Preparation of 13X zeolite powder and membrane: investigation of synthesis parameters impacts using experimental design

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Keywords: 13X zeolite powder, gel composition, zeolite membrane, hydrothermal synthesis, gas permeation

Abstract

The Plackett—Burman method was used to identify and rank most affective parameters on hydrothermal synthesis and properties of the 13X zeolite powder with gel composition of Al₂O₃:aSiO₂:bNa₂O:cH₂O. The affective parameters of SiO₂/Al₂O₃ ratio, synthesis mixture alkalinity, synthesis temperature, and water content were selected for further study of their impacts and gel composition optimization using the Taguchi method. The synthesized powders were characterized by XRD and SEM analysis. Synthesis temperature and mixture alkalinity were found as the most affecting parameters on the 13X zeolite synthesis at the best gel composition of Al₂O₃:5.4SiO₂:13Na₂O:840H₂O. Then 13X zeolite membranes were synthesized on the seeded supports using the optimum gel composition and impacts of synthesis temperature and time and coating layer number on their H₂ and CO₂ permeances and ideal H₂/CO₂ selectivity were studied. The optimum 13X zeolite membrane for H₂/CO₂ separation was obtained by three layer coatings at 80 °C for 16 h with H₂ permeance of 2.88 cm³ cm⁻².Pa.s and ideal H₂/CO₂ selectivity of 4.72.

1. Introduction

Hydrogen as a fuel is noteworthy due to its high energy content, environmental friendliness, and also numerous applications in petroleum and chemical processing industries and many attentions have been paid to its production and purification. Nowadays, hydrogen is mainly produced by natural gas (i.e. methane) steam reforming units in oil refineries and petrochemical plants [1–6]. Hydrogen has many applications in the oil refineries such as catalytic conversion processes, i. e. for fuel octane number enhancement in isomerization, Iso max, and unit. Accompanying of carbon dioxide with hydrogen stream may produce water where results in isomerization catalyst’s deactivation or damage, hence the catalytic reactors’ hydrogen feed must be CO₂ free [7, 8]. These facts reveal the importance of necessity of hydrogen different pollutions removal and its purity in the oil and gas industries. In addition to the important task of hydrogen purification, CO₂ removal/capture due to its large emission and global warming effects is also another important task. Investigation of efficient and economical processes for greenhouse gases emission reduction has attracted many attentions in recent years [9, 10].

Pressure swing adsorption (PSA) is extensively employed process, i. e. more than 85% of global hydrogen production units utilize the PSA process for hydrogen purification to higher than 99.95% [11].

Zeolites and molecular sieves are used in PSA units of the oil and gas processing industries for product impurities’ removal from and/or different streams drying, e. g. in isomerization and hydrogen units [12, 13]. Zeolites are the aluminosilicate crystalline materials and their structures and properties have a distinct relation with their Si/Al ratio. The zeolites basic units are usually tetrahedrons of [SiO₄]⁴⁻ and [AlO₄]³⁻ which are...
connected by their common oxygen atoms. The zeolites pores are determined by their context nature and interconnected by windows apertures [14–16].

Separation of undesired reforming reactions’ by-products such as CO2 and CO is usually carried out by their absorption on the amine absorbents, however, zeolites such as faujasite (FAU) are also good selections for of the produced hydrogen polishing process. Sodium cations in 13X zeolite are in charge of balancing its zeolite framework negative charges due to the Si-O-Al and also create an electrostatic field in the zeolite structure environment. Large quadrupole moment of CO2 molecules, as $4.30 \times 10^{-26}$ esu.cm$^2$, has strong interaction with the dipole electrostatic field of 13X zeolite leading to large CO2 adsorption amount inside the zeolite pores and cavities [15,17,18]. Other gas separation tasks, like normal/branched hydrocarbons such as n-pentane/iso-pentane after conversion of heavy hydrocarbons and benzene opening ring reactions in isomerization units, can also be carried out by proper zeolites such as 5 A and/or 13X [19].

