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Optimization of Synthesis Procedure for NaX Zeolite by Taguchi Experimental Design and its Application in CO_2 Adsorption

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Abstract

A series of experiments were designed to utilize the Taguchi method for investigating the effects of important parameters on the synthesis of NaX zeolite and to find the best conditions of synthesis. An L9 orthogonal design of Taguchi approach was applied to design experiments consisting of 9 trails. The effect of molar composition, including SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios, and the crystallization conditions, including temperature (T) and time (t) on crystallinity and also phase purity of NaX zeolite were investigated. The results revealed that the temperature of crystallization and alkalinity (Na_2O/Al_2O_3) of initial mixture were the most influencing parameters for desirable synthesis of NaX zeolite. To examine the validation the result of Taguchi experiment design, the most crystalline sample was resynthesized and characterized by XRD, SEM and N2 adsorption-desorption methods. At the end, the capability of the obtained sample for CO2 adsorption was determined by the static volumetric method.

Keywords: CO_2 adsorption; NaX zeolite; Taguchi experimental design; Volumetric gas adsorption; Zeolite synthesis.

Introduction

Zeolites are one of the most important categories of porous materials with unique structural features, including high surface area, large pore volume, interconnected channel and cavities of molecular dimension [1]. Due to their particular structural and chemical properties, they are widely used in industry as ion-exchanger, shape-selective catalysts, petrochemical catalysts, detergents, and adsorbents [2-4]. One of the beneficial types of zeolite is NaX, which belongs to Faujasite (FAU) family of zeolites. Its framework forms by connecting Sodalite cages through double-6-member ring (D6R) leading to provide a large pore diameter (7.4 Aº) [5, 6]. High aluminum content of NaX zeolite framework enables it to strong sorption of polar molecules such as CO_2,

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CO, H_2O and H_2S [7-9]. Especially, the capability of NaX zeolite for separation of carbon dioxide as a global concern [10, 11] has been reported previously [12, 13]. Investigating the zeolites formation process and involved factors is important in order to optimize their industrial production. These parameters include crystallization temperature and time, SiO_2/Al_2O_3 ratio, alkalinity and primary aging of reaction mixture [14-16]. The synthesis of pure phase of zeolite is very important from the characterization and application points of view. Previous studies show that, producing a pure single phase of NaX is difficult and other phases such as NaA or NaP zeolites may form as an impurity during the hydrothermal synthesis process [17-19]. Although a large number of studies have been made on NaX zeolites formation, but there is no obvious conclusion about the percent of effectiveness of parameters and relationship between them on the final product. So, determining the parameter which has the greatest impact on the final products is critical to control the purity of the obtained zeolite. On the other hand, the traditional way used for investigation of the effect of parameters on zeolites synthesis is one-factor-at-a-time-method (OFAT), which attempts to obtain information about one factor in each experiment [20]. This method is time consuming and is also unable to identify any possible interactions between parameters. The experimental design introduced by Taguchi based on orthogonal arrays is a strong mathematical and statistical tool for studying the various parameters affecting the process, simultaneously and is also more economical.

It is used for determining the factor which has the most influence on product quality with a significant reduction in number of experiments, thus leading to save time and resources. Analysis of variance (ANOVA) on obtained data is applied to estimate new values of parameters in order to optimize the process [21-23]. Dargahi *et al.* [24] have reported the effects of crystallization time and temperature, water content and organic template concentration on the synthesis of SAPO-34 zeolite by employing an L_9 Taguchi orthogonal design which decreased a total of 81 series of experiments down to 9, so that decreased cost, time, and work. Savaş *et al.* [25] have reported applications of Taguchi method for production of Al–B master alloys using boron oxide. In the present work, zeolite NaX, have been synthesized by conventional hydrothermal method. In addition, the impact of effective parameters on the crystallization and the purity of the synthesized product has been studied by the means of Taguchi statistical design. Finally, sample of optimum conditions is synthesized again to ensure its producibility, and then examined for its ability in CO_2 adsorption by using a volumetric gas adsorption apparatus. The obtained results are compared with commercial type as a standard.

