the dissolution of the MK, which leads to the formation of an aluminosilicate gel and subsequently the nucleation and growth of crystals. The presence of impurities in the kaolin is considered to affect not only the reactivity, but also the quality of the final products.

Previous researches have shown from metakaolin, it is possible to obtain high quality zeolites and low silica content such as zeolites A, X, Y.

Breck in 1974, exposes different aspects related to the synthesis of zeolites from Kaolin. For the synthesis, it is necessary to calcine the kaolin between 500 and 600 ºC for its transformation into metakaolin. Zeolites with low Si / Al ratio synthesized from metakaolin require specific conditions for each type of zeolite. For example, zeolite X with Si / Al ratio of 2.12: 3.0 of large pore size 6-8 Å [32], crystallization around 100 ° C for 24 hours and an aging of the same time.

Torres, J [33] conducted a study with the objective of production of metakaolin from heat treatment of kaolins of colombian origin. Based on background information indicating the presence of kaolinite as responsible for the structural transformation to metakaolin, they considered 5 samples of different kaolins, to which they subjected different analyzes in order to determine the presence of kaolinite. These analyzes were: chemical analysis, differential thermal analysis, X-ray diffraction, infrared analysis and electron microscopy. After heat treatment at 700^{o}C for 2 hours, by means of X-ray diffraction they verified that the samples with greater content of kaolinite produce a metakaolin of greater activity, meanwhile the low content of this mineral does not make the obtaining metakaolin. They argue that kaolins containing kaolinite the order of 50% or more when being heat treated originate metakaolin from good quality.

In this experiment, kaolin is used under different conditions and variables, in order to get a better synthesis results and increases the exchange capacity of the zeolite.

7. Experimental procedure

The goal of this project was to obtain Zeolite X by synthesis. In order to do so, it was crucial to find the best recipe, materials and equipment available. Two different but very promising recipes were found and therefore two separate syntheses were performed:

7.1 First synthesis [32]

Materials:

- 3,79 g of sodium hydroxide
- 32,80 g of deionized water
- 4,00 g of Metakaolin

Procedure:

4,00 g Kaolin was heated to 600 °C for approximately 30 minutes. This turns the crystalline Kaolin into the amorphous metakaolin. The crystalline Kaolin is not very reactive, whereas the amorphous metakaolin is very reactive. After heating the metakaolin, it was allowed to cool to room temperature.

The first step consisted on the adding of 3,79 g of sodium hydroxide to 32,80 g of deionized water and mixing until everything was dissolved.

The amount of water was calculated from the molar composition:

$3.3\ Na_2O: Al_2O: 3SiO_2: 132H_2O$

Then, the metakaolin was added to the solution and thoroughly mixed. The mixture has been divided equally in four glass tubes. Hydrothermal synthesis of the aged sample was followed in an autoclave oven at around 100^{o} C. . Each of the tubes were taken out at a different time, being the first one after approximately 3 hours. Afterward, the samples were taken out consecutively after 3, 4, 5, 6 and 7 hours. Once the hydrothermal reaction was over, the samples were accurately washed with deionized water four times and filtered. Once they were dried out, X-ray diffraction was performed in order to determine the structure and analyze the samples.

7.2 Second synthesis [32]

Materials:

- 3,81 g of sodium hydroxide
- 32,53 g of deionized water
- 4,00 g of Metakaolin

Procedure:

A second synthesis was performed. The procedure of the first synthesis was followed as indicated in the original recipe “Effect of temperature on the synthesis of zeolite X from Ahoko Nigerian Kaolin using novel metakaolinization technique” [32].

However, 4,00 g Kaolin was heated to 700 °C for approximately 30 minutes this time, since no crystals were formed.

7.3 Third synthesis [35]

Materials:

One difference in the materials used was in the density of sodium silicate solution, which in the recipe was 1,37 g/mL meanwhile ours was 1,33 g/mL.

- deionized water
- sodium hydroxide (99% NaOH)
- alumina trihydrate (65% Al_2O_3)
- sodium silicate solution (27,35% SiO_2; 8,30% Na_2O; 1,33 g/mL.

Procedure:

The original recipe consisted of large amounts of substrates, which would then result with a big quantity of the product. Therefore, we decided to weight out 1/10 of all of them.

