Synthesis and Characterization of Zeolite Obtained from Natural Kaolinite in the Jabal Nafusah, Libya

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Abstract

Zeolite NaA materials were synthesized successfully by hydrothermal method using the Jabal Nafusah kaolinite. In the first step, kaolinite [20g,125µm-particle size] has been calcined at 600 °C for 2h. confirm the transformation to the metkaolinite phase which has been detected during the calcination process in muffel funnece. As a second step, the zeolitisation experiments have been carried out under hydrothermal conditions. The metkaolinite obtained has been reacted with 200 ml of NaOH solutions of different concentrations in autoclaves /reflex at 105 °C for 2 h. The reaction product was found to be essentially sodium metakaolinate with the NaOH solution of 4 N. In third step filtration- filter the sodium metakaolinate and then dry. Prepation of sodium silicate- take 5 grams of NaOH and 5 grams of Sio2 in 25ml of distilled water, heat and stir the contents gently. Prepation of sodium aluminate - take 5 grams of NaOH and 5 grams of Al(OH)3 in 25ml of distilled water, heat and stir the contents gently mixing of sodium silicate and sodium aluminate until optimum solubility , in the fourth step-thermal-method; heat the mixture of sodium metakaolinate, sodium silicate, and sodium aluminate at 600 °c for 2 h the products obtained from the experiments have been characterized by using infrared spectroscopic, x-difraction analysis and electron microscopc methods. Zeolite NaA can be obtained from kaolinite under the conditions applied showing that a metakaolinisation can be achieved at 600 °C which is much lower than the temperatures given in the literature, 700-900 °C and also the time necessary for formation of zeolite NaA is less than that of the previous works.

Keywords: *Zeolite NaA; Kaolinite;* Characterization Synthesis*; hydrothermal synthesis;* X-ray diffraction

INTRODUCTION

The paper industry generates a significant amount of solid wastes requiring appropriate disposal. Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals. The frameworks are composed of [SiO4]4 and [AlO4]5 tetrahedra, which corner-share to form different open structures. Negative charge of lattice is compensated by the positive charge of cations located at specific positions of zeolite framework (Bekkum et al., 1991; Breck, 1974). In most of zeolites the compensating cations are usually mono- and bi-valent metal ions and/or their combinations (e.g. Engelhardt and Michel, 1987; Takaishi et al., 1995; Earl and Deem, 2006). In accordance with the Loewenstein's rule (Loewenstein, 1954), Al-O-Al bonds do not exist in aluminosilicate frameworks of zeolite. Instead of the tetrahedrally bonded atoms Si and Al, so-called ''T-atoms'', others such as P, Ga, Ge, B, Be, etc. can exist in the framework as well (McCusker and Baerlocher, 2001; Takaishi et al., 1995). The synthesis of zeolites in forms suitable for industrial applications is of great importance. The first synthesis of zeolite was attempted by St. Claire-Deville in 1862. Barrer's pioneering work in 1948 demonstrated that a wide range of zeolites could be synthesized from aluminosilicate gels.

At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes (Breck, 1974; Szoztak, 1998). However, the preparation of synthetic zeolites from chemical sources of silica and alumina is expensive. Such costs may be reduced by the use of clay minerals, volcanic glasses (perlite and pumice), rice husks, diatoms, fly ash or paper sludge ash as starting materials (e.g. Adamczyk and Bialecka, 2005; Querol et al., 1997; Saija et al., 1983; Tanaka et al., 2004; Walek et al., 2008; Wang et al., 2008). Zeolite has also been developed by the transformation of one zeolite type into other zeotypes (Rios et al., 2007; Sandoval et al., 2009).

Previous work has shown that kaolin is not stable under highly alkaline conditions and different zeolitic materials can form, and that kaolin is usually used after calcinations to obtain a more reactive phase (metakaolin). After dehydration (endothermic dehydroxylation), kaolin is transformed into amorphous metakaolin (Fialips, 1999; Gougazeh and Buhl, 2010; Smykatz-Kloss, 1975). Raw kaolin and metakaolin have been used as the Al and Si sources for synthesis of zeolite Linde Type A, X, Y, P, 4A, NaA, KI, cancrinite, sodalite, hydroxysodalite, faujasite, phillipsite, chabazite and several other types of zeolites (e.g., Buhl and Loens, 1996; Covarrubias et al., 2006; Dudzik and Kowalak, 1974; Gualtieri et al., 1997; Lin et al., 2004; Loiola et al., 2012; Marcelo et al., 2007; Mon et al., 2005; Rees and Chandrasekhar, 1993; Sanhueza et al., 1999; Vilma et al., 1999; Zhao et al., 2004).