Materials and Methods

Sodium aluminate (Al_2O_3: 50-56%, Na_2O: 40-45%, Sigma-Aldrich), colloidal silica (AM-30, SiO_2:30%, Sigma-Aldrich), sodium hydroxide pellets (99%, Merck) are reactants used for preparation of zeolite. All chemicals were used as purchased, without further purification. Distilled water was used for dissolving the materials, for preparing the gel and for washing purpose. As a standard, commercial type of zeolite 13X (Zeochem-Z10-02/13X) was used for evaluating the CO_2 adsorption capability of our synthesized zeolite.

Preparation of NaX zeolite

NaX zeolite was synthesized by hydrothermal method from a milky homogeneous solution. The starting gel was formed using the following procedure: at first, appropriate amount of sodium hydroxide pellets, were dissolved in distilled water, and then gradually sodium aluminate was added to obtain a clear solution. Afterwards colloidal silica was added. The generated hydrogel was stirred at room temperature for 30 minutes before hydrothermal treating. Then it was poured in a Teflon-lined stainless steel autoclave and kept at different temperatures and durations in an oven. The solid product was separated by filtration and washed several times with distilled water until the pH reached around 9. Then it was dried at 110 °C for 3 h.

Characterization

To identify the phase purity and crystallinity of the products, X-ray powder diffraction (XRD) data were acquired on a Philips 1830 diffractometer. The data were collected from 5º to 45° (2θ) with a resolution of 0.02° and a count time of 2°/min second at each point. The morphology and crystal size of the resynthesized sample was determined by scanning electron microscopy (SEM) using VEGA-TESCAN apparatus. Then its BET surface area and pore size were measured by means of N_2 adsorption-desorption isotherms at -196 °C using micrometrics model ASAP 2010 sorptometer. Prior to N_2 adsorption, the samples were evacuated at 250 °C.

Taguchi experimental design

In order to design the experiments Taguchi approach,

Table 1. Experimental variables and their levels

Factor number	Parameter	Level 1	Level 2	Level 3
1	Relative alkalinity(Na_2O/ Al_2O_3) of the reaction mixture	3.5	3.9	4.6
2	SiO_2/Al_2O_3 ratio of the reaction mixture	2	3	3.5
3	Temperature of crystallization T(°C)	80	90	100
4	Duration of crystallization t(h)	5	8	12

Table 2. Design of experiment for synthesized zeolites according to Taguchi L_9 orthogonal array

Number of experiment	Product sample	Experiment condition			
		Na_2O/ Al_2O_3	SiO_2/Al_2O_3	Time (h)	Temperature (^{0}C)
1	D_1	3.5	2	5	80
2	D_2	3.5	3	8	90
3	D_3	3.5	3.5	12	100
4	D_4	3.9	2	12	90
5	D_5	3.9	3	5	100
6	D_6	3.9	3.5	8	80
7	D_7	4.6	2	8	100
8	D_8	4.6	3	12	80
9	D_9	4.6	3.5	5	90

Qualitek-4 software was utilized. The capability of this software is the use of L_4 to L_{64} orthogonal arrays [21]. In this work the impact of four factors (duration of crystallization, temperature of crystallization, SiO_2/Al_2O_3 ratio and alkalinity of the reaction mixture), and each factor in three levels, on the synthesis of NaX zeolite were studied. Experimental variables and their levels are presented in Table 1. By using the option of Automatic Design in Qualitek-4 software an L_9 orthogonal array with 9 trails was selected. The phase crystallinity of NaX zeolite was taken as the measured response. Table 2 shows the nine induced experiments from Taguchi orthogonal design and their conditions.

CO2 adsorption measurement

Carbon dioxide adsorption measurements were carried out with a volumetric adsorption apparatus by set up shown in Figure 1.