In a glass beaker, we added 10,00 g of sodium hydroxide to 10,00 g of distilled water and mixed until being completely dissolved. Afterwards 9,75 g of alumina trihydrate was added and stirred at 100° C, until all alumina trihydrate was dissolved (from a white dense solution to a less dense one) and it was cooled down to room temperature. 20,255 g of distilled water were added. 10,01 g of the obtained mixture were taken, and 5,91 g of sodium hydroxide and 61,2 g of water was added and mixed until dissolved.

To a new glass flask, we added 22,64 g of sodium silicate solution, 60,535 g of water and 5,91 g of sodium hydroxide and it was mixed till everything dissolved. Lastly, the contents of the two flasks were combined quickly and stirred for half hour.

The given gel was divided among 6 glass tubes and in 2 small polyethylene bags. All of the glass tubes and one of the bags were heated to 91° C. The first glass tube was taken after 4 hours, the other ones at 5, 6, 7, 8 and 24 hours. The bag was take out after 8 hours. The other bag was heated to 104° C for 8 hours in order to be able to compare it with the one that was heated to 91 °C.

After all of the samples have been taken out, they have been filtered and washed (the pH of the sample before the washing had a value of 14). At the end all the samples were dried in an oven at 104 °C. Once they were dried out, X-ray diffraction was performed in order to determine the structure and analyze the samples.

8. Results and discussion

8.1 First synthesis ‘

The synthesis was performed as indicated in the original recipe “Effect of temperature on the synthesis of zeolite X from Ahoko Nigerian Kaolin using novel metakaolinization technique” [32]. It was proceed to take out the first sample after approximately 24 hours. However, no crystals were formed in any of the samples. This could be due to a bad quality of metakaolin since the Kaolin did not disappear in the Metakaolin.

8.2 Second synthesis

In order to see if the synthesis of zeolite X was a success, the samples taken out during the performed experiment were analyzed with X-ray powder diffraction (XRD). Since such apparatus is not present at Roskilde University, we had to send the obtained product to DTU

Risø Campus for analysis. The given results were analyzed with a specific program named Powdercell as well as in Excel.

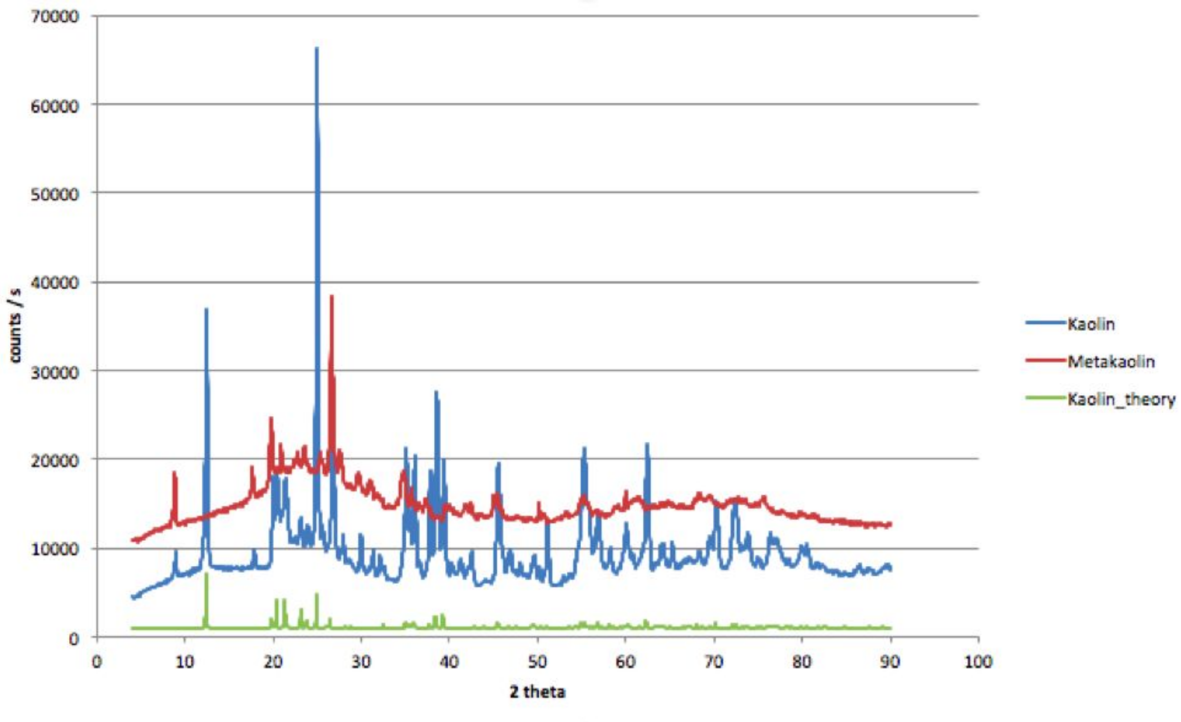


Figure 14. XRD patterns of kaolin, metakaolin and theoretical kaolin.