NaA Zeolite is of great industrial importance due to its molecular sieving, ion exchange and water adsorption properties. With the molar ratio Si/Al nearly equal to one, kaolin is an ideal raw material for preparing NaA zeolite. Kaolin was one of the most versatile industrial minerals and was used extensively for many applications (Murray, 1991). The synthesis of NaA zeolite from kaolin source was started from the 1970s (Breck, 1974; Barrer, 1978) by the hydrothermal reaction of dehydroxylated kaolin with sodium hydroxide solution.

No attempt has been made previously to produce zeolite type A from natural Jordanian kaolin. In this work, Zeolite A was hydrothermally synthesized from Jordanian kaolin, and the effect of NaOH concentration (1.0, 1.5, 2.0, 2.5, 3.5 and 4 M NaOH) was investigated. The synthesized products were characterized by X-ray diffraction (XRD) scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

RESULTS AND DISCUSSION

The kaolin used was fully characterized (mineralogical and chemical composition, thermal behavior and particle size distribution) and the results were similar with previous study by Gougazeh and Buhl (2010). The grain size analysis of bulk kaolin sample was separated by Atterberg methods. The quantitative analysis of the mineral content of the natural Jabal

Nafusah in Libyan kaolin has been worked out by a combination of XRD and XRF investigations. The physical, chemical and mineralogical properties of the kaolin under study are presented in Table 1 with Figure 1-6. The XRD pattern of metakaolin obtained by heating the kaolin for 3 h at 650° C resembled others, except for the peaks due to admixed impurities. The properties of the reaction intermediates and products were determined by various techniques to give the following results.

Results on the graphic and phase identification of the sample#0.09 mic on Figure 1 and semi quantitative analysis (see Table A1).

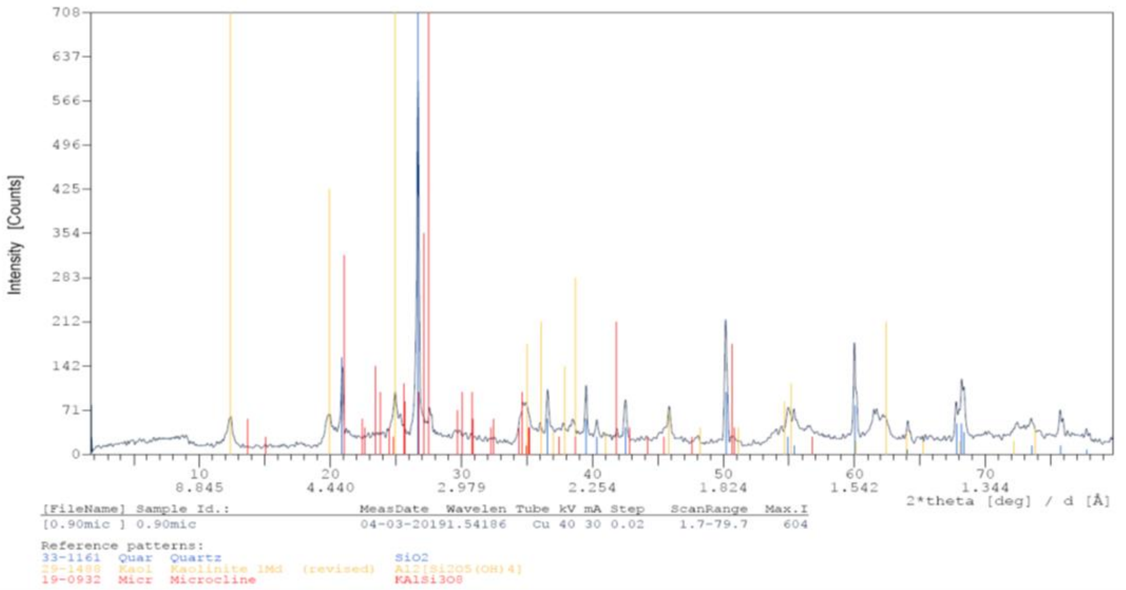

Figure 1. XRD patterns of quartz, kaolinite and, microcline and associated phases obtained by hydrothermal synthesis.