The volumetric gas adsorption measurement is a simple, low cost and easy assemblage method which widely used for study gas adsorption on solid sorbents [26]. At first adsorption cell was filled with 1 gram of adsorbent and attached to the system. Then the gas inside the system was evacuated by passing Helium. All the gases used in this study have purity > 99%. Before each experiment in order to remove the water or other gas impurities which may occupy zeolite pores, the adsorbent was preheated under vacuum condition. For this purpose valves 1, 2 and 3 were opened and other valves were kept closed. Then vacuum pump was turned on and the system was vacuumed for 3 h under the temperature of 250 °C. The equilibrium adsorption experiments were carried out under different temperatures (25, 35 and 45 °C) and pressure ranging of 1-20 bar. CO_2 was adsorbed by opening the valve 2 and 3 and closing other valves. Calculation of volumetric method is based on pressure drop which needs to measure dead volume (including connection volume and void volume of adsorption cell) by using Helium. A pressure transducer (ECO-1, WIKA) was used to measure the pressure. Temperature of the system was controlled by a water bath (LCP-R133, Lab Tech) with a fluctuation of ±0.3 K.

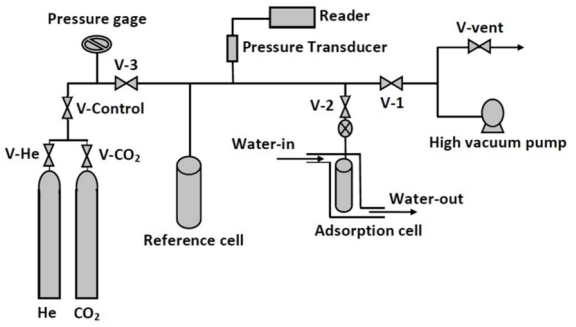

Figure 1. Set-up of apparatus for gas adsorption measurement

Results and Discussion

XRD characterization

The XRD patterns of produced samples prepared hydrothermally based on the Taguchi experimental design are illustrated in Figure 2. The major peaks to confirm the formation of zeolite X intensify at 2θ=6.1º,

Table 3. Molar composition of reaction mixture, percent crystallinity and detected phase for each sample

Product sample	Gel formula	Percent crystallinity of NaX zeolite	Detected phase
D_1	$3.5Na_2O:Al_2O_3:2SiO_2:156H_2O$	0	Amorphous
D_2	$3.5Na_2O:Al_2O_3:3SiO2:156H_2O$	27	NaX+NaA
D_3	$3.5Na_2O:Al_2O_3:3.5SiO_2:156H_2O$	70	NaX
D_4	$3.9Na_2O:Al_2O_3:2SiO_2:156H_2O$	35	NaX+NaA
D_5	$3.9Na_2O:Al_2O_3:3SiO_2:156H_2O$	100	NaX
D_6	$3.9Na_2O:Al_2O_3:3.5SiO_2:156H_2O$	0	Amorphous
D_7	$4.6Na_2O:Al_2O_3:2SiO_2:156H_2O$	22	NaX+NaP
D_8	$4.6Na_2O:Al_2O_3:3SiO_2:156H_2O$	0	NaP
D_9	$4.6Na_2O:Al_2O_3:3.5SiO_2:156H_2O$	0	Amorphous

10º, 15.5º, 20.1º, 23.3º, 26.7º, 29.3º, 30.5º, 31.0º and 32.1º [27]. The relative crystallinity of samples is calculated by equation (1):

(1)

$$\%\ \text{Crystallinity} \frac{\text{sum of peak intensities for the sample}}{\text{sum of the peak intensities for the re ference pattern}}$$

The molar composition, obtained phases and relative crystallinity of samples are presented in Table 3.

In the XRD patterns of samples D_5 and D_3, characteristic peaks of NaX zeolite with high intensity are observed indicating the successful formation of NaX zeolite.