Figure legend:
Blue- Kaolin used in the experiment
Red- Metakaolin
Green- Kaolin (theoretical)

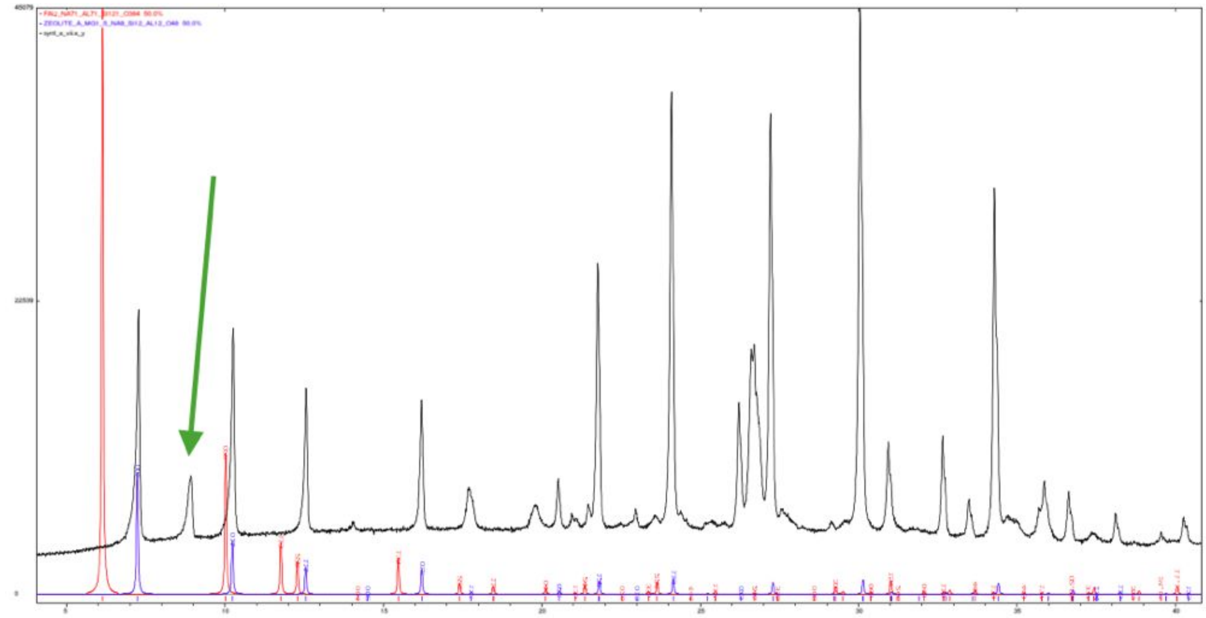


Figure 15. XRD patters of the synthesized compound (first experiment), zeolite A (theoretical) and zeolite X (theoretical).

Figure legend:
Blue- Zeolite A (theoretical)
Red- Zeolite X (theoretical)
Black- synthesized compound
Green arrow- it is the extra phase from the Kaolin and there are more of those peaks.

