

Comparison the Properties of Zeolite Nay Synthesized by Different Procedures

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ABSTRACT- This research was aimed to compare the morphology, crystallinity, chemical composition Si/Al and Na/Al of seven samples of NaY zeolite prepared by different procedures and different silicon sources. Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy, Energy Dispersive analysis (EDA), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) were selected to characterize the prepared samples. The FTIR results indicated that the position, height, and width of the peak are nearly identical for all synthesized samples. According to SEM results, the frame work of homoionic sodium form NaY zeolite was not widely affected, via treatment with NaCl. The EDS output indicated that, Si/Al were in the following order: NaY type 1 > USY > NaY type 3 > NH₄Y > NaY type 2 > Regenerated NaY > Homoionic sodium form. XRF analysis show that the major components of laboratory synthesized zeolites are SiO₂, Al₂O₃, Na₂O and H₂O, along with a small quantity of CaO and trace amounts of K₂O, Fe₂O₃, P₂O₅ and MgO.

KEYWORDS: NaY zeolite, Kaolin, zeolite characterization techniques, hydrothermal crystallization.

I. INTRODUCTION

Utilization of zeolite in most industrial applications required certain specifications. In this context synthetic zeolites can be tailored to meet the strict specifications imposed in adsorption and catalytic processes. (1). The sources for early synthesized zeolites were standard chemical reagents. The main problem in zeolite researches the availability and cost of raw material specifically the silica source. Zeolites have been synthesized from a variety of natural silicate. Clay minerals (2) such as kaolin, illite, smectite, interstratified illite-smectite, montmorillonite, and bentonite are widely used for zeolites synthesis. The benefits of using kaolin as an aluminosilicate source in zeolite synthesis widely known (3). Many techniques have been identified for the characterization of zeolite such as (4): FTIR, XRF, XRD, BET isotherm, EPR spectroscopy. Liu et al (3) studies NaY zeolites which are in-situ synthesized from coal-based kaolin via the hydrothermal method. Their results have shown that the crystallization temperature and the amount of added water play an important role in the formation of the zeolite. Christidis et al (5) studies the synthesis of pure FAU-type zeolite Y from a SiO₂-sinter and perlite glass. It has been concluded that inexpensive raw materials such as volcanic glasses can be used for the production of high added value zeolite Y. Recently, Krisnandi et al (6) have studied the synthesis of Na-Y nanozeolite of glassy carbon by seeding method. The variation on number of seed layers on GC (1, 2 and 3 layers), observed by SEM, shows that homogenous structure and crystal size are obtained with 1 layer of seeds. Moreover, in 2013 Smith and Gamal (7) oriented their research towards the development of greener processes for the synthesis of commercially important products. For example, they have shown that reusable zeolite catalysts can have advantages in para-regioselective nitration, halogenation, acylation and alkylation reactions of simple aromatics and hetero aromatics.

II. MATERIALS AND METHODS

2.1. Zeolite Synthesis

In the present investigation three types of zeolites: Na Y prepared by steam hydrothermal crystallization, NH₄Y and ultra stable Y (USY) zeolites were prepared in scientific laboratories in Fakultät Umweltwissenschaften und verfahrenstechnik Lehrstfuehrlluft chemie und Environmental poirutionturtr einhaltuns, Berlin, Germany(8,9). Another type of NaY zeolite

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was prepared employing the procedure followed by XuYongquan et al (10), with some modification in the step of mixing structure-directing agent with initial solution. Moreover, the homoionic sodium form NaY zeolite was prepared. In order to obtain, as far as possible, this form, the NaY zeolite, as prepared, was contacted with (1M) solution of NaCl at 60°C. The zeolite was then washed each time with (2L) of hot deionized water and oven-dried at 100°C for 24 hours. The procedure was repeated four times. Locally available natural source of silica, kaolin, was used to synthesis NaY zeolite (11). Finally, regenerated NaY zeolite was synthesized from kaolin source NaY zeolite which was used as a cation exchanger and then regenerated by (2M) Ammonium acetate solution (12). All the prepared Zeolites were collected to applied as an ion exchangers.