Sample D_5 shows the highest degree of crystallinity of NaX zeolite in comparison with other samples. Although sample D_2, D_4 and D_7 consist of NaX zeolite, but other phases such as NaA or NaP are generated as impurity during the crystallization process. XRD pattern of sample D_8 demonstrates complete transformation of NaX zeolite to NaP (GIS) phase. For samples D_1, D_6 and D_9 any peak was observed, suggesting formation of the amorphous phase. According to literature, in most cases during the synthesis of NaX other types of zeolites such as NaP or NaA may co-form or it may completely transform to the mentioned phases. This phenomenon is because of metastability of NaX zeolite. Zhang *et al.* [14] have shown that lower temperature and duration of crystallization leads to formation of NaA instead of NaX zeolite. Also lower concentration of Si favors the formation of NaA zeolite. This behavior is due to more complex secondary building units (D6R) of NaX, which require more energy, time and Si concentration to be formed. In an opposite way, Xing-dong *et al.* [28] have reported the formation of NaX during NaA zeolite synthesis. They have shown that the higher alkalinity of the reaction mixture and longer crystallization time is favorable for the formation of NaX zeolite. Chaves *et al.* [29] have reported that increasing the alkalinity of reaction in mixture is a key parameter to produce high crystalline FUA type zeolite with reduction its crystal size, but there is a limitation for alkalinity and exceeding its limitation may cause the transformation FUA to NaP zeolite. This kind of behavior was confirmed by XRD patterns of sample D_8.

Analysis of Taguchi design of experiment

After performing the experiments, the measured characteristics of them were used to analyze the relative effect of different parameters. The crystallinity of final products was considered as the quality characteristic and measured response. In order to assess the impact of selected parameters and determining the optimum level of them, analysis of variance (ANOVA) was employed. Calculation of ANOVA is based on the total and factors sum of squared deviations which are given by following equations [30]:

Total sum of square:

$$(2)\quad S_T = \left[\sum_{i=1}^{N}(Y_i)^2\right]\frac{T^2}{N}$$

Where Y_i is i-th obtained data value, N is the number of observations and T is the total of all observations.

Factor sum of square due to parameter A:

$$(3)\quad S_A = \left[\sum_{i=1}^{K_A}\left(\frac{A_i^2}{n_{A_i}}\right)\right] - \frac{T^2}{N}$$

Where K_A is the number of levels for parameter A, A_i is the sum of results (y_i) where parameter A_i is present, and n_{Ai} number of experiments where i-th level of factor A is present. Other given data in ANOVA table are calculated based on sum of squares. For each factor they are as fallow:

Mean square:

$$(4)\quad V_A = \frac{S_A}{f_A}$$

Pure sum of square:

$$(5)\quad S_A' = S_A - V_e \times f_A$$

Table 4. Analysis of variance (ANOVA)

Parameter	DOF (*f*)	Sum of squares	Variance (V)	Pure sum	Percent (P (%))
Na_2O/ Al_2O_3	2	2144.22	1072.11	2144.22	22.75
SiO_2/Al_2O_3	2	1044.22	522.11	1044.22	11.08
Temperature of crystallization (°C)	2	5707.55	2853.77	5707.55	60.57
Duration of crystallization (h)	2	526.88	263.44	526.88	5.59
Total	8	9422.88	-	-	100%

Table 5. Optimum condition and performance for NaX zeolite synthesis

Parameters	Level Description	Level	Contribution
Na_2O/ Al_2O_3	3.9	2	17.88
SiO_2/Al_2O_3	3	2	15.22
Temperature of crystallization (°C)	100	3	33.55
Duration of crystallization (h)	5	1	6.22
Expected Result at Optimum Condition	-	-	99.99

Percent influence:

(6) $$P_A = \frac{S'_A}{S_T} \times 100$$

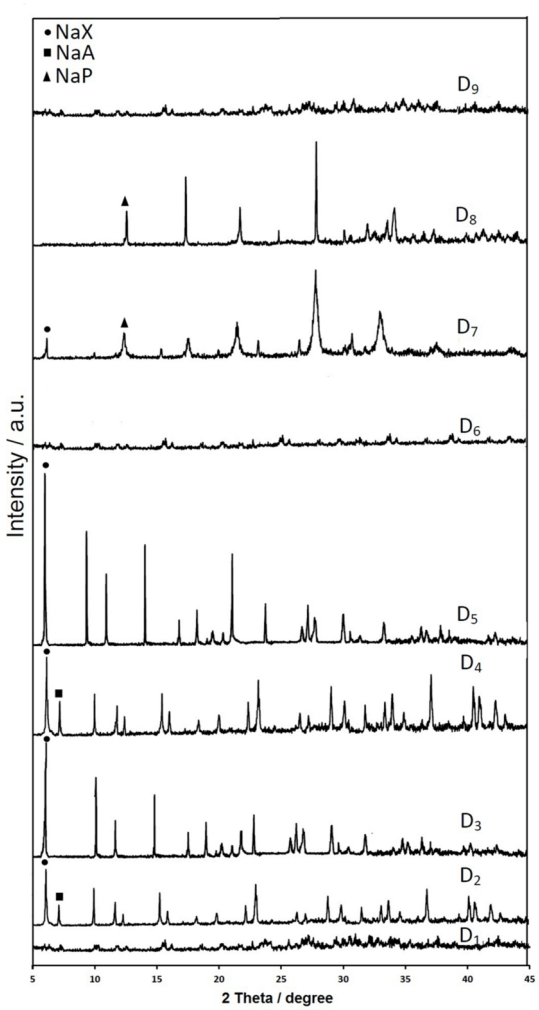

Figure 2. XRD patterns of synthesized samples

Where V_A is variance and f_A degree of freedom of factor A. V_e is the variance of error which calculated by means of error sum of squares and dividing by error degrees of freedom. The degree of freedom for the Taguchi array is defined as follows [21]:

(7) DOF parameter number of factor levels − 1

Table 4 shows the most effective parameters on the synthesis of NaX zeolite are temperature and alkalinity (Na_2O/Al_2O_3) of the reaction mixture. Si_2O/Al_2O_3 ratio stands as the third effective parameter. Time of crystallization didn't show any significant effect on crystallinity of the final product. Also the optimum conditions for achieving the maximum crystallinity of NaX zeolite are summarized in Table 5.

According to the results obtained from XRD and Taguchi orthogonal design following conclusion is achieved. In addition the main effects of parameters are shown in Figure 3.

Temperature of crystallization is the most effective parameter on the formation of NaX zeolite. Higher temperature provides bigger energy for polymerization of silicate and aluminate species, thus accelerates the dissolution and transformation of gel. Cundy *et al.* [31] have demonstrated that temperature notably influences the rate of crystal growth and nucleation of zeolites. Figure 3a shows that increasing the temperature of synthesis leads to formation expected phase. So the main reason which makes samples D_1 and D_6 amorphous is their insufficient temperature of crystallization.

Second parameter that has a great impact on zeolite formation is alkalinity (Na_2O/ Al_2O_3) of the reaction mixture. Although crystallization temperature of sample