A large number of variables can affect the synthetic zeolites crystallinity and phases’ purity, i.e., synthesis procedure, SiO2/Al2O3 molar ratio, synthesis solution alkalinity (H2O/Na2O) and water content (H2O/Al2O3), synthesis temperature (Tn, °C) and time (tR, h), aging time (tA, h), template (if any) and seeding [20–22].

13X zeolite is one of the microporous crystalline hydrophilic FAU and the sodium X zeolite type with large super cages and windows aperture pores of around 13 and 7.4 Å [14]. A lot of investigations have been carried out over recent years on the 13X zeolite preparation and characterization [23, 24]. Generally, the 13X zeolite is prepared by sodium aluminosilicate gels, using a wide range of silica and alumina sources via hydrothermal synthesis route. Several researchers used 13X zeolite as adsorbent for CO2, N2, CH4 and H2 separation [25], as binderless 13X zeolite beads for bindery CO2/CH4 mixture separation [26], as CO2 adsorbent in its modified state by amine-grafting [27], and as high-grade detergents due to its high magnesium ion exchange/removal capacity from water [28].

In the current study, some affective parameters on the 13X zeolite hydrothermal synthesis were systematically investigated by the Plackett—Burman experimental design method. Sodium silicate and colloidal silica sol were used as the Si source and sodium aluminate was employed as the Al source of the zeolite synthesis mixture. Other important parameters of Si/Al, H2O/SiO2, H2O/Na2O molar ratios, synthesis temperature (Tn), synthesis time (tR) and aging time (tA) were changed in the ranges of 2.9–8.1, 52–105, 30–70, 80–110 °C, 5–16 h, and 12–24 h, respectively. The selected Plackett—Burman parameters of Si/Al (in term of SiO2/Al2O3), H2O/SiO2 (in term of H2O/Al2O3), H2O/Na2O (in term of Na2O/Al2O3), H2O/Na2O molar ratios and synthesis temperature impacts on the synthesized zeolite powders’ crystallinities and zeolitic phase contents were further studied by the Taguchi method of experimental design. Finally the most affecting parameters of the synthesis temperature (Tn), the synthesis time (tR), and the coated zeolite layer number were further studied for their impact(s) on the 13X zeolite supported membranes’ H2/CO2 separation performance.

2. Experimental

2.1. Materials

Sodium silicate (Na2SiO3 as 27% SiO2, 8% Na2O, 65% H2O from Sigma Aldrich), sodium hydroxide pellets (99% purity from Sigma-Aldrich), aqueous colloidal silica (Ludox Hs-30, Sigma-Aldrich), and sodium aluminate (53% Al2O3 and 42.5% Na2O) were purchased and directly used as received without any further purification. Homemade deionized (DI) water was used for different solutions preparation. H2 and CO2 gases with purities of 99.99% purchased from Varian Gas Services and used as the membrane feed gases.

2.2. Experimental design

2.2.1. The Plackett—Burman experimental design method

The Plackett—Burman method of experimental design was used to identify and rank the most affecting parameters on the 13X zeolite hydrothermal synthesis and properties [29]. The most important affecting parameters were selected based on the literature [30–32] and are reported in table 1 based on the Plackett—Burman method. The selected parameters minimum and maximum levels were coded as (−1) and (+1), respectively. The coded parameters’ real values are also reported in table 1 and the zeolite powders were synthesized accordingly.

2.2.2. The taguchi experimental design method

As the affective parameters were determined by the Plackett—Burman method, they were systematically evaluated by L9 orthogonal array of the Taguchi experimental design method to obtain an optimum gel composition for 13X zeolite synthesis. The selected parameters and their levels are reported in table 2.
Table 1. Carried out experiments for 13X zeolite synthesis based on the Plackett—Burman experimental design method.