III. RESULTS AND DISCUSSION

3.1. Synthesized Zeolite Characterization

The structural formulae, the bulk chemical composition, morphology, crystallinity, functional groups, types of linkages, Si/Al and Si/Na of the synthesized samples were analyzed using: FTIR, SEM, EDS, XRF and XRD.

3.1.1. FTIR Spectrometry

The FTIR spectra of the synthesized NaY zeolite crystals with different morphologies were shown in Figure 1. The bands at 478 – 482 cm^{-1} assigned to the structure insensitive internal TO_4 (T-O) tetrahedral bending mode and a shoulder located at 432 cm^{-1} was the characteristics of a pore opening of external linkages. The peak at 565 cm^{-1} is attributed to the double ring external linkage peak assigned to zeolite Y in literature (13). Bands in the region 773 cm^{-1} , 690 cm^{-1} and 571– 460 cm^{-1} were attributed mainly to the symmetric stretching, double ring and T-O bending vibrations, respectively. A sharp band around 767–772 cm^{-1} was the main band characteristics of external or internal symmetric stretching, and the band 608– 611 cm^{-1} was the band characteristics of double-six-ring vibration. Lee et al. (14) and Sang et al. (1) reported that a band at 500 – 600 cm^{-1} is related to the topological arrangement of secondary units of structure in zeolites that contain the double 4 and 6 rings external linkage peak associated with the FAU structure and also observed in all the zeolite structures. The band in the range 1020 – 1098 cm^{-1} corresponded to the internal vibrations of T-O-T (T = Si, Al) tetrahedral structure (13). The vibration band at 1638 cm^{-1} was referred to bending vibration of adsorbed water molecule and the band with a peak at 3487 cm^{-1} was assigned to OH stretching (1). Finally the FTIR results indicated that the position, height, and width of each peak are nearly identical for all synthesized samples.

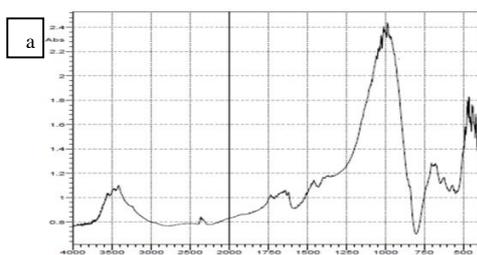


Figure 1a: FTIR Spectrum of laboratory synthesized NaY, type 1, zeolite prepared at 30 °C.

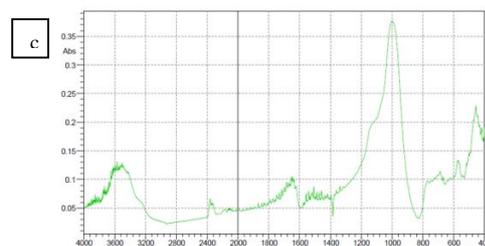


Figure 1c: FTIR Spectrum of laboratory synthesized NaY type 2, zeolite prepared at 30 °C.

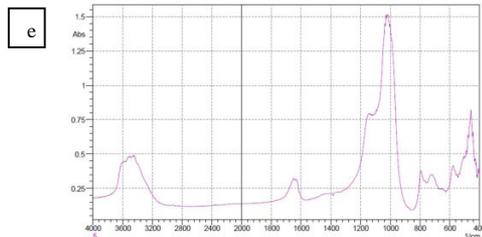


Figure 1e: FTIR Spectrum of laboratory synthesized NaY, type 3, zeolite prepared at 30 °C.

