

## Incorporation of organic surfactant in the porous network of NaX zeolite

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### ABSTRACT/RESUME

**Abstract:** Today, microporous solids, such as zeolites, occupy a prominent place in the industrial field and are an interest potential in various applications; Such as include gas drying, purification, refining, catalytic and ion exchange processes, the environment and even in the nuclear industry. It is because of their very remarkable properties "Adsorbents" that these materials have invaded our life.

In fact, the microporous systems of these materials are at the origin of numerous filtration and purification processes in liquid phase as well as in the gas phase, due to their excellent adsorption capacity; Capacity linked to their large surface area and the development of their porosity. In addition, the recycling and regeneration of adsorbed products are relatively easy, the long service life of the adsorbent solids is also a considerable advantage.

The aim of this work is the elaboration of a NaX zeolite modified by the incorporation of organic complex in the porous network.

Incorporation of the surfactant into the zeolite framework slightly increased the specific surface area of the modified NaX material. The surface area increases from 32 to 64 m<sup>2</sup>/g, but the surface area increases to 405 m<sup>2</sup>/g after calcination of the modified NaX material.

### I. Introduction

Zeolites are crystalline, microporous solid minerals with small pores 1 to 20 Å in diameter [1]. These materials include crystallized aluminosilicates hydrated alkali or alkaline earth metals. Today, the term zeolite is no longer restricted to aluminosilicates, but refers to any crystallized microporous silica-based solid in which part of the silicon is substituted by other elements such as trivalent elements (Al, Fe, B, etc.) or tetravalent (Ge, Ti ...). Currently, 161 different structural types of zeolite materials, including phosphate materials, are classified according to a three-letter code by International Zeolite Association base IZA [2]. Features or properties that are common to them are:

- Low density and large pore volumes;
- Molecular sieves (geometric selectivity);
- Crystalline stability in the dehydrated state;
- Cation exchange properties;
- Uniform pore size;
- Adsorbents and adsorption properties of gases and vapors;
- Separation;
- Catalytic properties;
- Solid of adjustable acidity;
- Thermal and chemical stability [3-5].

Zeolites synthetic are mainly obtained by hydrothermal treatment of a reaction mixture, at basic pH (11-14) or near neutral (5-9), respectively, in the presence of OH<sup>-</sup> or F<sup>-</sup> ion as a mineralizer at

temperatures between 60 and 200 °C. This reaction mixture, called a "gel", contains: a source of silica, an alumina source (in the case of aluminosilic zeolites), mineralizing agent and cations of alkali or alkaline-earth metals. Zeolites with Al/Si ratio of 1:1, such as zeolite A, zeolite P and zeolite X, find applications especially in the field of ion exchange [6-8].

Among the thousands of zeolites applications, they are also found in the treatment and management of radioactive waste. For example, radio isotopes ( $\text{Cs}^+$  and  $\text{Sr}^+$ ) derived from nuclear fission by products are stored in zeolites [9]. In the majority of cases, zeolites synthesis also requires the presence of organic structants (salts of quaternary amines, amines, quaternary ammoniums, alcohols, etc.). The use of these organic species introduced into the synthesis media made it possible to obtain a large number of zeolites having an increasing Si/Al molar ratio. The zeolites modification with a cationic surfactant can take place via two routes, namely the post-synthesis or extra-synthesis route.

The purpose of post-synthesis treatments is to adjust the characteristics of active centers. The most important is the exchange of the alkaline cations present in the synthetic zeolite, generally by protons which will catalyze the acid reactions, sometimes by other alkaline cations such as cesium which will give the zeolite a basic character. Or by other alkaline, alkaline earth cations or by an organic complex ..... etc [10, 11].

In the present work, we will proceed to the preparation of the mesoporous NaX and NaX zeolites by incorporating an organic surfactant, Cetyltrimethyl ammonium bromide (CTAB) into the starting gel.

We emphasize here that the elaboration of mesoporous NaX and NaX zeolites by the incorporation of an organic surfactant CTAB in the starting gel is intended for their application in the recovery of ferric ions from radioactive effluents and to see even their performance.