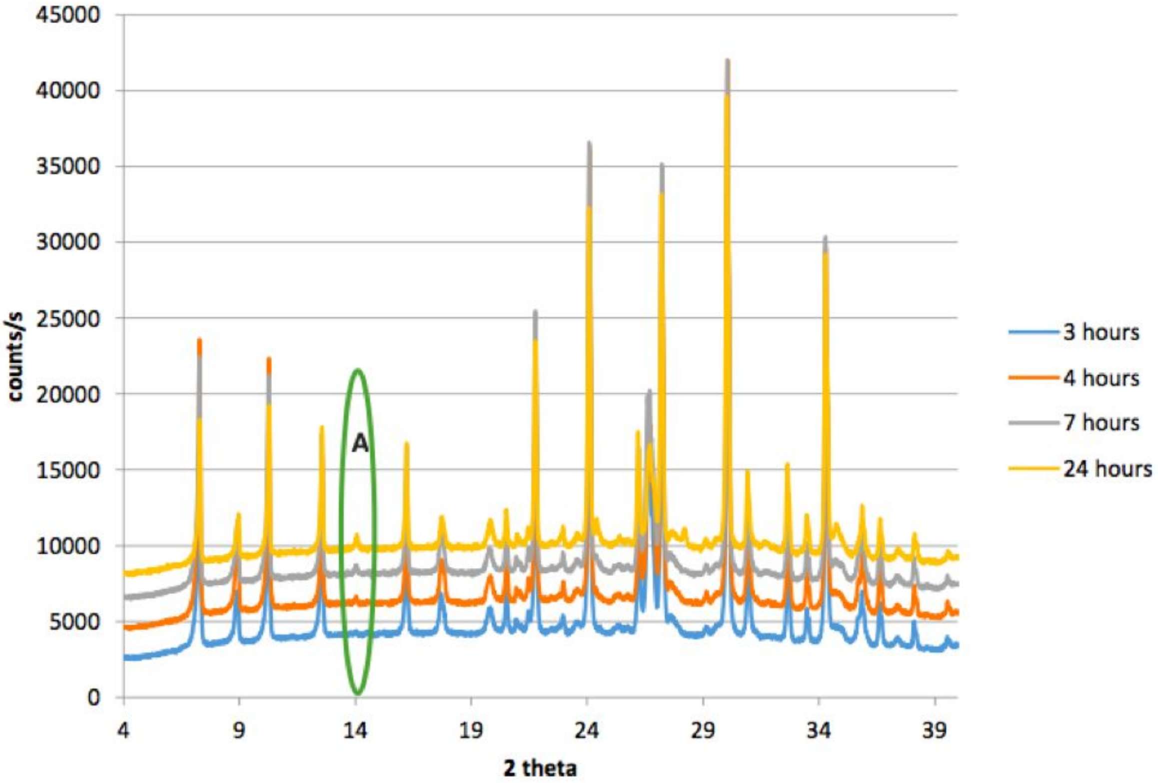


Figure 16. Comparison of XRD patterns of all the samples in the first synthesis, taken respectively at: 3,4,7 and 24 hours.

It was observed that after 3 hours most of the material is crystallized, however from the peaks, it could be noticed that there is a reflection at 2theta= 14,05 ° (A) which is getting higher over time. This reflection might be a small amount of a different compound which is still crystallizing (a second phase was observed).

From the results in *figure 15,* we were able to deduce that the experiment was not successful as we obtained zeolite A instead of zeolite X, which we can see from the fact that the peaks of the obtained compound correspond to the ones of zeolite A. There is also an extra phase present which was not able to be identified (we would need more reflections in order to determine the compound). Looking at the results, it can also be concluded that the second unidentified phase is not affected by the heating.

After realizing that the synthesis was unsuccessful, we decided to analyze with the XRD method the kaolin used (Figure 14). It is seen that there is a second phase present, it means that we have an unidentified compound in our Kaolin, and because we assumed that it was pure, we have less Metakaolin in our synthesis than we expected. Therefore, it means that we have a different ratio between SiO_2, Al_2O_3 and Na_2O, which is probably why we do not get zeolite X but zeolite A. However, the Kaolin disappears in the Metakaolin, which means that the heating is making the Kaolin active by making it non-crystalline.

Below, a compositional diagram for NaO2-Al2O3-SiO2 system is shown, in order to demonstrate the low chances to obtain zeolite X by changing the ratio between the compounds mentioned comparing to zeolite A (Figure 17).

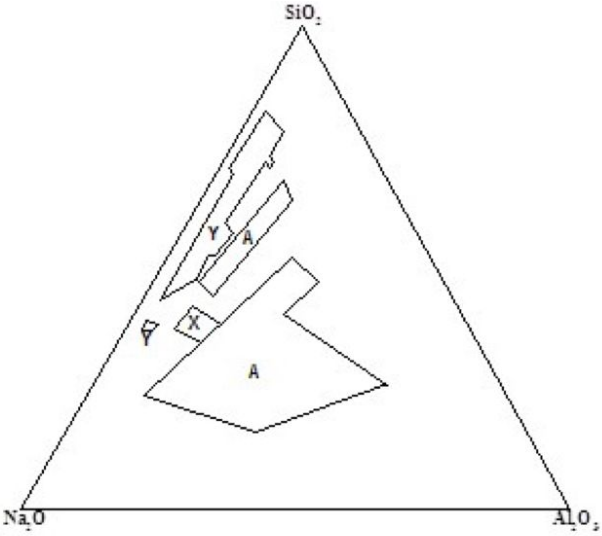


Figure 17. Ternary compositional diagram for NaO2-Al2O3-SiO2 system for synthesis of zeolite A, X and Y [46.]