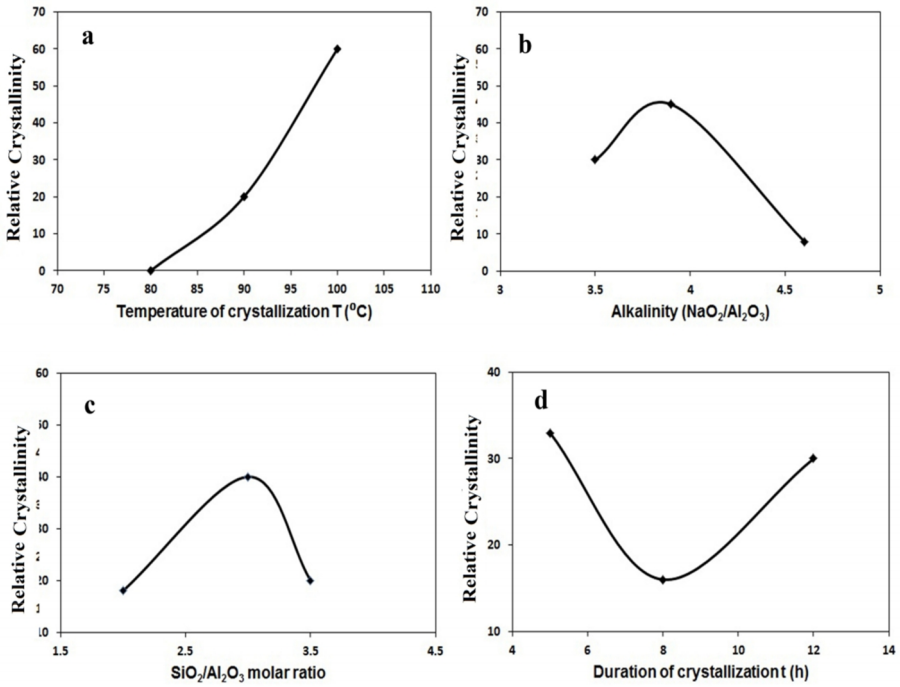

Figure 3. Main effects of selected parameters

D_8 is low, but its high alkalinity and longer time are barriers against making it an amorphous phase and leads to the formation of NaP (GIS type). Higher content of Na_2O causes more dissolution of NaX zeolites which behaves as an aluminasilicate precursor for NaP formation. Figure 3b shows the dependency of the crystallinity of zeolite NaX on Na_2O/Al_2O_3. Furthermore, longer time of crystallization for sample D_8, is another reason for phase transformation of NaX to NaP.

Mid temperatures of samples D_2 and D_4 result in the formation of NaA zeolite as an impurity phase. On the other hand by comparison of these samples, it's clear that longer time and higher alkalinity make the sample D_4 to have more content of NaX zeolite.

High temperature and appropriate amount of alkalinity are the most important reason for the successful synthesis of pure NaX phase of samples D_5 and D_3. Lower crystallization of sample D_3 in comparison with sample D_4 may be due to its lower alkalinity.

Figure 3c illustrates the effect of the Si_2O/Al_2O_3 ratio on NaX content of final products. According to the obtained results, decreasing SiO_2/Al_2O_3 ratio favors formation of NaA phase. This phenomenon can be explained by the fact that lowering the concentration of Si results in the formation of small silicate species (D4R) of NaA zeolite. This behavior can be observed in sample D_4.

By comparing sample D_3 and D_2, it can be concluded that longer duration of crystallization, bigger SiO_2/Al_2O_3 ratio and higher temperature lead to the transformation of NaA to NaX phase.

The contribution of each parameter on the crystallinity of final products is shown in Figure 4.

Validation the result of Taguchi experimental design

To validate the results of Taguchi experimental design, sample D_5 was synthesized again to confirm its reproducibility. Figure 5 illustrates XRD pattern of new synthesized sample D_5 indicating the successful formation of pure phase NaX zeolite with high crystallinity. Also, SEM images of resynthesized sample are shown in Figure 6. Octahedral morphology of particles were distinguished, indicating formation of NaX zeolite crystals with the size of 0.75 to 1.51 µm,

