

**Synthesis of Zeolite Beta Using Seawater Instead of Deionized Water**

Djamal Dari\*, Azzeddine Farid Houari, Christian Beling, Fatiha Djafri, Abdelkader

Bengueddach, Mohamed Sassi

*Laboratory of Materials Chemistry, Department of Chemistry, University of Oran1 Ahmed Benbella, PB 1524 El Mnaouer Oran, Algeria.*

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**Abstract**

In this paper, zeolite Beta (BEA structure) was successfully obtained by hydrothermal synthesis, using seawater as a solvent and a Na source. The effect of the Si/Al molar ratio, Si source and water source upon the synthesis of the Beta zeolite was studied. The synthesized materials were characterized by X-ray diffraction and thermogravimetry. The main results of this investigation show that Beta zeolite was obtained from aluminosilicate gels as well as in the absence of aluminium. However, when seawater was replaced with deionized water in the absence of NaCl, no zeolitic structure was formed. This result reveals that the sodium cation contained in the seawater plays a crucial role in the crystallization of Beta zeolite.

Keyword: zeolite synthesis, Beta zeolite, seawater, deionized water, characterization.

**1. Introduction**

Zeolites are crystalline aluminosilicates with a regular framework which leads to an ordered pore structure with size of less than 2 nm. Due to the controlled porosity and diversity of structures, zeolites are extensively used in ion exchange, separation or adsorption and catalysis [1].

Zeolites are generally synthesized under hydrothermal conditions using hydrogels prepared from aluminate, silicate, alkaline cation, quaternary ammonium salts, mineralizing agent ( $\text{OH}^-$  or  $\text{F}^-$ ) and deionized water [2].

Among hundreds of zeolitic structures, Beta (BEA structure) is one of the several zeolites having realized industrial application, especially in the petroleum industries and fine chemical reactions, due to its controlled acidity and thermal stability [3-5]. Beta is a large pore zeolite with a three-dimensional structure. It was first synthesized by Wadlinger et al. from a gel containing the tetraethylammonium hydroxide (TEAOH) as the structure-directing agent [6].

The objective of this work is to examine possibility of using seawater instead of deionized water in laboratory synthesis of Beta zeolite from silica and alumina commercial sources.

Up to now, only a few papers report the use of seawater during the hydrothermal synthesis of artificial zeolite from fly ash [7-10] and volcanic ash [11] as a source of silica and alumina. The synthesizing process for zeolite from these materials requires an alkaline treatment using NaOH at high temperatures to assure the conversion of the fly ash and volcanic ash into zeolite. Whereas the use of pure species of silica and alumina does not require this treatment. In this case, seawater constitutes the only source of sodium. Therefore it is possible to verify the role played by the Na contained in seawater in the synthesis of zeolites.

The use of seawater in the synthesis of zeolites could cut down the costs for large-scale utilization of demineralized water. In addition, the presence of sodium in seawater may have a role in zeolite formation [12-14]. Recently, it has been reported that Na affects both the nucleation and the growth processes of zeolites [15].

Our study can provide a starting-point to develop a new economically advantageous method for the production of useful materials (zeolites) using seawater. The experiments involved were performed using both seawater and demineralized water, separately. Therefore, the role played by Na of

\*Corresponding author e-mail: [dari\\_djamel@yahoo.fr](mailto:dari_djamel@yahoo.fr)

Receive Date: 28 November 2021, Revise Date: 02 February 2022, Accept Date: 24 March 2022

DOI: 10.21608/EJCHEM.2022.104358.4956

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seawater can be verified.

## 2. Experimental

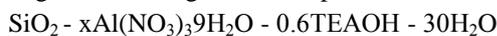
### 2.1 Synthesis

Seawater was collected at the seaside of Tlemcen state in Algeria, and its chemical composition was performed by 881 Compact IC pro ion chromatography (Table 1), with column metrosep C4-100 for the determination of cations and with column metrosep A Supp 250 for the determination of anions.

Table 1. Chemical composition of the seawater (g/l)

pH	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
8.2	13.555	0.411	0.384	1.729	22.359	2.174

The Beta zeolites was synthesized from gels having the following molar composition:



Where x varied from 0 to 0.1.

The reaction mixtures were prepared as follows: aluminum nitrate hydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Merck) and tetraethylammonium hydroxyde (TEAOH, Liquid 35%, Alfa Aisar) were dissolved in seawater and then colloidal silica (Ludox AS40, Liquid 40%, Sigma-Aldrich) or silica gel (Diasil 200, Diatom) was added to the solution. After mixing for 30 minutes, the resulted homogeneous gel was heated at 150 °C for 5 days in a PTFE-lined stainless-steel autoclave, under static conditions. The solid product was recuperated by filtration, washed with distilled water and finally dried at 80 °C for 6 hours.