Table A1: Properties of Jabal Nafusah kaolin on Figure 1.

Phase%	SUM 100.00	Quar 23.23	Kaol 32.71	Micr 44.06
K_2O%	7.46			7.46
SiO_2%	66.99	23.23	15.22	28.54
Al_2O_3%	20.99		12.92	8.07
H_2O%	4.56		4.56	
LOI %	4.56	0.00	4.56	0.00

Results on the graphic and phase identification of the sample#0.75 mic on Figure 2 and semi quantitative analysis (see Table A2).

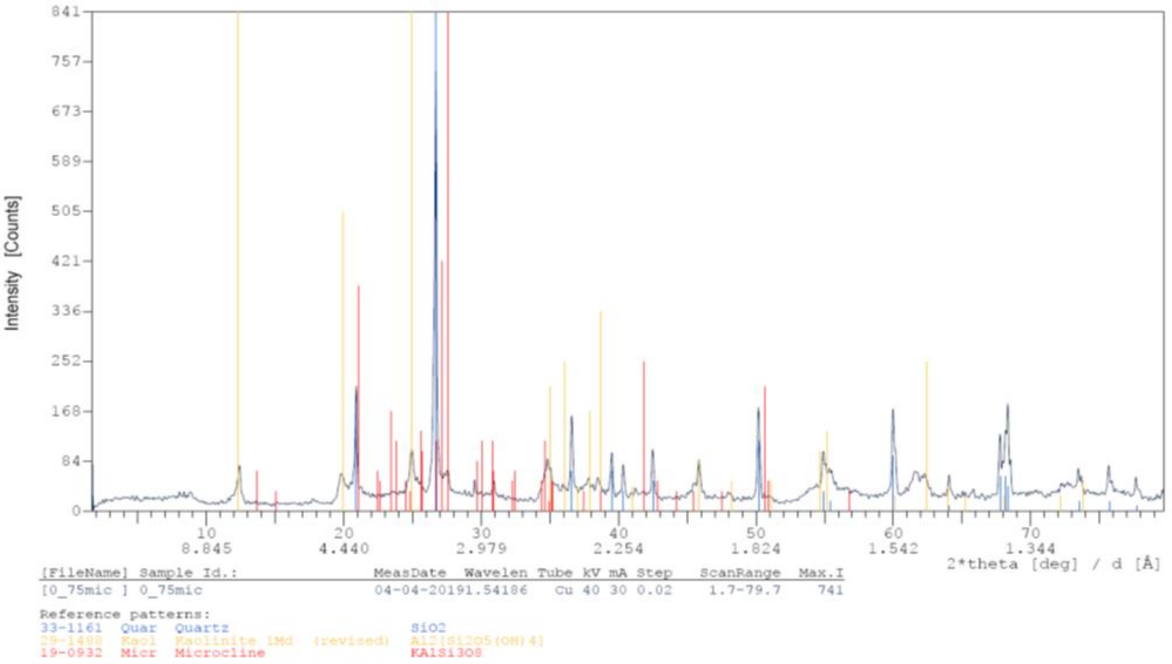

Figure 2. XRD patterns of quartz, kaolinite and, microcline and associated phases obtained by hydrothermal synthesis.

Table A2: Properties of Jabal Nafusah kaolin on Figure 2.

Phase%	**SUM 100.00**	**Quar 24.73**	**Kaol 29.70**	**Micr 45.56**
K_2O%	7.71			7.71
SiO_2%	68.07	24.73	13.83	29.51
Al_2O_3%	20.08		11.73	8.35
H_2O%	4.15		4.15	
LOI %	4.15	0.00	4.15	0.00

Results on the graphic and phase identification of the Sample#125 mic on Figure 3 and semi quantitative analysis (see Table A3).