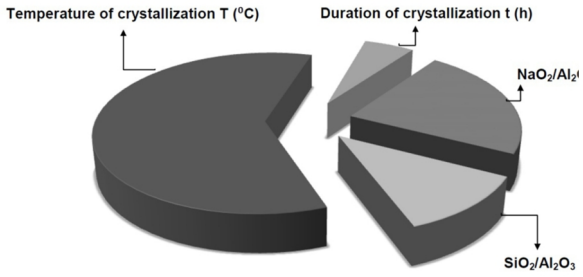

Figure 4. Percent contribution of parameters

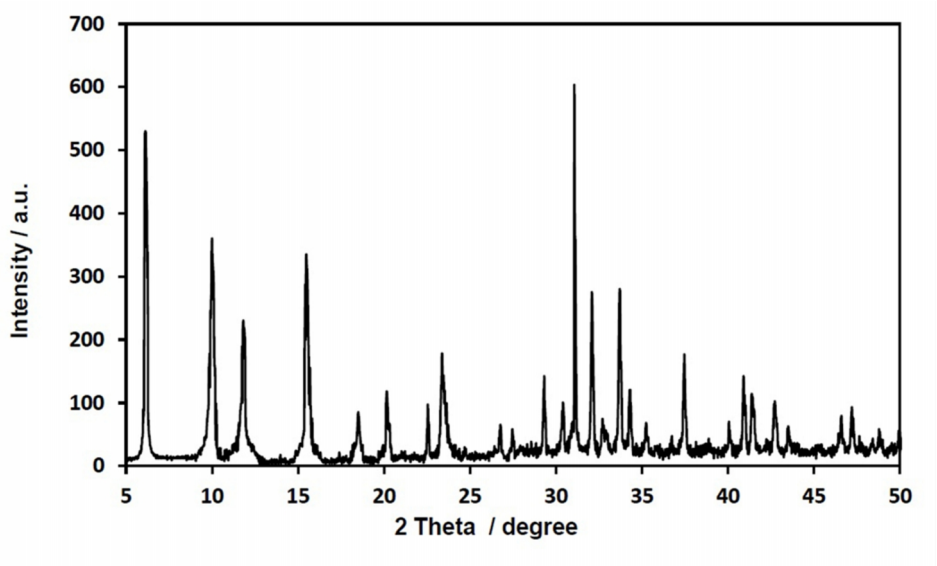

Figure 5. XRD pattern of resynthesized NaX zeolite

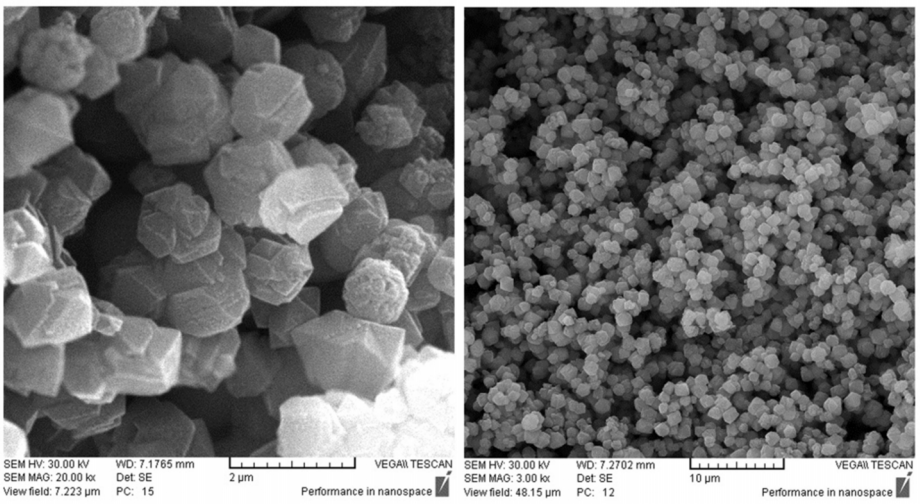

Figure 6. SEM image of resynthesized NaX zeolite

and it is in agreement with previous results [14].

N_2 adsorption-desorption measurement

N_2 adsorption-desorption isotherm of resynthesized NaX zeolite is depicted in Figure 7. The isotherm of synthesized zeolite is of type I which is the characteristic of microporous according to the IUPAC definition [32].

Assessment of surface areas was performed using BET (Brunauer–Emmett–Teller) method. The micropore surface area as well as external surface area and micropore volume obtained from t-plot method. Textural characteristics of synthesized NaX zeolite are summarized in Table 6. In addition, the surface area was similar to reported values in literature [14].

CO_2 adsorption Isotherms

Adsorption isotherms of CO_2 on commercial type 13X (Zeochem Z10-02/13X) and resynthesized NaX zeolite at the different temperatures (25, 35, and 45ºC) and pressure in the range of 0-20 bar are exhibited in Figure 8 and 9 respectively. It is clear that the adsorption capacity of CO_2 decreased by increasing the temperature. Also the trend of increasing CO_2 adsorption was very sharp up to pressure of 1.55 bar, but after 1.55 bar it is lowered, indicating better performance of the synthesized zeolite at low pressures. For better describing of CO_2 adsorption, Langmuir equation was fitted to the experimental data. The Langmuir isotherm is expressed by equation (8) [33]:

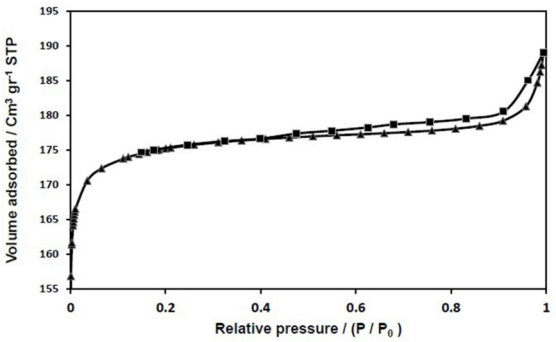

Figure 7. N_2 adsorption–desorption isotherm

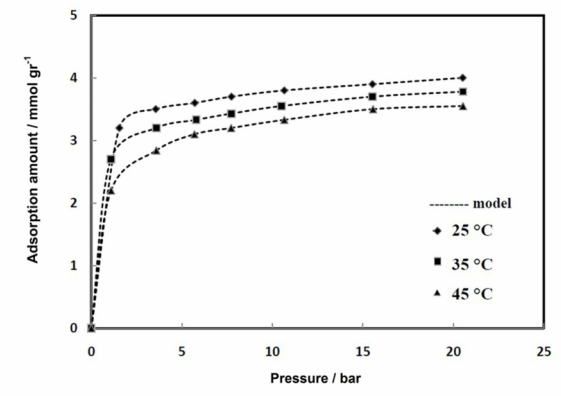

Figure 8. Adsorption isotherms of CO_2 for commercial 13X

$$(8)\quad q = \frac{q_{max}\, b\, P}{1+b\, P}$$

Where q (mmol gr^{-1}) is the amount of gas adsorbed at equilibrium pressure of P (bar), q_{max} is the maximum capacity of adsorption, b (bar^{-1}) is equilibrium constant of adsorption. Equilibrium parameters of Langmuir equation for CO_2 adsorption on both adsorbent and correlation coefficients R^2 for linear regression of data are presented in Table 7, and show that amount of q_{max}

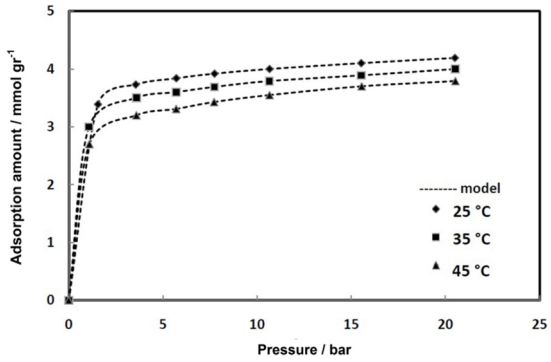

Figure 9. Adsorption isotherms of CO_2 for synthesized NaX zeolite

for both adsorbents are almost in a relative close range, suggesting that our produced NaX zeolite can be used as an adsorbent for CO_2. The high values of correlation coefficients R^2, ranging from 0.997 to 0.998, shows good agreement between experimental data and Langmuir model.

Conclusions

In this research, a Taguchi L_9 design was applied in order to study the impact of environmental and operational parameters and finding the optimum range of them for the synthesis of NaX zeolite. The influence order of the investigated parameters on the content of NaX zeolite in the final product is: temperature of crystallization > alkalinity (Na_2O/Al_2O_3) > Si/Al and duration of crystallization. The obtained results showed that by decreasing the temperature and SiO_2/Al_2O_3 ratio, NaA zeolite phase may co-form, or by increasing the alkalinity, NaX may transform to NaP phase. Furthermore, measuring amount of CO_2 adsorption on the produced sample under optimum conditions and comparing it with the commercial type indicates its capability of being used as an effective CO_2 adsorbent.

Table 6. Textural characteristics of resynthesized zeolite NaX

Adsorbent	BET surface area ($m^2\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)	External surface area ($m^2\ g^{-1}$)
resynthesized NaX	620.0899	0.255972	585.8834	34.2065

Table 7. Parameter of Langmuir equation for CO_2 adsorption at 25, 35 and 45 ^0C

Adsorbent	T (^0C)	q_{max} (mmol gr^{-1})	B (bar^{-1})	R^2
Commercial 13X	25	3.99	2.63	0.999
	35	3.66	2.35	0.999
	45	3.35	2.24	0.997
NaX	25	4.05	2.51	0.998
	35	3.69	2.66	0.997
	45	3.39	1.48	0.999

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