### 2.2 Characterization

Powder X-ray diffraction (XRD) data were obtained by a Panalytical-Empryean diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The percentage of crystallinity of synthesized zeolites was evaluated by the ratio of the sum of the areas of the characteristic peaks of the Beta zeolite at 2 theta of 7.38, 21.09 and 22.19°, and that taken as a reference (100% crystallinity). The reference sample had the highest sum of areas (sample 08).

$$\% \text{Crystallinity} = 100 \times \frac{\sum (\text{area peak at } 2\theta \text{ of } 7.38, 21.09 \text{ and } 22.19^\circ)}{(\text{area peak at } 2\theta \text{ of } 7.38, 21.09 \text{ and } 22.19^\circ)_{\text{Ref}}}$$

The thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on a thermal analyser model Labsys EVO. The experiments were performed in the temperature interval from 30 to 800 °C, with heating speed of

10 °C/min and under nitrogen flow. Flame Photometer model PFP7 Jenway was used to measure the Na content of zeolites Beta. The percent synthesis yield was evaluated using the following formula:

$$\% \text{Yield} = 100 \times \frac{(\text{Weight of product} - \text{mass loss from TG})}{(\text{Weight of SiO}_2 + \text{Weight of Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})} \quad [2]$$

## 3. Results and discussion

### 3.1 Synthesis

Table 2 shows the synthesis conditions and the obtained results at different Si/Al, TEAOH/Al and NaCl/Si molar ratios, compared with the results obtained using the same hydrothermal method but in the presence of deionized water.

Synthesis tests carried out in the presence of silica gel and from a gel of molar ratio Si/Al = 10 have led to different results (Table 2). The crystallization of cristobalite and the zeolite Beta were observed (sample HB02) for a molar ratio TEAOH/Si = 0.6, while the Beta zeolite is formed with zeolite Na-P1 (GIS structure), when the molar ratio TEAOH/Si = 1 (sample HB03). Additionally, the synthesis carried out in the presence of deionized water and NaCl also led to the crystallization of cristobalite and the Beta zeolite (HB01 sample).

Syntheses performed in the presence of Ludox as silica source led to the crystallization of pure Beta zeolite (samples HB04 and HB05). However, only the amorphous phase was obtained if seawater was replaced by deionised water, in the absence of NaCl (sample HB07). These results reveal that the sodium contained in the seawater is an important factor in the synthesis of BEA zeolite.

The results mentioned above show that alkaline cations are the key factor for the crystallization of zeolite from gels of low Si/Al molar ratio. In this case, the alkaline cation plays both the role of structure directing agent by promoting the formation of certain building units and charge balancing agent of the negative charge of Si-O-Al<sup>-</sup> species [16, 17]. The charge properties, geometric configuration and atomic size of the alkaline cation also affect the polymerization of aluminosilicates gel and the crystallization of the zeolite [18].

The Si/Al molar ratio and the source of silica also constitute an important parameter: with relatively large amounts of Al (at the Si/Al of 10) the use of ludox leads to the formation of pure Beta zeolite. Whereas, cristobalite was produced together with

Beta zeolite, when the silica gel was used as the silica source.

Table 2. Compositions of the gels and results of the syntheses

Samples	Water source	Si source	Si/Al	TEAOH/Al	NaCl/Si	Obtained phase
HB01	deionized water	Silica gel	10	0.6	0.2	BEA+cristobalite
HB02	seawater	Silica gel	10	0.6	0	BEA+cristobalite
HB03	seawater	Silica gel	10	1	0	BEA+GIS
HB04	deionized water	Ludox	10	0.6	0.2	BEA
HB05	seawater	Ludox	10	0.6	0	BEA
HB06	seawater	Ludox	10	1	0	BEA
HB07	deionized water	Ludox	10	0.6	0	amorphous
HB08	seawater	Silica gel	50	0.6	0	BEA
HB09	deionized water	Silica gel	50	0.6	0	Cristobalite
HB10	seawater	Silica gel	50	0.3	0	BEA+ UIP*
HB11	seawater	Silica gel	$\infty$	0.6	0	BEA
HB12	seawater	Silica gel	$\infty$	0.07	0	Cristobalite

\*: unidentified phase

In the four syntheses carried out in the presence of seawater and from gels of molar ratios Si/Al = 10,50 and  $\infty$  (samples HB05, HB06, HB08, HB11), only the pure Beta phase of structure BEA has been formed. Note that in the presence of deionized water, the synthetic product was cristobalite (HB09 sample). This result shows that the Na cations contained in seawater play a significant role in the crystallisation of Beta zeolite.