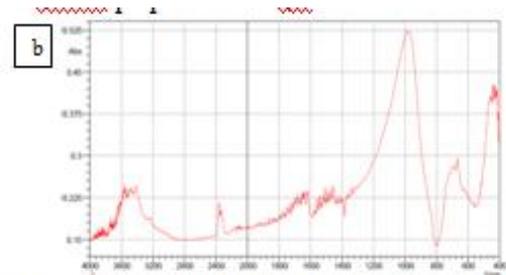


Figure 1b: FTIR Spectrum of laboratory synthesized homoionic sodium NaY, prepared at 30 °C

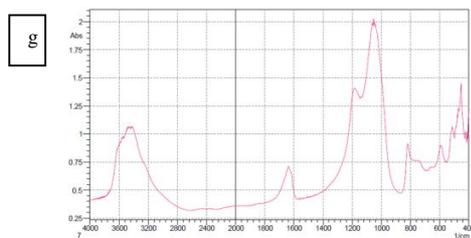


Figure 1g: FTIR Spectrum of laboratory synthesized USY zeolite prepared at 30 °C.

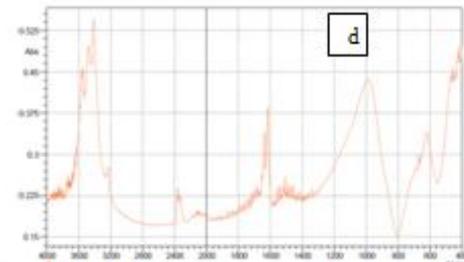


Figure 1d: FTIR Spectrum of laboratory synthesized Regenerated NaY, prepared at 30 °C

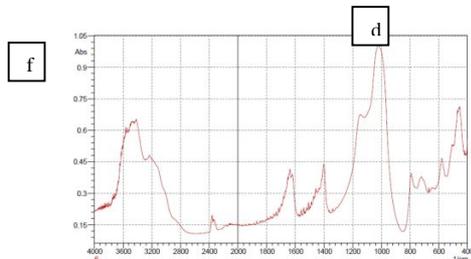


Figure 1f: FTIR Spectrum of laboratory synthesized NH₄Y zeolite, prepared at 30 °C.

3.1. 2. Scanning Electron Microscope (SEM)

Shape and size of NaY particles laboratory synthesized by different procedures were studied by SEM and images with a scale bar of 10 μm displayed in Figure 2. The SEM images (Figure 2 a & b) show, the solid product contained a mixture of multi-faced spherules crystals with an ice hockey shape with different particle diameter along with round amorphous particles. Since some particles apparently connected with other particles, the particle size distribution was expected to be large. In consequence of, they may be dissolved and oligomerized after crystal collapse time for hydrothermal zeolite NaY synthesis. This influence is caused by a long time of reaction with heating, as the mechanism of zeolitization is closely related to this effect. The SEM images of zeolite samples indicate the formation of some crystals with sharp edges and large sizes. Our results were in good agreement with that reported in literature (15). This observation is in agreement with the X-ray diffraction analysis results, and all of the synthesized samples were noticeably identified as the desired zeolite NaY morphology. Comparison of SEM image of NaY zeolite synthesized from kaolin (Figure 2c) with those of NaY synthesized via modified hydrothermal crystallization procedure and homoionic sodium form zeolite NaY respectively (Figure2 a&b), indicates that there were minimal differences between the morphology, crystal shapes and sizes. It can generally be suggested that the framework of homoionic sodium form NaY zeolite is not widely affected, via treatment with NaCl, albeit the sodium bonds are broken down inside its atomic structure.

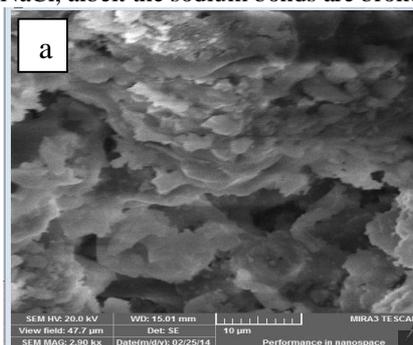


Figure 2a: SEM patterns of laboratory synthesized NaY, type 1, prepared at 30 °C.