## II. Materials and methods

The hydrothermal syntheses of the NaX and NaX-CTAB zeolites were carried out in stainless steel autoclaves coated with a Teflon liner.

The molar compositions expressed as follows: for the zeolite NaX  $4.54 \text{ Na}_2\text{O} \text{ Al}_2\text{O}_3 \text{ 3.44SiO}_2 \text{ 180.7 H}_2\text{O}$  [12] and for the NaX CTAB material:  $4.54 \text{ Na}_2\text{O}_3.44 \text{ SiO}_2 \text{ 1 Al}_2\text{O}_3 \text{ 180 H}_2\text{O} \text{ 0.14 CTAB}$  n dodecane. The gel allowing the synthesis of the zeolite NaX and NaX-CTAB are obtained according to the following two methods, the first; in a beaker containing sodium hydroxide solution and water and with stirring, the necessary amount of the aluminum source is added in the cuttings form, the latter being allowed to stir until the total dissolution of the aluminum. After the silica source, the gel

thus obtained is stirred for hours and left to settle for 24 hours and then it is introduced into the Teflon jacket of an autoclave.

The second synthesis is the same as the previous one except after the addition of the silica, cetyl trimethyl ammonium bromide (CTAB) ( $\text{C}_{19}\text{H}_{42}\text{BrN}$ ) is added, after one hour of stirring, the dodecane is added dropwise, the mixture is stirred until homogenized and allowed to mature for two weeks.

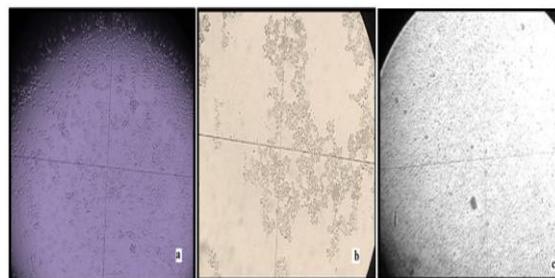
The latter are placed in a furnace heated to a fixed temperature for a period of six hours. After crystallization, the autoclave is cooled with running water and the product is recovered by filtration, washed with distilled water to  $\text{pH} = 7$ , and dried at 80 °C in an oven. The NaX materials and an amount of NaX-CTAB were calcined at 600 °C. After each use, the Teflon liners are placed in 40% hydrofluoric acid for 24 hours and then rinsed with distilled water; this ensures complete destruction of any residual crystals coming from an earlier synthesis.

## III. Results and discussion

### III.1. Optical microscopy

The synthesized materials have been characterized by different analytical techniques. The experiments carried out allowed us to have pure materials under the operating conditions.

We notice from optical microscopy very homogeneous forms of very small morphologies, hence the first observation that the materials elaborated are not amorphous as shown in the photo a of Figure 1. The incorporation of CTAB in the structure of the NaX zeolite post-synthesis did not alter the crystallinity of the initial material (see photo b). Calcining of the NaX-CTAB material also did not alter the crystallinity of the material (photo c).



**Figure 1.** Optical microscopy of samples; a) NaX; b) NaX-CTAB; c) calcined NaX-CTAB.

### III.2. X-ray diffraction

NaX and NaX-CTAB materials purity is verified by X-ray diffraction. The diffractograms are compared with the simulated NaX structural type [13, 14]. The phases obtained are well of NaX type (Figure 2 a and b). Peaks located at  $2\theta$  are respectively;

10; 11.7, 15.5; 23.5; 27 and 30° and are characteristic of the NaX zeolite and appear clearly on the diffractogram of the NaX and NaX-CTAB material with very high crystallinity, even the results found in the literature [15,16]. For NaX-CTAB material, the diffractogram indicates no presence of another compound or amorphous, and suggests that the selectivity to zeolite formed during the synthesis is very high.

