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Preparation of zeolites by different bases with 1.5 of initial ratio Si/Al: the effect of crystallization temperature

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Abstract: *In this study, the behavior of prepared zeolites with a 1.5 Si/Al ratio in different crystallization temperatures was investigated. In this work, the samples were synthesized from hydrogel solution which being prepared using silica solution and sodium aluminate powder as precursors in the presence of different bases. The sodium hydroxide, potassium hydroxide and ammonium hydroxide are the most bases used in the present paper. The amount of precursor's materials which used in resulting hydrogel with appropriate mole ratio was calculated. All samples for this research were prepared by agitation at room temperature for one hour then the mixture was aged for one day at the same temperature. All others parameters of the synthesis were stayed the same. The crystallization temperature was done at 60,80, and 100 °C for 24 hours. The obtained product is dried in an oven at 100°C for 8-12H.*

Keywords*: Crystallization temperature, Sodalite, Zeolite, Bases.*

I. Introduction

Zeolites are the mostly hydrated aluminolicates of alkalines elements. Alkaline soils elements , or on rare occasions other cations, such as these material find wide application in diverse area, that's return to their proprieties(sorption[1], catalytic,molecular-sieve ,ion exchange[1] ,and other proprieties)are the results of the specific structure of its alumniosilicate skeleton, this zeolitic structure comprises a system of channels and cavities , which are the results of sequential combining of alumino-silico-oxygen tetrahedra rings. These tetrahedral rings form so-called secondary building units (SBU) which are the most often used criteria for zeolite separation into different structural types.

One of the most distinguished types of synthesized structural zeolites is sodalite[2]. The first describe doft he mineral sodalite with chemical composition Na_8 $(Al\text{-}SiO_4)_6Cl_2$ was in 1811 by Thompson, and its structure was solved in 1930 by Pauling[3]. The framework of sodalite is completely made up of regular truncate doctahedral cages called sodalite cages. These cages consist of six four-member rings and eight six-member rings. Therefore, the largest pore size is about 2.4Å. The smallest among all zeolites. In addition to many studies on the theoretical and experimental principles of zeolite chemistry, there have been wide investigation on industrial applications of sodalite in different filed of pigments , synthesis of nano-composites and special ,synthesis of nanocomposites and special host matrices for quantum dot materials,and waste management[4-9].

Aluminosilicate sodalites can be synthesized by low-temperature condensation reactions in basic solution [10–12], high-temperature, solid states interring [13], or structure transformation[14,15] .

In the other hand we find an other important structural zeolite is the LTA (Linde Type A) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is small at 4.2Å. This leads into a larger cavity of minimum free diameter 11.4Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure. The unit cell is cubic (a = 24.61Å) with Fm-3c symmetry. Zeolite A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700ºC. [16, 17, 18].

Such as Zeolite A is of much interest because its supercage structure is useful in spacio-specific catalysis. The inner cavity is large enough for structure changing reactions to take place, but the small pore means only a specific structure can get into the cavity for reaction, typically n-paraffins and olefins. One use is in paraffin cracking. The small entry pore is selective towards linear paraffins, and cracking can occur on sites within the supercage (alpha-cage) to produce smaller chain alkanes. Zeolite A is also widely used in ion exchange separation. [19]

Zeolite A, like other zeolites, is synthesized in a gelling process. Sources of alumina (usually sodium aluminate) and silica (usually sodium silicate) are mixed in basic aqueous solution to give a gel. The alkali agent can be NaOH or solutions of quaternary ammonium salts, amines, or other polar organics. The gel is then heated

to 70-300ºC to crystallize the zeolite. The zeolite is normally synthesized in the Na^+,K^+ Na^+ and NH_4^+ Na^+ form. [18]

The present study comprehends a systematic study of the synthesis A zeolite and zeolite-sodalite by a hydrothermal process in a basic solution (sodium hydroxide , potassium hydroxide, or ammonium hydroxide), and the behavior of structure's transformation in different temperature, such as the aim of this work is to investigate the effect of temperature on a prepared zeolite with a 1.5 Si/Al ratio by different bases.