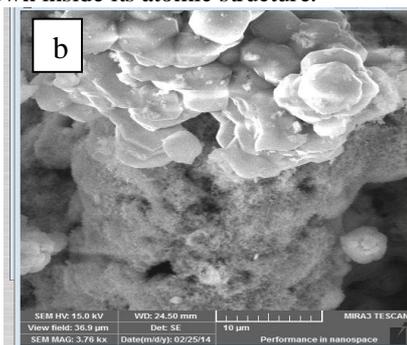


Figure 2b: SEM patterns of laboratory synthesized homoionic sodium NaY, prepared at 30 °C.

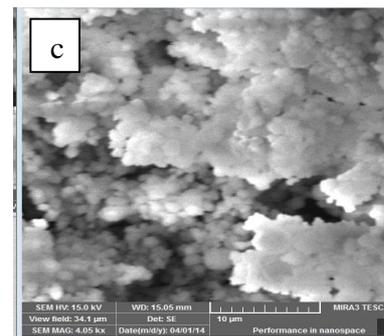


Figure 2c: SEM patterns of laboratory synthesized NaY type 2, prepared at 30 oC.

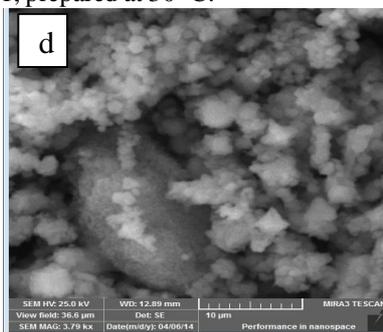


Figure 2da: SEM patterns of laboratory synthesized Regenerated NaY, prepared at 30 oC.

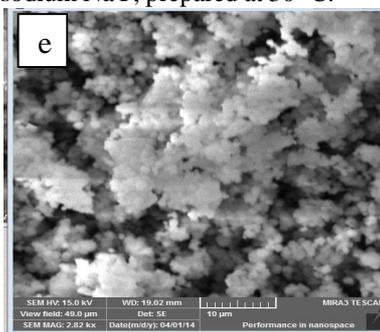


Figure 2e: SEM patterns of laboratory synthesized NaY, type 3, prepared at 30 °C.

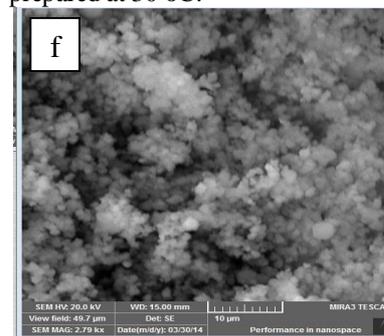


Figure 2f: SEM patterns of laboratory synthesized NH₄Y zeolite, prepared at 30 °C.

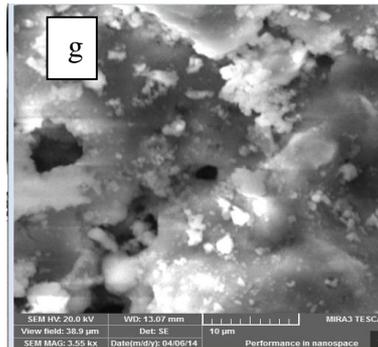


Figure 2g: SEM patterns of laboratory synthesized USY zeolite, prepared at 30 °C.

3.1.3. Energy Dispersive Spectroscopy (EDS)

EDS analysis can provide the elemental analysis (e.g. Al, Si, O, Na, etc) on the selected spots located on the external surface of a crystal. EDS allows one to identify what those particular elements are and their relative proportions in the sample. The output of an EDS analysis of the synthesized NaY zeolites by different procedures at 30 °C were shown in EDS spectra in Figure 3 and Table 1. EDS spectra of the studied samples show strong elemental signal of oxygen, silicon, aluminum and sodium. Data in Table 1 show that Si content of the synthesized zeolites were in the following order: USY > NH₄Y > NaY type 3 > NaY type 2 > homoionic sodium NaY > Regenerated > NaY type 1. This implies the three procedures employed in Germany laboratory were applicable to prepare zeolite with high Si content. The NaY zeolite prepared from kaolin, yields zeolite with 27.31 percent Si. The home modified procedure for NaY zeolite preparation yields zeolite with 17.03 percent Si, which can be increased to 20.56 or to 27.31 respectively, by either treating the prepared zeolite with (1M) NaCl to convert it to homoionic sodium form or by regenerating it.