### III.3. SEM

The micrograph obtained by scanning electron microscopy (Figure 3.a) illustrates the morphology of the product produced. The crystals of the NaX material are in cubic form [17], characteristic of the NaX zeolite and similar to that reported in the literature [18], having a dimension of the order of 1 μm. The crystals have regular geometric shapes. This micrograph shows only one crystalline phase. EDS microanalysis of the elaborated NaX material allowed the qualitative determination of its chemical composition as shown in Figure 3.b and the results are shown in Table 1. Si/Al molar ratio

of the NaX elaborated material is 1.5; This ratio is in agreement with the ratio of faujasite X (Si/Al = 1.5) [19].

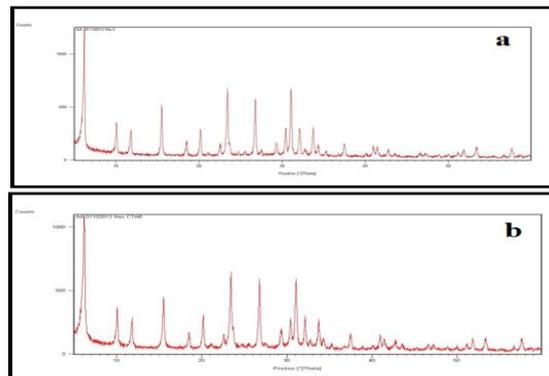


Figure 2. X-ray diffractograms of materials; a) NaX, b) NaX-CTAB

Table 1. Anhydrous chemical composition of NaX material

Elaborate material NaX	% By mass of oxides			% By mass of elements			Mass ratio	
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Si	Al	Na	Si/Al	Na/Al
	112.5	62.08	22.48	52.46	32.87	16.68	1.5	0.5

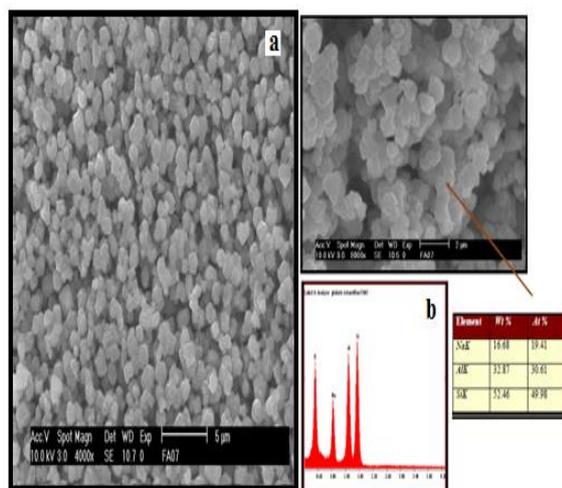


Figure 3. SEM; a) Micrograph of NaX-developed material and b) Energy spectra and chemical compositions of NaX material

### III.4. TGA and DSC

Thermogravimetric analysis (TGA) results of the calcined NaX and NaX-CTAB and calcined NaX-CTAB materials carried out under a stream of nitrogen are shown in the following figures. TGA curves of Figures 4 and 6 for NaX and calcined NaX-CTAB samples show a total mass loss of order of 20.8 and 21% successively, from 50 to 200 °C. These different mass losses can be interpreted by the departure of water molecules (dehydrating water) for NaX and calcined NaX-CTAB samples, the DSC curves show that the process is endothermic. Beyond 200 °C the masses of two samples remain stable. This indicates that both materials have a very stable structure up to 900 °C.

For NaX-CTAB sample, analysis result of thermogravimetry (TGA) is shown in Figure 5, this curve shows a total loss of mass of approximately 24%. From 50 to 200 °C the mass loss (22.48% of the total mass) can be interpreted by the departure of water molecules, and then between about 400-500 °C (loss of mass of 1.25%, can be attributed to the desorption of organic molecules (structurant decomposition) (CTAB). DSC curve shows that the reactions are endothermic.