II. Experimental

A) Material

In the present work, silica solution ($Na_2Si_3O_7$, 27 % SiO_2, 17% NaOH) was used as a silica source. Sodium Aluminate (65% Al_2O_3), distilled water and sodium hydroxide, potassium hydroxide or ammonium hydroxide were also used to prepare alumina source solution. These two prepared solutions were needed to get synthesis (hydrogel) for the synthesis of different products in different temperatures.

B) Preparation of zeolites samples by using hydrothermal process:

In order to prepare synthetic zeolite by hydrothermal process, hydrogel solution (synthesis gel) was prepared by agitation of 0,786 g of silica source and 0,522 g of Alumina source in a polyethylene flask containing water and Sodium hydroxide, potassium hydroxide, or ammonium hydroxide, with mechanic stirring at 250 rpm for one hour at room temperature, then the resulting hydrogel was aged for 24 hours at room temperature.

After aging the mixture was transferred to a sealed container and put into oven to hydrothermal crystallize, at different temperatures for 24 hours .After completing crystallization, the resultant precipitate was separated from the mother liquor by vacuum filtration and washed with distilled water until reaching pH range of 9-10 and dried at 100 C° for 8-12 hours.

C) Characterization of prepared zeolite by X-Ray diffraction

X-ray powder diffraction data were collected with diffractometer Shimadzu 6100 using CuKα radiation and a monochromator. The measured 2 theta range (5–60°) was scanned in steps of 0.02° with a counting time of 3s/step. The aperture and the soller slits were set at 1.0°.

III. Results and discussion

A. Effect of crystallization temperature on zeolite formation by sodium hydroxide

In this study of the effect of crystallization temperature, it can be observed that when the hydrogel solution was crystallized at 60°C for 24 hr, the zeolite formed is the zeolite NaA. Then the temperature was increased to 80ºC, we obtain a mixture of phases: zeolite NaA and Sodalite. Finally the sodalite is the favorable sample in 80°C.

In the XRD patterns in Fig.1, all the peaks confirmed the presence of zeolite NaA. In Fig.2, the peaks at 14º, 24º, 31º, 35°, 37° and 42° are typically the 2θ values of the sodalite. The Fig3 shows the XRD pattern of sodalite.

The table I summarizes the results.

Table I: Effect of crystallization Temperature on Zeolite obtained by sodium hydroxide.

Crystallization temperature	**Zeolites phases and other synthesis products**
60 °C	Zeolite NaA
80°C	Zeolite NaA +Sodalite
100 °C	Sodalite

B. The effect of crystallization temperature on zeolite formation by potassium hydroxide

According to the XRD spectra, when the crystallization temperature is 60°C the product zeolite is the amorphous phase with some unknown peaks (fig 4). And when the crystallization temperature increases to 80°C and 100° the product zeolite is Unnamed Zeolite (fig 5,6).

The results are listed in Table II.

Table II: Effect of crystallization Temperature on Zeolite obtained by potassium hydroxide

Crystallization temperature	**Zeolites phases and other synthesis products**
60 °C	amorphous
80°C	Unnamed Zeolite
100 °C	Unnamed Zeolite

C. The **effect of crystallization temperature on zeolite formation by ammonium hydroxide**

The effect of crystallization temperature on zeolite preparation with ammonium hydroxide was studied by varying temperature from 60ºC, 80ºC and 100ºC (.Fig 7, Fig. 8 and fig 9). We note the apparition of some peaks with amorphous phase at 60 °C. When the temperature increase to 80ºC for 24hrs, the product obtained is only NH_4NaA. At 100ºC, we can note the formation of sodalite. The table III gives the zeolite formed in different crystallization temperature.