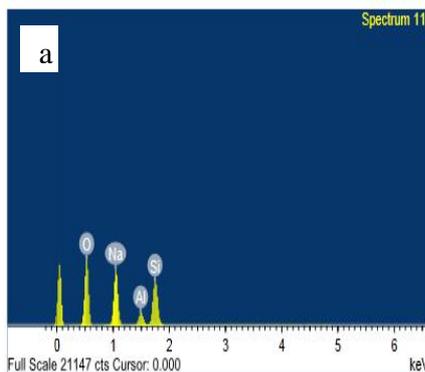


Figure 3a: EDS patterns of laboratory synthesized NaY, type 1, prepared at 30 °C.

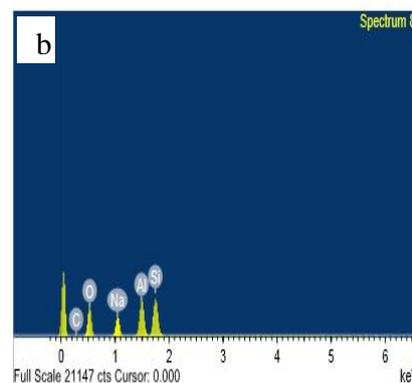


Figure 3b: EDS patterns of laboratory synthesized homoionic sodium NaY, prepared at 30 °C.

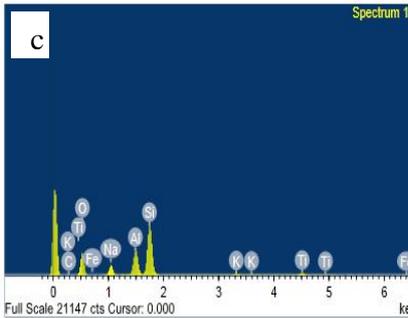


Figure 3c: EDS patterns of laboratory synthesized NaY type 2, prepared at 30 °C.

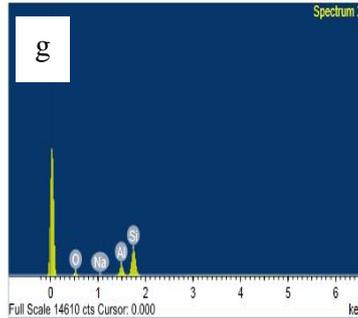


Figure 3g: EDS patterns of laboratory synthesized USY zeolite, prepared at 30 °C.

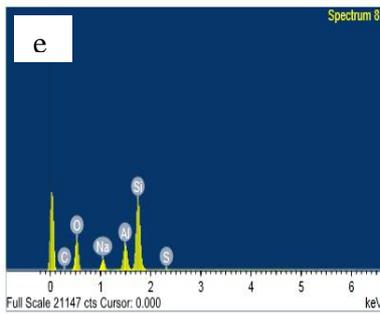


Figure 3e: EDS patterns of laboratory synthesized NaY, type 3, prepared at 30 °C.

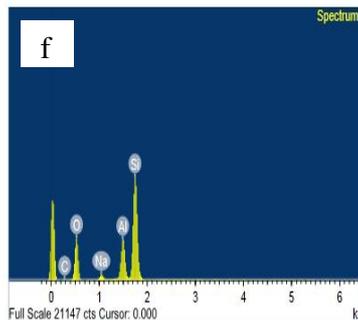


Figure 3f: EDS patterns of laboratory synthesized NH₄Y zeolite, prepared at 30 °C.

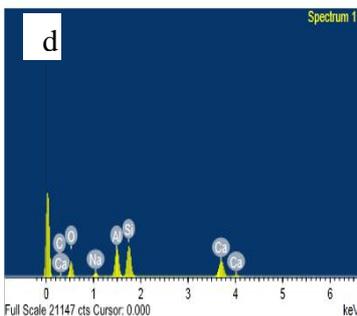


Figure 3d: EDS patterns of laboratory synthesized Regenerated NaY, prepared at 30 °C.