| RUN no. | SiO$_2$/Al$_2$O$_3$ | H$_2$O/SiO$_2$ | H$_2$O/Na$_2$O | $T_k$ (°C) | $t_e$ (h) | $t_A$ (h) | Silica Source (Dummy factor) |
|---------|---------------------|----------------|----------------|----------|----------|----------|-----------------------------|
| 1       | 8 (+1)              | 105 (+1)       | 70 (+1)        | 80 (-1)  | 16 (+1)  | 12 (-1)  | Lodux (-1)                 |
| 2       | 2.9 (-1)            | 105 (+1)       | 70 (+1)        | 110 (+1) | 5 (-1)   | 24 (+1)  | Water glass (+1)           |
| 3       | 2.9 (-1)            | 52 (-1)        | 70 (+1)        | 110 (+1) | 16 (+1)  | 12 (-1)  | Water glass (+1)           |
| 4       | 8 (+1)              | 52 (-1)        | 30 (-1)        | 110 (+1) | 16 (+1)  | 24 (+1)  | Water glass (+1)           |
| 5       | 2.9 (-1)            | 105 (+1)       | 30 (-1)        | 80 (-1)  | 16 (+1)  | 24 (+1)  | Lodux (-1)                 |
| 6       | 8 (+1)              | 52 (-1)        | 70 (+1)        | 80 (-1)  | 5 (-1)   | 24 (+1)  | Water glass (+1)           |
| 7       | 8 (+1)              | 105 (+1)       | 30 (-1)        | 110 (+1) | 5 (-1)   | 12 (-1)  | Water glass (+1)           |
| 8       | 2.9 (-1)            | 52 (-1)        | 30 (-1)        | 80 (-1)  | 5 (-1)   | 12 (-1)  | Lodux (-1)                 |

Table 2. The selected effective parameters on the 13X zeolite synthesis and their levels.

| Parameter | Level 1 | Level 2 | Level 3 |
|-----------|---------|---------|---------|
| SiO$_2$/Al$_2$O$_3$ | 2.9 | 5.4 | 8 |
| Na$_2$O/Al$_2$O$_3$ (Relative Alkalinity) | 2.13 | 13 | 28 |
| H$_2$O/Al$_2$O$_3$ | 150.7 | 495.35 | 840 |
| Crystallization Temperature($T_k$, °C) | 80 | 95 | 110 |

2.2.3. Analysis of variance (ANOVA)

ANOVA separates total variability of the response into percent contribution of each selected parameter. ANOVA employs quantities such as sums of squares (SS), degrees of freedom (DOF), mean square (MS), associated F-test of significance (F) and percent contribution (P) where can be calculated using the following equations [33]:

$$SS_A = \left[ \frac{\sum_{i=1}^{N} A_i^2}{n_{A_i}} \right] - \frac{T^2}{N}$$

(1)

where $K_A$ is the A’s parameter levels number, $n_{A_i}$ is all experiments number at ith level of parameter A, $A_i$ is A’s parameter sum for all the experiments in it’s ith level and T is sum of the all experiments measured values.

Also, sum of the squared error (SS$_e$) is given by the following equation [33]:

$$SS_e = SS_T - (SS_A + SS_B + \ldots)$$

(2)

where $SS_T$ is the all observations’ squares sum and calculated using the following equations [33]:

$$SS_T = \sum_{i=1}^{N} \gamma_i^2 - \frac{T^2}{N}$$

(3)

where $\gamma_i$ is the ith observation. Mean square (MS) is calculated by dividing SS to DOF. DOF, F-ratio and P are calculated using the following equations [33]:

$$DOF_A = K_A - 1$$

$$F_A = MS_A/MS_e$$

$$P(\%) = \frac{SS_A - (DOF \times MS_e)}{SS_T} \times 100$$

(4)

where $MS_e$ is the error variance [33].

2.3. 13X zeolite powder synthesis

In order to prepare the 13X zeolite synthesis solution, alumina and silica sources were mixed in a polypropylene bottle. Initially, sodium hydroxide pellets were dissolved in deionized water, and then the solution was divided into two equal parts. The silicate solution was prepared by dissolving sodium silicate (Na$_2$SiO$_3$)/Lodux in one part, and the aluminate solution was prepared by mixing sodium aluminate in another part.

In the next step, the silica source was slowly added to the alumina source. The final solution was stirred at the ambient temperature for 12–24 h. The solution was then transferred into an autoclave and placed inside an oven. The zeolite powders were crystallized at temperatures range of 80–110 °C for crystallization times of 5–16 h. After the prescribed crystallization time duration based on the experimental design, the autoclave was exited from the oven and leaved at the room temperature for natural cooling. Then the cooled suspension was
filtered and the crystallized zeolite powders were washed by deionized water for several times until the drained water’s pH reached 7. Finally the gathered powder dried at 100 °C for 3 h.