8.3 Third synthesis

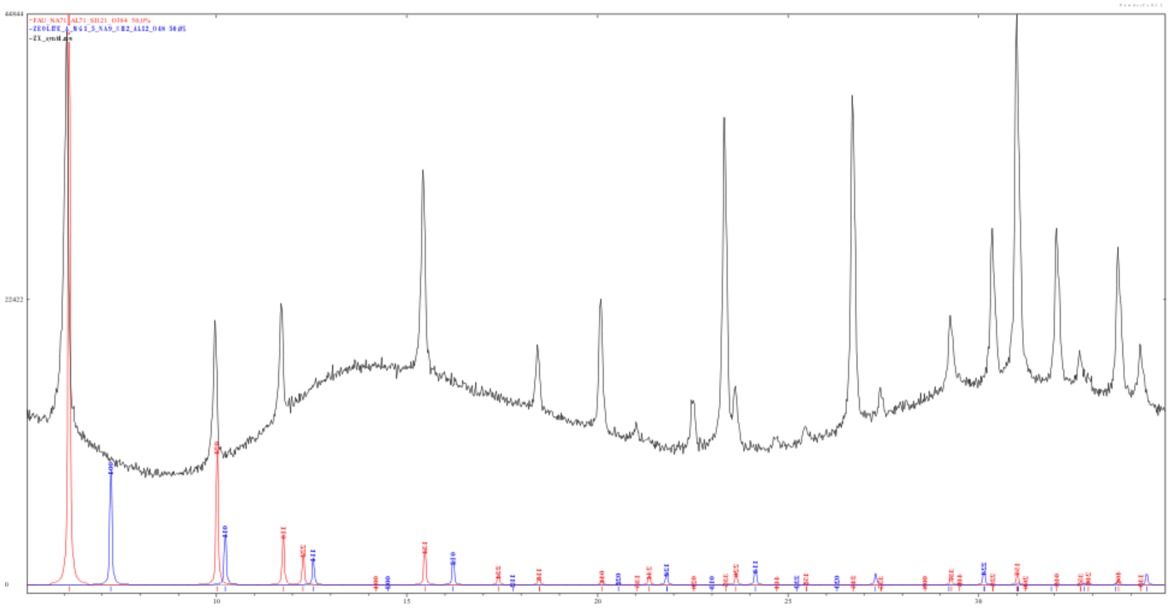


Figure 18 XRD patters of the synthesized compound (second synthesis), zeolite A (theoretical) and zeolite X (theoretical).

Figure legend:
Blue- Zeolite A (theoretical)
Red- Zeolite X (theoretical)
Black- synthesized compound