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In order to obtain an acceptable comparison among the synthesized samples, the weight percentages of the elements on the selected spots located on the external surface of a crystal was taken according to higher Si/Al ratios for each sample and summarized in

| Sample number | Si (Wt %) | Al (Wt %) | Na (Wt %) | O (Wt %) | Ratio Si/Al | Ratio Na/Al |
|---------------|-----------|-----------|-----------|----------|-------------|-------------|
| 1 | 17.03 | 4.72 | 25.25 | 35.00 | 3.60 | 5.35 |
| 2 | 20.56 | 16.51 | 12.42 | 45.76 | 1.23 | 0.75 |
| 3 | 27.31 | 11.50 | 7.05 | 45.05 | 2.37 | 0.61 |
| 4 | 17.49 | 13.49 | 3.52 | 44.02 | 1.29 | 0.26 |
| 5 | 30.95 | 9.64 | 6.25 | 48.21 | 3.21 | 0.64 |
| 6 | 33.37 | 10.90 | 2.09 | 48.46 | 3.06 | 0.19 |
| 7 | 52.40 | 15.59 | 1.18 | 30.83 | 3.36 | 0.07 |

Table 1. The molar values of Si/Al and Na/Al ratios were then calculated from the appeared weight percent values of elements in the EDX-spectra, and the results are listed in Table 2. The EDS output indicated that, the molar values of Si/Al were in the following order: NaY type 1 > USY > NaY type 3 > NH4Y > NaY type 2 > Regenerated NaY > Homoionic sodium form. Additionally, the EDS output indicated that, the molar values of Na/Al were in the following order:

NaY type 1 > Homoionic sodium form > NaY type 3 > NaY type 2 > Regenerated NaY > NH4Y > USY.

Table 1: The chemical content based EDS for laboratory synthesized zeolite samples at 30 °C.

3.1.4 X-Ray Diffraction

X-ray diffraction analysis was used to determine morphologies and the degree of crystallinity of synthesized samples. A 2 theta range of 3° to 50° is usually adequate to cover the most important regions of the XRD pattern, and each peak represents at least the one diffraction (2). The relative intensities of the peaks are related to the level of sample crystallization, and are determined by the type and position of all atoms in the unit cell (8). The widths of the peaks are related to the size of crystallite, i.e. they can give an indication of the crystalline quality of the sample. The XRD patterns of laboratory synthesized NaY zeolite prepared by modified hydrothermal crystallization, homoionic sodium form zeolite and NaY, prepared from natural material (Kaolin) zeolite samples prepared at 30 °C are illustrated in Figure 4. The peak positions are measured in 2-theta from 0° to 50°.

Figure 4 clearly indicates the formation of NaY zeolite in the three samples as the major peaks of identification on XRD pattern were located on $2\theta = 23.6^\circ$, 26.9° , and 31.3° . The XRD pattern also indicates that the peak in the range of $2\theta = 20-35^\circ$, which is an indicative of degrees of crystallinity (16, 17). This indicates that the most of amorphous material was being crystallized. The XRD results were further confirmed by the SEM images of the studied samples in Figure 2.

The background of a powder pattern can also give an indication about the amorphous materials, whether they are present in the sample or not. As a rule, a highly crystallized zeolite samples must have quite a flat baseline (18). Subsequently, NaY zeolite prepared from natural material (Kaolin) has a comparatively highest degree of crystallinity among the three samples. The degree of crystallinity of the studied samples as shown in their XRD patterns in Figure 4. were in the following order:

NaY, prepared from natural material (Kaolin) > NaY prepared by modified hydrothermal crystallization > homoionic sodium form NaY zeolite.