2.4. 13X zeolite membrane synthesis

2.4.1. Preparation procedure

Different methods were developed for the zeolitic membranes preparation such as hydrothermal method where is simple and at the same time is the most conventional and economical method. In this method, the 13X zeolite crystal layer grew on a properly conditioned and seeded porous support using appropriately composed mixture as the synthesis gel where came into contact with the support in an autoclave to initiate the zeolite crystallization process and form the 13X zeolitic selective layer.

2.4.2. Zeolitic membrane preparation

In this study, α–alumina supports (diameter of 2.1 cm, thickness of 1.8 mm and mean pore size of 4 μm) were used for as the 13X zeolitic membrane support. All the supports’ surface were smoothen using SiC polishing paper numbers of 800, 1000 and 1500, consecutively, to polish their surface topology. The supports then washed several times with distilled water for dust removal and after that they were ultrasonicated for 2 h using KUDOS SK3310HP ultrasonic bath to completely remove the remained polishing dust and finally the cleaned supports were dried at 90 °C for 1 h.

Proper amount of the previously synthesized zeolite powders were fined using a ball mill and then passed through mesh No. of 400 and the screened particle were suspended in distilled water by 3 wt% for the polished supports seeding. One side of supports were covered by Teflon tape to inhibit the seeded zeolite crystals penetration into the pores on that side and guarantee one side zeolite formation.

The 13X zeolite synthesis solution was prepared based on the Taguchi method’s DOE run No. 5, as sample S<sub>n</sub> then the one face seeded supports were placed vertically in a Teflon autoclave using a PTFE holder. After that, the sealed autoclave was inserted in an oven at the prescribed temperature and time duration based on the DOE method. At the end of synthesis time, the supports with grown zeolite layers on their top surface existed from the autoclave and washed several times with deionized water until their drained water pH neutralization. Finally the coated membranes were dried at 100 °C for 3 h.

2.5. Characterization and analyses methods

2.5.1. X-ray diffraction (XRD) analysis

The prepared zeolite powders were characterized by XRD analysis to determine their zeolite phase contents. The samples’ XRD patterns were recorded using Philips PW1140/90 diffractometer and Cu Kα target (40 kV, 25 mA) at scan rate of 1 °min<sup>-1</sup> in 2θ angels range of 4–90° with 0.02° step size.

2.5.2. Scanning electron microscopy (SEM) analysis

Scanning electron microscopy (SEM) micrographs were taken using TESCAN scanning electron microscope (15 kV). All the samples were initially gold coated.

2.5.3. Gaseous penetrants permeances measurement

In order to evaluate gas separation performance of the prepared zeolitic membranes, a setup was assembled as schematically shown in figure 1. The feed flow rate was controlled by manual valves and measured using bubble flow meters. The transmembrane pressure was kept constant at 1 bar using another valve. All the experiments were carried out at operating temperature of 25 °C.

3. Results and discussion

3.1. Experimental results of the Plackett—Burman and the taguchi methods

The 13X zeolite powder’s standard XRD pattern is presented in the zeolite XRD pattern collection of Treacy and Higgins [34] and those of gathered for the prepared 13X zeolite powders based on the Plackett—Burman DOE method are shown in figure 2. The prepared zeolites crystallinities were calculated by comparison of the most intense peaks’ intensities of the gathered XRD patterns and those of the standard patterns and the results are reported in table 3 [34, 35].

The calculated zeolites crystallinities synthesized based on the Plackett—Burman DOE method are given in table 4. The calculations were done based on table 1 experiments results and gathered data of the zeolites’ crystallinities by multiplying each row’s crystallinity value to that row’s level of the selected variable. All individual table column’s reported values were added and their sum was reported in lowest cell of that column. Based on the Plackett—Burman method’s instruction, the evaluated variables should be ranked in order of the
Figure 1. Experimental Lab. scale setup used for the membranes’ gaseous penetrant permeance measurement.