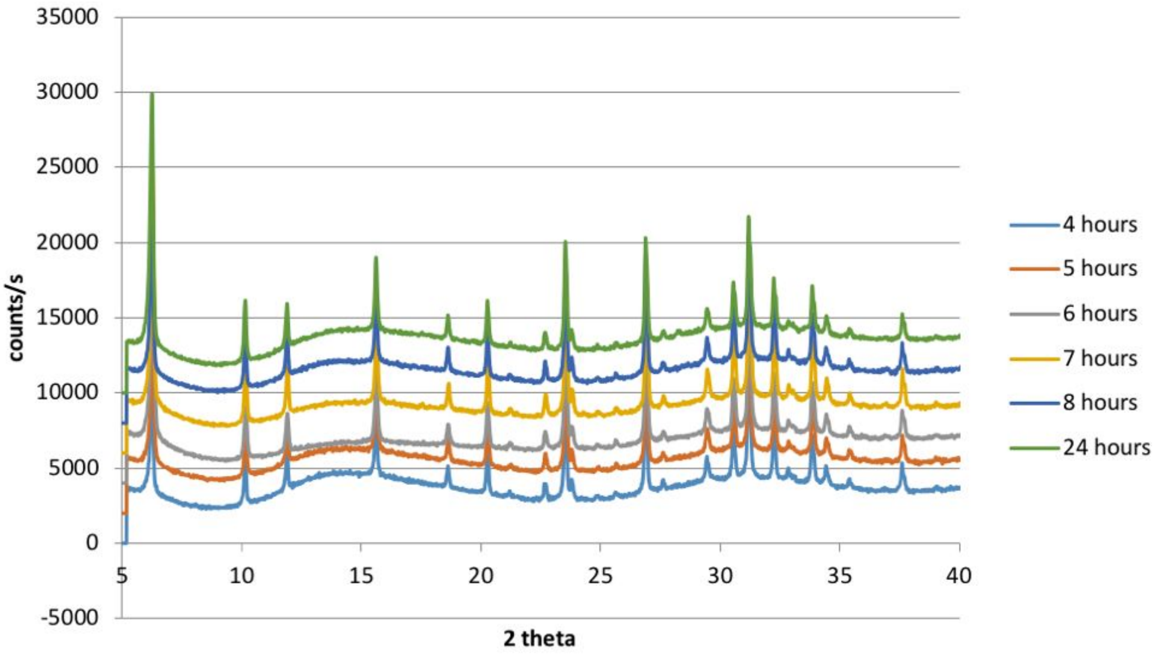


FIgure 19**.** XRD patterns of all the taken samples, taken respectively at: 4,5,6,7,8 and 24 hours.

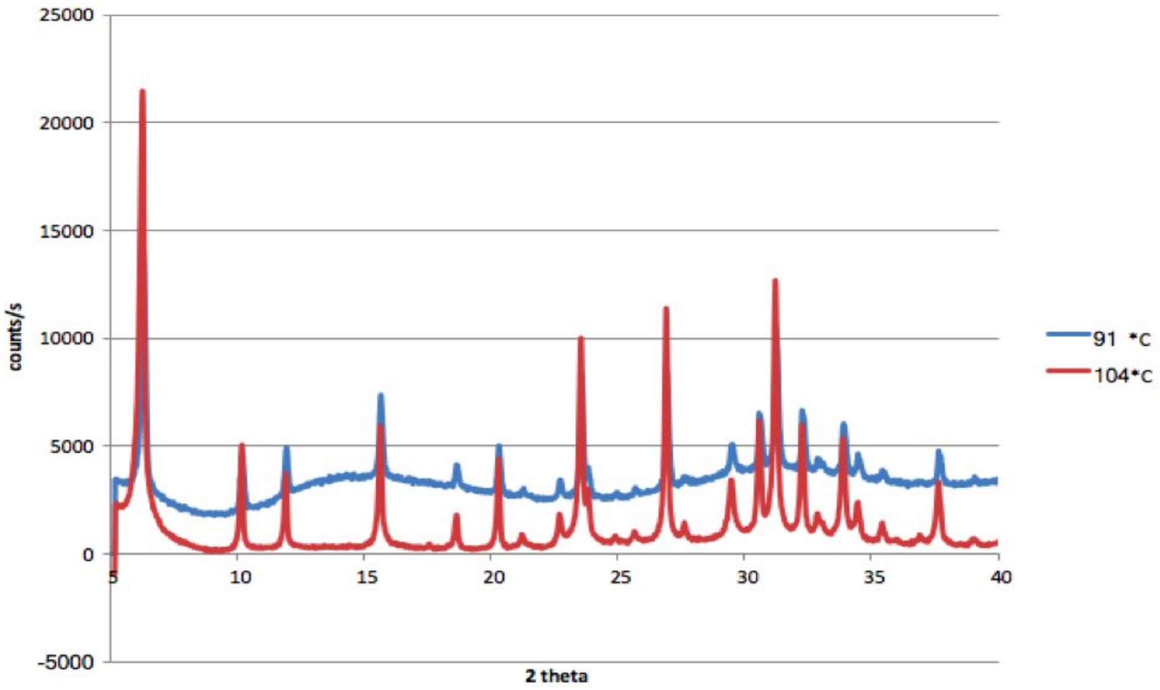


Figure 20. XRD patterns of the samples that were in the bags, one was at 91° C and the other one at 104° C.

From figure 19 we can see that, since there is not visible difference between the different samples, the complete crystallization had already occurred at 4 hours, even if in the recipe it was said that it would occur at 8 hours. Additionally, from figure 20 it is visible that there are no differences between the sample at 91° C and the one at 104° C, so the synthesis can occur at a higher temperature.
By analyzing figure 18, it is possible to conclude that zeolite X was obtained. It can be stated that, since the peaks of the obtained material correspond with the ones of the theoretical zeolite X.
In figure 18, 19 and 20 it is seen, that the background of all samples except the red one in figure 20, is wave like, whereas the red one in figure 20 is (more or less) a flat line. Normally a wave like background indicates amorphous material present in the sample, but in this case, it is the sample holder. The red dataset in figure 20 was measured on a deep sample holder, that contained more material. All the other samples were measured on a different type of sample holder. The sample holder had a glass plate and there were only used a little material for the measurement. The wave like background comes from the amorphous glass plate.