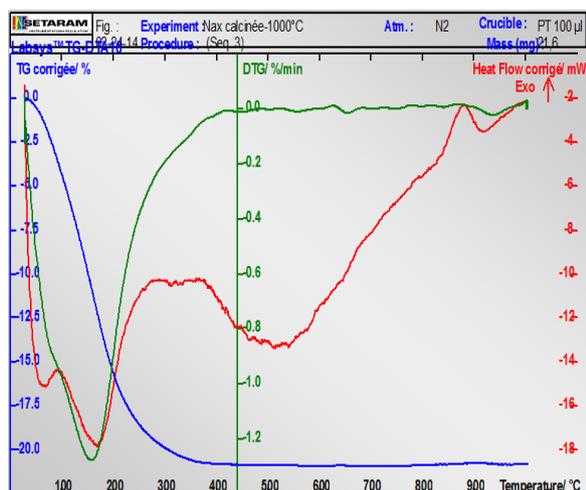


Figure 4. TGA and DSC spectrum of NaX material.

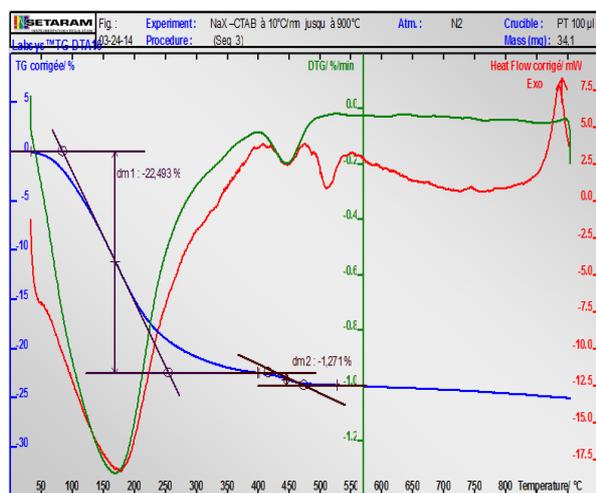


Figure 5. TGA and DSC spectrum of NaX-CTAB elaborate material.

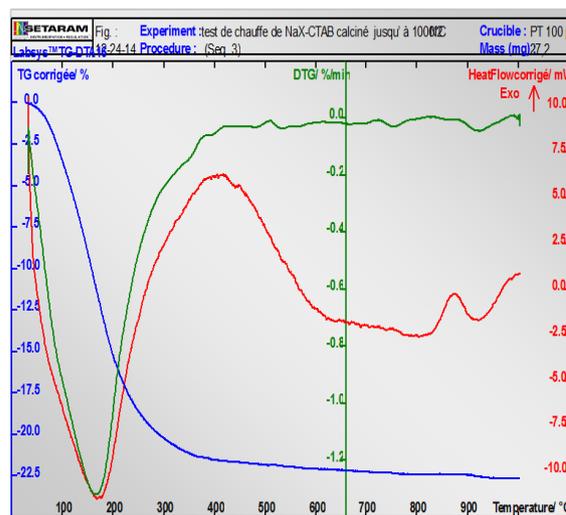


Figure 6. TGA/ DSC diagrams of calcined NaX-CTAB material

### III.5. BET

Nitrogen adsorption made it possible to evaluate the specific surfaces of NaX, NaX-CTAB and calcined NaX-CTAB materials. Brunauer, Emmet and Teller (BET) have designed a multilayer adsorption model of nitrogen molecules. For NaX material, the surface area value is about 32.78 m<sup>2</sup>/g, it reaches 64.21 m<sup>2</sup>/g for NaX-CTAB material, but about NaX-CTAB calcined specific surface is increasing considerably to 405.5 m<sup>2</sup>/g. According to these results, surfactant incorporation into the zeolitic framework increased the surface area both materials NaX-CTAB and calcined NaX-CTAB.

#### IV. Conclusion

Zeolites NaX and NaX-CTAB were developed hydrothermally. Then thermal analyzes DSC and TGA made it possible to determine the thermal stability at 900 °C for all these elaborate materials. Si/Al ratio of pure zeolite NaX synthesized is equal to 1.5 determined by the dispersive energy spectroscopy (EDS) technique. Analysis by scanning electron microscopy shows well-formed crystals having a cubic form characteristic of a faujasite type zeolite having a dimension order of 1 µm. Furthermore crystals have regular geometric shapes.