Figure 2. XRD patterns of the synthesized 13X zeolite powders based on the Plackett—Burman method. The main peaks of 13X zeolite, sodalite and NaA zeolite are shown with full squares, blank triangles and blank lozenges, respectively.
Based on the results of the Plackett—Burman DOE method, the synthesis gel SiO$_2$/Al$_2$O$_3$ molar ratio, alkalinity (H$_2$O/Na$_2$O) and water content (H$_2$O/SiO$_2$) and the zeolite synthesis temperature were found as the most affective parameters on the synthesized zeolites’ crystallinities. Hereafter, these variables were selected for further study based on the Taguchi method’s L9 orthogonal array. Accordingly, another set of experiments were carried out to find the optimum 13X zeolite crystallinity and separation performance as the membrane top selective layer. The designed experiments and their related variable levels are listed in table 5. As the above results revealed, the gel aging and the synthesis reaction times are also important affecting parameters on the 13X zeolite formation and its crystallinity. However, in the Taguchi experimental design results, since reaction and aging times were found to have similar impacts on the selected response, their values were kept fixed at 16 and 24 h, respectively, and instead Si/Al molar ratio was selected as the fourth affecting parameter in the Taguchi method.

Molar gel compositions of the Taguchi experimental design are given in table 6. XRD patterns of the hydrothermally synthesized 13X zeolite samples are shown in figure 3. As mentioned above, the main peaks intensities were compared with those of the standard 13X zeolite pattern and their relative crystallinities were calculated and are reported in table 6.

As it is observed in the second experiment run in table 3 and the first and the second experiment runs in table 4, 13X zeolite formation is favored by lower silica content. Probability of the NaA zeolite formation at lower

| Table 3. Gel composition, zeolite type and crystallinity of the synthesized zeolites. |
| RUN no. | Gel composition | Zeolite types and crystallinities (%) |
|-----------------|-----------------|----------------------------------|
| 1               | Al$_2$O$_3$:8SiO$_2$:12Na$_2$O:840 H$_2$O | 13X = 78 |
| 2               | Al$_2$O$_3$:2.9 SiO$_2$:4.35 Na$_2$O:304.5 H$_2$O | 13X = 52, NaA + NaP |
| 3               | Al$_2$O$_3$:2.9 SiO$_2$:2.154 Na$_2$O:150.78 H$_2$O | Amorphous |
| 4               | Al$_2$O$_3$:8 SiO$_2$:13.86 Na$_2$O:416 H$_2$O | Sodalit |
| 5               | Al$_2$O$_3$:2.9 SiO$_2$:10.15 Na$_2$O:304.5 H$_2$O | 13X = 20 + Sodalit + NaP + NaA + Amorphous |
| 6               | Al$_2$O$_3$:8 SiO$_2$:5.943 Na$_2$O:416 H$_2$O | Amorphous |
| 7               | Al$_2$O$_3$:8 SiO$_2$:28 Na$_2$O:840 H$_2$O | Amorphous |
| 8               | Al$_2$O$_3$:2.9 SiO$_2$:5.027 Na$_2$O:150.08 H$_2$O | Amorphous |

| Table 4. Investigation of different variables impacts on the 13X zeolite synthesis. |
| RUN no. | Si/Al | H$_2$O/SiO$_2$ | H$_2$O/Na$_2$O | $T_R$ (°C) | $t_R$ (h) | $t_A$ (h) | Crystallinity |
|--------|------|--------------|-------------|-----------|--------|--------|--------------|
| 1      | 624  | 8190         | 5460        | −6240     | 1248   | −936   | 78           |
| 2      | −150.8 | 5460        | 3640        | 5720      | −260   | 1248   | 52           |
| 3      | 0    | 0            | 0           | 0         | 0      | 0      | 0            |
| 4      | 0    | 0            | 0           | 0         | 0      | 0      | 0            |
| 5      | −58  | 2100         | −600        | −1600     | 320    | 480    | 20           |
| 6      | 0    | 0            | 0           | 0         | 0      | 0      | 0            |
| 7      | 8    | 0            | 0           | 0         | 0      | 0      | 0            |