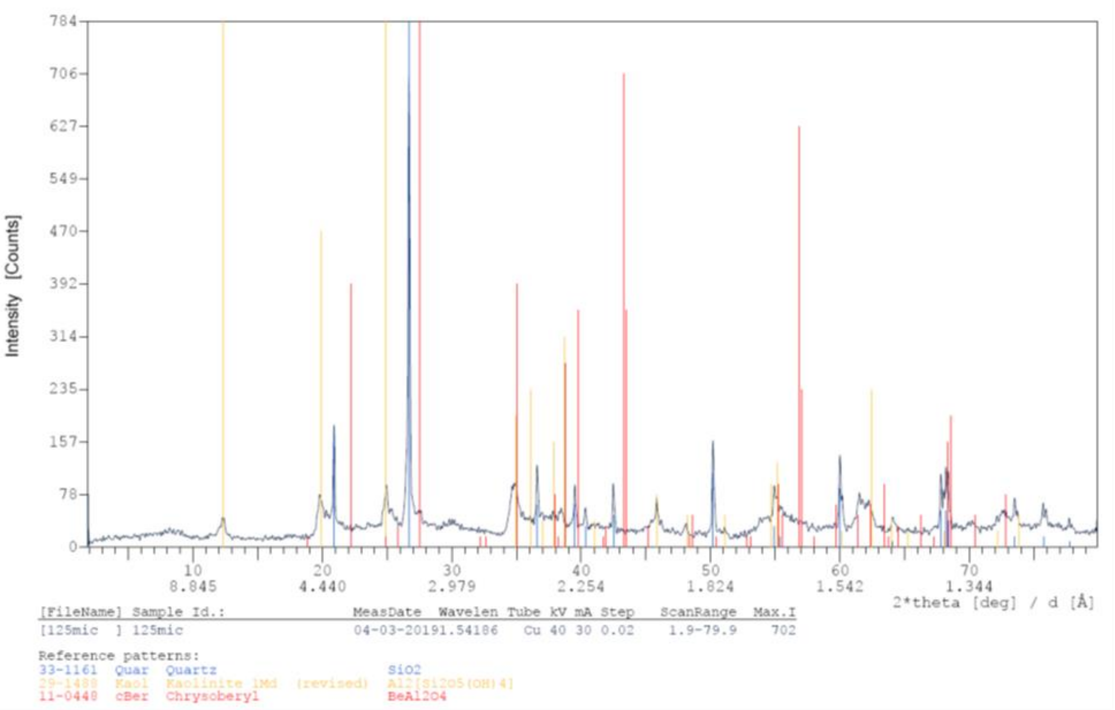

Figure 3. XRD patterns of quartz, kaolinite and, chrysoberyl and associated phases obtained by hydrothermal synthesis.

Table A3: Properties of Jabal Nafusah kaolin on Figure 3.

Phase%	**SUM 100.00**	**Quar 27.84**	**Kaol 39.59**	**cBer 32.57**
SiO_2%	46.27	27.84	18.43	
Al_2O_3%	41.79		15.64	26.15
BeO%	6.42			6.42
H_2O%	5.53		5.53	
LOI %	5.53	0.00	5.53	0.00

Results on the graphic and phase identification of the sample#355 mic on Figure 4 and semi quantitative analysis (see Table A4).