The calculated ratio of Silica: Alumina is 4:1, meanwhile the measured weight of the samples was 4,85g, which was bigger than the expected one. This means, that when it was weighed out, it was not completely dried.

9. Conclusion

It was possible to obtain zeolite A and Faujasite type X from metakaolin and a sodium silicate solution (27,35% SiO_2; 8,30% Na_2O; 1,33 g/mL), respectively, of high purity and characteristics similar to those reported in the literature. The final result of the synthesis is influenced by the nature of the silicon source, whose reactivity depends on the composition of the synthesis mixture.

On one hand, zeolite A was obtained from metakaolin with a ratio higher than the unit. The hydrothermal activation with NaOH converts metakaolin into a zeolitic type material. The results show a second phase and some impurities (hydroxisodalite impurities). It is possible to retain a greater amount of hydroxides in the structure. The use of the furnace, in the conditions mentioned in the experimental procedure, favored the formation of zeolite A in less time than using conventional heating.

On the other hand, it has been possible to obtain zeolite X with a silicon / aluminum molar ratio 4:1, with a high degree of crystallinity and in a relatively short synthesis time.

During all this time of synthesis study, two important criteria were concluded. Firstly, the higher Si / Al ratio of the zeolite to synthesize, higher is the reaction temperature. The second is that the higher is the crystallization temperature, the lower the porous volume of the zeolite. Additionally, the synthesis not only depends on the conditions of pressure and temperature, but also on the chemistry related to the synthesis gel (very important factor) and the nature of the cations present in the reaction medium.

10. References

1. D.W. Breck. Zeolite Molecular Sieves: Structure, Chemistry and Use. (1975). *Analytica Chimica Acta*, 75(2), p.493.

2. Leinonen, H. (1999). Removal of harmful metals from metal plating waste waters using selective ion exchangers.

3. Margeta, K., Zabukovec, Logar, N., Siljeg, M. and Farkas, A. (2012). *Natural zeolites in water treatment- how effective is their use*.

4. Baerlocher, C., McCusker, L. and Olson, D. (2007). Atlas of Zeolite Framework. Sixth Edition.

5. Smeets, S. and Zou, X. (2017). Zeolite structures.

6. Davis, M. and Lobo, R. (1992). Zeolite and molecular sieve synthesis. *Chem. Mater.*, pp.756−768.

7. Nils, E., Zimmermann and Haranczyk, M. (2016). History and Utility of Zeolite Framework-Type Discovery from a Data-Science Perspective.

8. George, T. (1989). Synthetic zeolites.

9. CHEN, N. and DEGNAN, T. (1988). ChemInform Abstract: Industrial Catalytic Applications of Zeolites. *ChemInform*, 19(26).

10. Tschernich (1992). Zeolites of the world.

11. Cundy, C. and Cox, P. (2005). The Hydrothermal Synthesis of Zeolites: Precursors, Intermediates and Reaction Mechanism. *ChemInform*, 36(37).

12. Currao, A. (2007). Understanding Zeolite Frameworks. *Journal of Materials Chemistry*.

13. JHA, B. (2018). *FLY ASH ZEOLITES*. [S.l.]: SPRINGER.

14. Wang, Y. and Li, H. (2014). Luminescent materials of zeolite functionalized with lanthanides. *CrystEngComm*, 16(42), pp.9764-9778.

15. Pauling, L. (1935). THE STRUCTURE OF CRYSTALS. *Science*, 82(2129), pp.372-372.

16. Milton, R. (1959). Molecular Sieve Adsorbents. (Patent 2882244).

17. Wang, S., Terdkiatburana, T. and Tadé, M. (2008). Adsorption of Cu(II), Pb(II) and humic acid on natural zeolite tuff in single and binary systems. *Separation and Purification Technology*, 62(1), pp.64-70.

18. Roland, E. and Kleinschmit, P. (2008). Zeolites. *Ullman's Encyclopedia of Industrial Chemistry*, 7th Edition.

19. McMonagle, J. (1995). Zeolites and related microporous materials: State of the art 1994 (Studies in Surface Science and Catalysis, vol. 84A-C). *Applied Catalysis A: General*, 124(1), pp.176-177.

20. Sumaya, Usman, K. (2018). Utilizing Silica from Rice Hull for the Hydrothermal Synthesis of Zeolite Y.

21. OZIN, G., BAKER, M., GODBER, J. and GIL, C. (1989). ChemInform Abstract: Intrazeolite Site-Selective Far-IR Cation Probe. *ChemInform*, 20(30).