Weightings 415.2 15750 8500 −2120 1308 792

| Table 5. Designed experiments based on the Taguchi method’s L9 orthogonal array for 13X zeolite synthesis. |
| RUN no. | SiO$_2$/Al$_2$O$_3$ | Na$_2$O/Al$_2$O$_3$ | H$_2$O/Al$_2$O$_3$ | $T_R$ (°C) |
|--------|---------------------|---------------------|---------------------|-----------|
| 1      | 2.9                 | 2.15                | 150.7               | 80        |
| 2      | 2.9                 | 13                  | 495.35              | 95        |
| 3      | 2.9                 | 28                  | 840.00              | 110       |
| 4      | 5.4                 | 2.15                | 495.35              | 110       |
| 5      | 5.4                 | 13                  | 840.00              | 80        |
| 6      | 5.4                 | 28                  | 150.7               | 95        |
| 7      | 8                   | 2.15                | 840.00              | 95        |
| 8      | 8                   | 13                  | 150.7               | 110       |
| 9      | 8                   | 28                  | 495.35              | 80        |

largest assigned number to the smallest one to indicate their order of effectiveness on the selected response(s), i.e. the synthesized zeolites crystallinities in the current study [29].

Based on the results of the Plackett—Burman DOE method, the synthesis gel SiO$_2$/Al$_2$O$_3$ molar ratio, alkalinity (H$_2$O/Na$_2$O) and water content (H$_2$O/SiO$_2$) and the zeolite synthesis temperature were found as the most affective parameters on the synthesized zeolites’ crystallinities. Hereafter, these variables were selected for further study based on the Taguchi method’s L9 orthogonal array. Accordingly, another set of experiments were carried out to find the optimum 13X zeolite crystallinity and separation performance as the membrane top selective layer. The designed experiments and their related variable levels are listed in table 5. As the above results revealed, the gel aging and the synthesis reaction times are also important affecting parameters on the 13X zeolite formation and its crystallinity. However, in the Taguchi experimental design results, since reaction and aging times were found to have similar impacts on the selected response, their values were kept fixed at 16 and 24 h, respectively, and instead Si/Al molar ratio was selected as the fourth affecting parameter in the Taguchi method.

Molar gel compositions of the Taguchi experimental design are given in table 6. XRD patterns of the hydrothermally synthesized 13X zeolite samples are shown in figure 3. As mentioned above, the main peaks intensities were compared with those of the standard 13X zeolite pattern and their relative crystallinities were calculated and are reported in table 6.

As it is observed in the second experiment run in table 3 and the first and the second experiment runs in table 4, 13X zeolite formation is favored by lower silica content. Probability of the NaA zeolite formation at lower
SiO2/Al2O3 molar ratios increases as can be observed in figure 2 (samples of S2 and S5) and figure 3 (samples of S1 and S2). Reduction in the synthesis solution silica content resulted in small double 4 member rings (D4R) formation of the NaA zeolite \([36, 37]\). Similar results were reported by Tanaka et al. \([38]\).

### 3.1.1. Analysis of variance (ANOVA) results

After synthesis of the zeolites powder, their properties were characterized. The synthesized powders crystallinities were considered as a desired response. Using ANOVA parameters where have significant effects on the synthesized 13X zeolite powder crystallinity can be selected. The main objective of ANOVA analysis is further investigation of the selected parameters significance in term of their impact(s) on the concerned response(s), i.e. the 13X zeolite content of produced powders here. As observed from table 7, the most affective synthesis parameter of the 13X zeolite content is the zeolite crystallization temperature. The second parameter, which

| RUN no. | a   | b   | c   | Zeolite type and crystallinity (%) |
|---------|-----|-----|-----|------------------------------------|
| 1       | 2.9 | 2.15| 150.70| NaA + NaP                          |
| 2       | 2.9 | 13.00| 495.35| 13X = 60, NaA + NaP                |
| 3       | 2.9 | 28.00| 840.00| Sodalite                           |
| 4       | 5.4 | 2.15| 495.35| Amorphous                          |
| 5       | 5.4 | 13.00| 840.00| 13X = 100                          |
| 6       | 5.4 | 28.00| 150.70| Amorphous                          |
| 7       | 8.0 | 2.15| 840.00| Amorphous                          |
| 8       | 8.0 | 13.00| 150.70| Sodalite                           |
| 9       | 8.00| 28.00| 495.35| Sodalite                           |