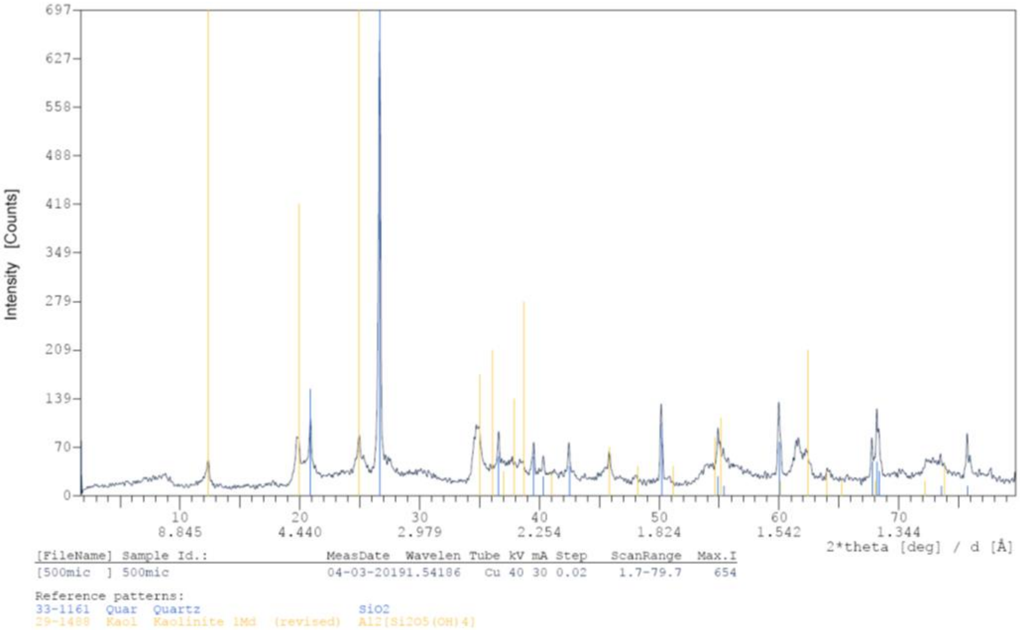

Figure 4. XRD patterns of quartz and, kaolinite and associated phases obtained by hydrothermal synthesis.

Table A4: Properties of Jabal Nafusah kaolin on Figure 4.

Phase%	SUM 100.00	Quar 35.20	Kaol 51.74	Tllr 13.07
TeO_3%	17.98			17.98
SiO_2%	59.28	35.20	24.08	
Al_2O_3%	20.43		20.43	
H_2O%	7.22		7.22	
LOI %	2.30	0.00	7.22	-4.92

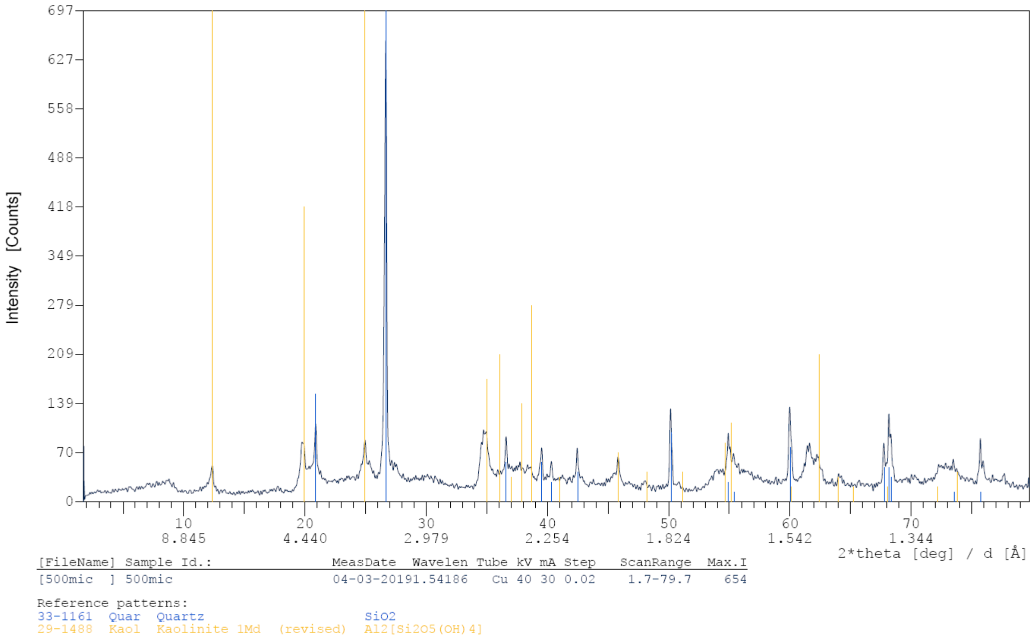

Figure 5. XRD patterns of quartz and, kaolinite and associated phases obtained by hydrothermal synthesis.

Results on the graphic and phase identification of the sample#500 mic on Figure 5 and semi quantitative analysis (see Table A5).

Table A5: Properties of Jabal Nafusah kaolin on Figure 5.

Phase%	**SUM 100.00**	**Quar 39.46**	**Kaol 60.54**
SiO_2%	67.64	39.46	28.18
Al_2O_3%	23.91		23.91
H_2O%	8.45		8.45
LOI %	8.45	0.00	8.45

Results on the graphic and phase identification of the sample#600 mic on Figure 6 and semi quantitative analysis (see Table A6).