22. Yunxia, Y., Zhang, J., Burke, N. and Huang, S. (2014). Influence of Charge Compensating Cations on Propane Adsorption in X Zeolites: Experimental Measurement and Mathematical Modeling.

23. Verhulst (1994). Zeolite Science 1994.

24. Filippidis, A., Godelitsas, A., Charistos, D., Misaelides, P. and Kassoli-Fournaraki, A. (1996). The chemical behavior of natural zeolites in aqueous environments: Interactions between low-silica zeolites and 1 M NaCl solutions of different initial pH-values. *Applied Clay Science*, 11(2-4), pp.199-209.

25. Arruebo, M., Coronas, J., Santamaria, J. and Tellez, C. (2008). Microporous and Mesoporous Materials. *4th International Zeolite Membrane Meeting*.

26. Giannetto, G., Guisnet, M. and Wang, Q. (1990). Zeolites. pp.10:301.

27. Petrov, I. and Michalev, T. (2013). Synthesis of Zeolite A.

28. Faraji, D., Sadighi, S. and Mazaheri, H. (2017). Modeling and Evaluating Zeolite and Amorphous Based Catalysts in Vacuum Gas Oil Hydrocracking Process. *International Journal of Chemical Reactor Engineering*, 16(1).

29. Vaughan, D. and Thomas, J. (1989). Hydrothermal Chemistry of Zeolites.

30. Laue, M. (1912). Max von Laue and the discovery of X-ray diffraction in 1912. *Annalen der Physik*.

31. Bogatyrev, B., Matveeva, L., Zhukov, V. and Magazina, L. (1997). Kaolinite and Halloysite Synthesis in the Gibbsite-Silica Solution System under Normal Conditions.

32. Kovo, A. (2012). Effect of temperature on the synthesis of Zeolite X from Ahoko Nigerian Kaolin using novel metakaolinization technique.

33. Torres, J., Ruby M. de Gutiérrez, Ricardo Castelló and Carmina Vizcayno (2010). Comparative study between five different Kaolins from various regions of Colombia

34. Bunaciu, A., Gabriela, E. and Aboul, Enein, H. (2015). X-Ray Diffraction: Instrumentation and Applications.

35. Lechert, H. and Staelin, P. (2001). Hans Lechert and Philip Staelin.

36. Kamal Masoudian, S., Sadighi, S. and Abbasi, A. (2013). Synthesis and Characterization of High Aluminum Zeolite X from Technical Grade Materials.

ONLINE SOURCES:

37. Lenntech.pl. (2018). *Zeolite structure and types - Lenntech*. [online] Available at: https://www.lenntech.pl/zeolites-structure-types.htm.

38. Lenntech.pl. (2018). *Zeolites applications - Lenntech*. [online] Available at: https://www.lenntech.pl/zeolites-applications.htm#ixzz5ZO9y8I68.

39. Sercalia.com. (2018). *Natural Zeolite - Sercalia*. [online] Available at: https://www.sercalia.com/en/natural-zeolite/.

40. Macedo, A. (2018). *Handbook of zeolite - Tudo sobre zeólitas*. [online] Ebah.com.br. Available at: https://www.ebah.com.br/content/ABAAAfAJIAL/handbook-of-zeolite?part=3%20Mention%20LTA%20briefly].

41. Hyperphysics.phy-astr.gsu.edu. (2018). *Bragg's Law*. [online] Available at: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html.

42. Slideplayer.com. (2018). *Zeolites. - ppt video online download*. [online] Available at: https://slideplayer.com/slide/6427680/.

43. (Mrl.ucsb.edu. (2018). *X-ray Basics | Materials Research Laboratory at UCSB: an NSF MRSEC*. [online] Available at: https://www.mrl.ucsb.edu/centralfacilities/x-ray/basics.

44. Xrpd.eu. (2018). *What is X-Ray Diffraction*. [online] Available at: http://www.xrpd.eu/.

45. Anten Chemical. (2008) and Xinyuan Molecular Sieve. (2011).

46. ThoughtCo. (2018). *What Is the de Broglie Equation?*. [online] Available at: https://www.thoughtco.com/definition-of-de-broglie-equation-604418 [Accessed 18 Dec. 2018].

47. Jin, X. (2013). *Neutron Diffraction. Principles, instrumentation and applications*. Nova Science Publishers.