The incorporation of surfactant Cetyltrimethyl ammonium bromide (CTAB) into zeolitic framework slightly increased surface area of NaX-CTAB material; which increases from 32 (for zeolite NaX pur) to 64 m<sup>2</sup>/g. However, this one increases to 405 m<sup>2</sup>/g after calcination of NaX-CTAB material.

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#### V. References

1. Scott, J.; Guang, D.; Naeramitnamsuk, K.; Thabuot, M.; Amal, R. Zeolite synthesis from coal fly ash for the removal of lead ions from aqueous solution. *Journal of Chemical Technology and Biotechnology*. (2001) 77, 63–69.
2. Database of Zeolites Structures. <http://www.iza-structure.org>. Accessed 22 June 2014.
3. Payra, P.; Dutta P.K. *Handbook Of Zeolite Science And Technologies*, Marcel Dekker (2003).
4. Plee, D.; Zeolites. *Engineering Technique, Treaty of Engineering Processes* (2003).
5. Walton, K.S.; Abney, M.B.; Levan, M.D. CO<sub>2</sub> Adsorption In Y And X Zeolites Modified By Alkali Metal Cation Exchange, *Microporous and Mesoporous Materials*. (2006) 91, 78-84.
6. Nah, I.; Hwang, K.; Jeonq, C.; and Choi, H.B. Removal of Pb ion from water by magnetically modified zeolite. *Minerals Engineering*. (2006) 19, 1452–1455.
7. Ichiura, H.; Okamura, N.; Kitaoka, T.; and Tanaka, H. Preparation of zeolite sheet using a papermaking technique Part II The strength of zeolite sheet and its hygroscopic characteristics. *Journal of Materials Science*. (2001) 36, 4921–4926.
8. Falamaki, C.; Afaran, M.S.; Aghaie, A. In-situ crystallization of highly oriented silicalite films on porous zircon supports. *Journal of the American Ceramic Society*. (2006) 89, 408–414.
9. Chelishchev, N. F. *Natural Zeolites 93' : Occurrence, Properties, use*, International Committee On Naturel Zeolites , Ed. Ming D.W, Mumpton A , Brockport, New York, 1995.
10. Akyil, S.; Aslani, M.A.A.; (Olmez) Aytas, S. *Journal of Alloys and Compounds*. (1998) 271-273, 769-773.
11. LubomiraTasheva. Licentiate Thesis. Lulea University of technology Sweden 1999.
12. Romero, M.D.; Ovejero, G.; Rodríguez, A.; Gómez. J.M. *Microporous and Mesoporous Materials*. (2005) 81(1), 313-320.
13. Treacy, M.M.J.; Higgins, J.B.; Elsevier (2001). Amsterdam, London, NewYork, Oxford-Paris-Shannon-Tokyo.
14. Doula, M.; Loannou, A.; Dimirkou, A. *Journal of Colloid and Interface Science*. (2002) 2, 245, 237-250.
15. Poltowicz, J.; Pamin, K.; Tabor, E.; Haber, J.; Adamski, A.; Sojka, Z. *Applied catalysis A: General* (2006) 299, 235-242.
16. Joshi, U.D.; Joshi, P.N.; Tamhankar, S.S.; Joshi, V.V.; Rode, C.V.; Shiralkar, V.P. *Applied Catalysis A: General* (2003) 239, 209-220.
17. Shuzhen, Liu.; Xuejing, Cao.; Liansheng, Li.; Caijin, Li.; Yanyan, Ji.; Feng-Shou, Xia o. *Colloids and surface A: Physicochemical Engineering Aspects*. (2008) 318, 269-274.
18. Coutinho, D.; Balkus, K.J.Jr. *Microporous and Mesoporous Materials*. (2002), 52, 79-91.
19. Breck, D.W. *Zeolite Molecular Sieves structure Chemistry and Use* Eds Wiley Interscience, New York (1974).

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