Table III :Effect of crystallization Temperature on Zeolite obtained by ammonium hydroxide

Crystallization temperature	Zeolites phases and other synthesis products
60 °C	Zeolite NH_4NaA + amorphous
80°C	Zeolite NH_4NaA
100 °C	Sodalite

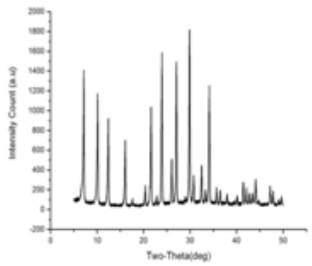

Fig 1: crystallization Temperature T=60°C. XRD spectrum of Prepared Zeolite with sodium hydroxide,

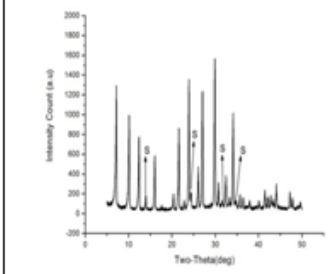

Fig 2: crystallization Temperature T=80°C. XRD spectrum of Prepared Zeolite with sodium hydroxide

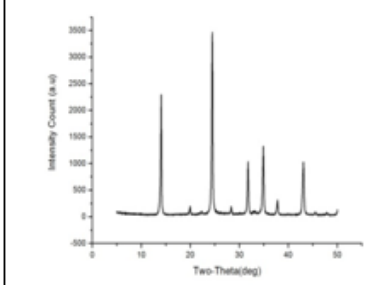

Fig 3: crystallization Temperature T=100°C. XRD spectrum of Prepared Zeolite with sodium hydroxide

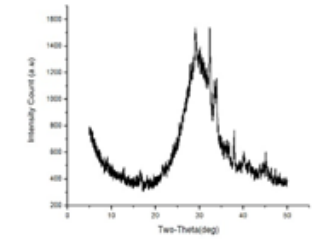

Fig 4: crystallization Temperature T=60°C. XRD spectrum of Prepared Zeolite with potassium hydroxide

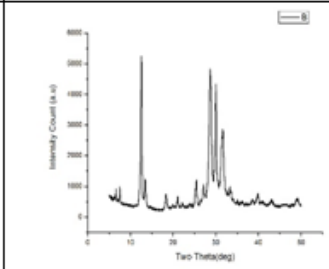

Fig 5: crystallization Temperature T=80°C. XRD spectrum of Prepared Zeolite with potassium hydroxide

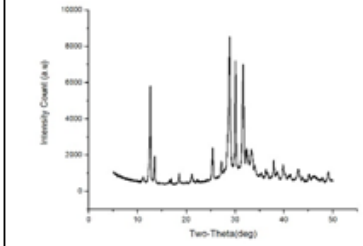

Fig 6: crystallization Temperature T=100°C. XRD spectrum of Prepared Zeolite with potassium hydroxide

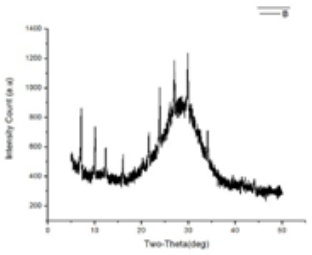

Fig 7: crystallization Temperature T=60°C. XRD spectrum of Prepared Zeolite with ammonuim hydroxide,

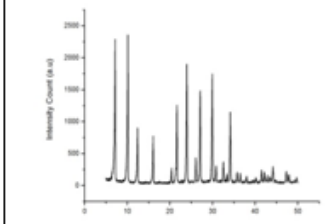

Fig 8: crystallization Temperature T=80°C. XRD spectrum of Prepared Zeolite with ammonuim hydroxide

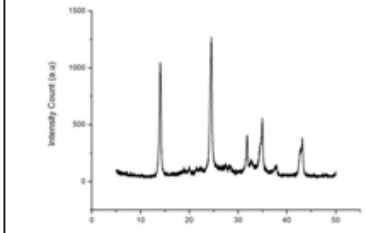

Fig 9: crystallization Temperature T=100°C. XRD spectrum of Prepared Zeolite with ammonuim hydroxide

IV. Conclusion

In the present work, it is concluded that the optimum conditions to prepare zeolite A depended on the bases and the crystallization temperatures. It is possible to synthesize the zeolite A with sodium hydroxide and the ammonium hydroxide as bases and 80°C as crystallization temperature. If we increase the temperature to 100°C, we obtain the sodalite. With our experimental conditions, we note the absence of the formation of zeolite A in the case of the of the potassium hydroxide.

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