The XRD patterns of Beta zeolites obtained are given in Figure 1. These diffractograms were compared to that of the simulated BEA structural type [2]. All peaks of the samples were attributed to the BEA type structure. X-ray diffraction shows that the products obtained are pure phases. However, the Beta zeolite obtained from a gel with a molar ratio Si/Al =10 is less crystallized than the Beta zeolites obtained from an aluminosilicate gel with a molar ratio Si/Al =50 and a pure silica system.

### 3.2 Characterization by TG

Figure 2 shows TG and DTA results of sample HB08, synthesized from a gel having a Si/Al molar ratio of 50, under nitrogen flow. The TGA profile for this sample has the same characteristics as the aluminosilicate Beta zeolite (Si/Al = 8) obtained by Nascimento et al. [19]. The total weight loss is approximately 12.5%, between ambient temperature and 800 ° C. The loss of mass, about 2%, observed up to 200 ° C can be attributed to the elimination of water.

The second mass loss of about 10.5% occurs between 200 and 500 ° C. This step corresponds to the desorption of the organic structure agent

(TEAOH) which is present in the porosity of the zeolite.

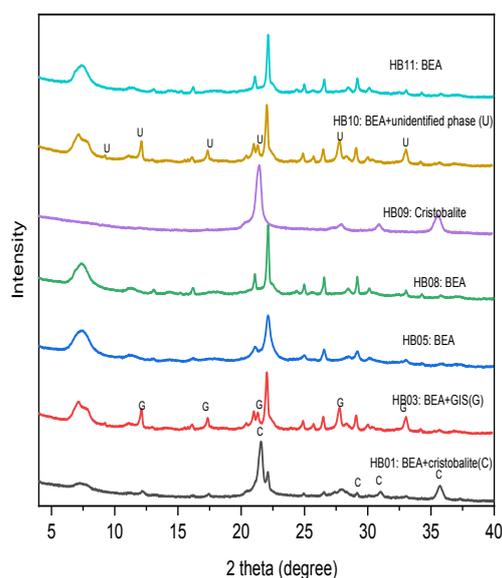


Fig. 1. X-ray diffractograms of the synthesized Beta zeolites produced by using different Si/Al molar ratio

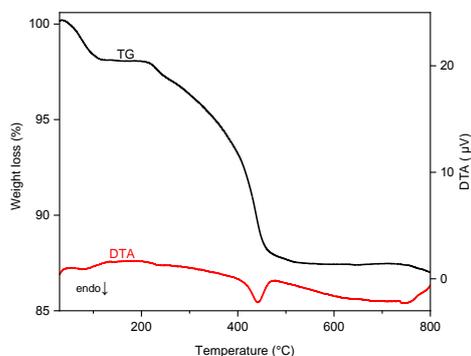


Fig. 2. TG and DTA curves of Beta zeolite synthesized at Si/Al=50

This weight loss is accompanied by a broad endothermic signal located at about 440°C [2,19].

As seen from table 3, the crystallinity degree is high and varied from 85% to 100%, and the optimal percentage was obtained from the synthesis realized from gel with a Si/Al molar ratio of 50. The results show that the values of the organic matter content of the obtained beta zeolites are very close (10–10.5 wt.%). It can be observed that there is

Sample	Si/Al	Crystallinity (%)	Yield (%)	Total organic (wt.%)	Na (wt.%)
HB05	10	85	62	10	1.48
HB08	50	100	63	10.5	1.60
HB11	∞	92	71	10.3	1.93

Table 3. characteristics of obtained beta zeolites in the presence of seawater

Table 3 shows that a positive correlation can be found between the amount of Na in the zeolite product and the Si/Al molar ratio. At first, it could be imagined that Na plays the role of charge balancing agent of the negative Al charge of the framework of the zeolite. But, the presence of a significant amount of Na in the pure silica zeolite clearly shows that there remains a net positive amount of Na. This result reveals that Na plays a crucial role in the crystallization of Beta zeolite, as well as charge balancing.

#### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgment

The authors thank The General Directorate of Scientific Research and Technological Development (DGRSDT) for providing funds through the project B00L01UN310120180015.

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proportionality between organic content and crystallinity. This shows the importance of TEAOH in the crystallization of zeolite Beta. Yield values show a positive correlation with the Si/Al molar ratio of the starting gel, however these values are close enough from 62 to 71%.

#### 4. Conclusion

Beta zeolites with different Si/Al molar ratios were obtained by hydrothermal method, using seawater as solvent. The replacement of deionized water with seawater rendered the synthesis even less expensive. It was observed that the sodium cation contained in seawater is an important factor governing the synthesis of Beta zeolite. The variation of the Si/Al molar ratio did not affect the phase purity of Beta zeolite. High yield and crystallinity were obtained at high Si/Al molar ratios.

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