The morphology of the three samples was confirmed by XRD patterns as compared with standard NaY zeolite (Fig. 5). The samples gave peaks at positions similar to that of the standard NaY. Although all the XRD peaks of our samples were similar to those of the standard NaX, but the sequence of intensities were different. This was not surprising because our samples contain Na and traces of other cation like K, Mg, Ca and Fe, as indicated in EDS and XDF results in Tables 1 and 2 respectively, while the standard only has the Na cation. It was previously reported that the sequence of peak intensities

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depended strongly on type of cations and the presence of other cations attenuated them (19). Finally, the obtained XRD-patterns refer to nearly crystalline zeolite-Y type, indicating the formation of NaY zeolite synthesis was successful.

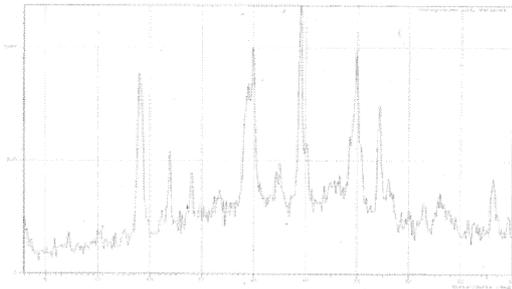


Figure 4a: XRD patterns of laboratory synthesized NaY, prepared by structure-directing agent, at 30°C.

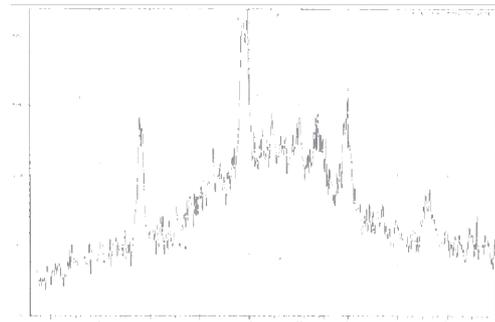


Figure 4b: XRD patterns of laboratory synthesized homoionic sodium NaY zeolite, prepared at 30°C.

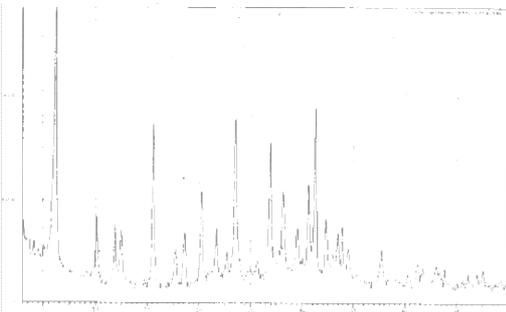


Figure 4c: XRD patterns of laboratory synthesized NaY, prepared from natural material (Kaolin) prepared at 30°C.

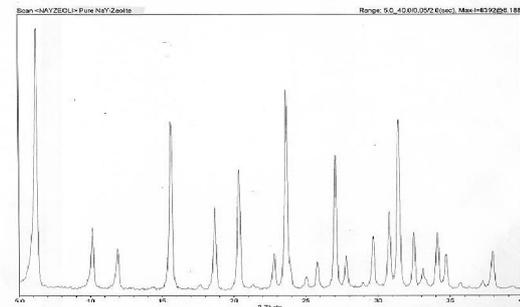


Figure 5. XRD pattern of commercial NaY zeolite powder (20).

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3.1.5. X-Ray Florescence

The structural formulae, the bulk chemical composition Si/Al of laboratory synthesized samples were determined using XRF analysis. The resulting SiO₂, Al₂O₃, Na₂O and H₂O contents and unit cell composition for different laboratory synthesized zeolites were summarized in Table 2 and Table 3.

The results of XRF analysis show that the major components of laboratory synthesized zeolites are SiO₂, Al₂O₃, Na₂O and H₂O, along with a small quantity of CaO and trace amounts of K₂O, Fe₂O₃, P₂O₅ and MgO.

The data in table 2 indicate that there is a small degree of correlation between the results obtained from EDS analysis in the amount of silicon, aluminum, sodium and oxygen for each sample, with that calculated from XRF analysis. This is attributed to the type of analysis EDS analysis represent a spot on the surface while XRF analysis represent the composition of the bulk. Moreover, a clear difference may be seen in data in Tables 2. and 3. between Si/Al-EDS value and Si/Al-XRD value for NaY zeolite prepared hydrothermal crystallization which indicates a partial collapse within the zeolite structure.