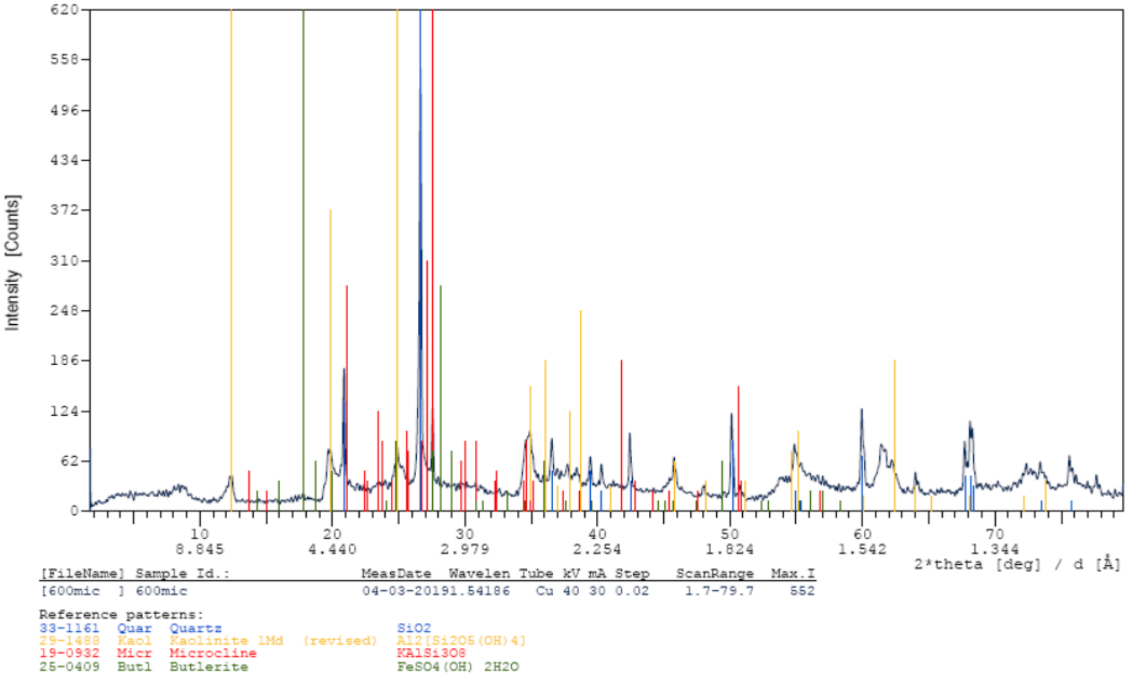

Figure 6. XRD patterns of quartz, kaolinite, microcline and, butlerite and associated phases obtained by hydrothermal synthesis.

Table A6: Properties of Jabal Nafusah kaolin on Figure 6.

Phase%	SUM 100.00	Quar 12.57	Kaol 20.22	Micr 28.13	Butl 39.07
Fe_2O_3%	15.22				15.22
K_2O%	4.76			4.76	
SO_3%	15.26				15.26
SiO_2%	40.21	12.57	9.41	18.22	
Al_2O_3%	13.14		7.99	5.15	
H_2O%	11.41		2.82		8.59
LOI %	26.67	0.00	2.82	0.00	23.85

CONCLUSIONS

Based on the results of XRD of zeolite produced by treating the activated metakaolin from natural Jabal Nafusah kaolin with various concentrations of NaOH at 600^o C for 20 h, some observations could be summarized as follows:

- The results indicated that the obtained kaolinite products contain Zeolite NaA as the major constituent phase, whereas hydroxysodalite (HS) and quartz were found as minor phases. With one exception untransformed metakaolin occurred only in considerable amounts at 1.0 M NaOH. Although the amount of untransformed metakaolin probably decreases with increasing NaOH concentration. On the other hand, amount of HS increases with the increasing NaOH concentration, which could account for the decrease in the amount of zeolite.
- The synthesized products were found to contain quartz phases as impurities coming from the natural kaolin samples (see XRD pattern in Figure 1-6).
- Zeolite was hydrothermally synthesized using kaolin as the raw material. The XRD analysis confirmed an excellent relative crystallinity.
- For a future research we are going to evaluate the efficiency of such zeolite materials in selective cation exchange as ion exchangers, adsorbents and catalysts.

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