Table 2. The chemical content based on XRF analysis laboratory synthesized zeolite samples at 30 °C.

| Sample number | Na ₂ O (Wt%) | Al ₂ O ₃ (Wt%) | SiO ₂ (Wt%) | P ₂ O ₅ (Wt%) | MgO (Wt%) | K ₂ O (Wt%) | CaO (Wt%) | Fe ₂ O ₃ (Wt%) | H ₂ O (Wt%) |
|---------------|-------------------------|--------------------------------------|------------------------|-------------------------------------|-----------|------------------------|-----------|--------------------------------------|------------------------|
| 1 | 2.065 | 30.233 | 28.497 | 0.058 | 0.048 | 0.003 | 7.305 | 0.085 | 31.706 |
| 2 | 1.626 | 41.993 | 31.946 | 0.069 | 0.162 | 0.086 | 7.287 | 0.082 | 16.749 |
| 3 | 0.420 | 20.221 | 30.807 | 0.110 | 0.123 | 0.020 | 7.446 | 2.066 | 38.787 |
| 4 | 0.986 | 29.861 | 52.866 | 0.080 | 0.077 | 0.007 | 7.257 | 0.050 | 8.816 |
| 5 | 1.156 | 39.572 | 32.614 | 0.074 | 0.239 | 0.009 | 9.065 | 0.084 | 17.187 |
| 6 | 0.359 | 34.693 | 58.721 | 0.073 | 0.144 | 0.015 | 7.246 | 0.060 | 1.311 |
| 7 | 0.386 | 37.984 | 63.012 | 0.092 | 0.156 | 0.015 | 7.247 | 0.060 | 8.952 |

Table 3. The unite cell of laboratory synthesized zeolite samples at 30 °C.

| Sample number | unite cell |
|---------------|---|
| 1 | 2.0Na ₂ O.30.2 Al ₂ O ₃ .28.4SiO ₂ .31.7 H ₂ O |
| 2 | 1.6Na ₂ O.41.9 Al ₂ O ₃ .31.9SiO ₂ .16.7 H ₂ O |
| 3 | 0.4Na ₂ O.20.2 Al ₂ O ₃ .30.8SiO ₂ .38.7 H ₂ O |
| 4 | 0.9Na ₂ O.29.8 Al ₂ O ₃ .52.8SiO ₂ .8.8 H ₂ O |
| 5 | 1.1Na ₂ O.39.5 Al ₂ O ₃ .32.6SiO ₂ .17.1 H ₂ O |
| 6 | 0.3Na ₂ O.34.6 Al ₂ O ₃ .58.7SiO ₂ .1.3 H ₂ O |
| 7 | 0.3Na ₂ O.37.9 Al ₂ O ₃ .63.0SiO ₂ .8.9 H ₂ O |

IV. CONCLUSIONS

- 1- FTIR results indicated that the position, height, and width of the peaks are nearly identical for all synthesized samples.
- 2-SEM results indicated that all of these samples were notice ably identified as the desired zeolite NaY morphology.

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- 3- Although most of the XRD peaks of our samples were similar to those of the standard NaX, but the sequence of intensities were different. The sequence of peak intensities depended strongly on type of cations and the presence of other cations attenuated them.
- 4- According to EDS analysis, NaY zeolite prepared by modified hydrothermal crystallization procedure has a higher molar Si/Al and Na/Al ratio and accordingly higher silicon and sodium content than other samples for the selected spots.
- 5- The obtained XRD-patterns refer to nearly crystalline zeolite-Y type, indicating the formation of NaY zeolite synthesis was successful.
- 6- The results of XRF analysis show that the major components of laboratory synthesized zeolites are SiO₂, Al₂O₃, Na₂O and H₂O, along with a small quantity of CaO and trace amounts of K₂O, Fe₂O₃, P₂O₅ and MgO.

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