**Table 6.** Molar composition of different 13X zeolite synthesis gels as '1Al2O3:aSiO2:bNa2O:cH2O' and their obtained zeolite phase contents and crystallinities based on the Taguchi method’s L9 orthogonal array.
Table 7. Analysis of variance (ANOVA) of carried out experiments in term of the synthesized zeolite powder crystallinity.

| Variable                  | DOF | Sums of Squares | Variance | F-Ratio | Pure Sum | Percent |
|---------------------------|-----|-----------------|----------|---------|----------|---------|
| SiO₂/Al₂O₃                | 2   | 1088.888        | 544.444  | 0       | 1088.888 | 10.652  |
| Na₂O/Al₂O₃               | 2   | 3488.889        | 1744.444 | 0       | 3488.889 | 34.130  |
| H₂O/Al₂O₃                | 2   | 688.888         | 344.444  | 0       | 688.888  | 6.739   |
| Crystallization Temperature | 2   | 4955.555       | 2477.777 | 0       | 4955.555 | 48.478  |
| Total                     | 8   | 10 222.222     | —        | —       | —        | 100     |

Table 8. The optimum conditions for the 13X zeolite synthesis with highest crystallinity.

| Parameters                  | Level no. (Value) | Contribution (%) |
|-----------------------------|-------------------|------------------|
| SiO₂/Al₂O₃ molar ratio      | 1 (5.4)           | 7.77             |
| Na₂O/Al₂O₃ molar ratio      | 2 (13)            | 27.77            |
| H₂O/Al₂O₃ molar ratio       | 3 (840)           | 7.77             |
| Temperature (°C)            | 1 (80)            | 31.11            |
| Expected Response at the Optimum Condition | —                | 99.99            |

great impact on the 13X zeolite formation, is the synthesis mixture’s alkalinity (Na₂O/Al₂O₃). The third parameter with the next significant impact on the 13X zeolite powder synthesis, is the synthesis gel SiO₂/Al₂O₃ ratio. Finally, the synthesis gel water content was found as the lowest significant effect on the synthesized zeolite crystallinity. Based on the results, the optimum conditions for the 13X zeolite synthesis with high crystallinity are reported in table 8 [39, 40].

3.2. Selected parameters effect(s) on the 13X zeolite synthesis

3.2.1. The synthesis temperature

It is noticeable that the zeolite synthesis should be considered in both thermodynamics and kinetic growth points of view. The both independent features of the zeolite crystallization should take into account to justify the observed phenomena at different synthesis times and temperatures [41, 42]. Crystallization temperature is the most affective parameter in 13X zeolite synthesis. In both series of the experiments conducted at temperature range of 80 °C–110 °C, it was found that an optimum synthesis temperature of the 13X zeolite is 80 °C. Increasing the zeolite synthesis temperature from 80 to 95 °C leads to formation of the other zeolite types such as A and P [30, 37]. At higher synthesis temperatures up to 100 °C, the hydroxysodalite zeolite crystals will be formed as is shown in figure 2 (samples S₁, S₄ and S₅). The higher thermodynamically stable hydroxysodalite zeolite seems to be formed by the metastable NaX zeolite conversion at higher synthesis temperatures. This is in agreement with the Ostwald’s law of successive transformation [37].

3.2.2. The synthesis time

As known, zeolites crystallinities are increased over their synthesis time. Increasing the 13X zeolite synthesis time from 5 to 16 h, significantly improved its crystallinity. As observed in figure 2, samples of S₁, S₄ and S₅, the 13X zeolite formation requires relatively long crystallization times. This behavior can be attributed to its framework formation by connecting sodalite cages through double 6 member rings (D6R) and sparser structure [52].

As observed, NaA is the most important zeolite phase can be formed in short crystallization times as it was formed in the second run (S₂) of the Plackett- Burman based experiments (table 3) [37]. Formation/dissolving of different zeolite phases can occur over the zeolite synthesis time then for obtaining the desired zeolite phase with proper crystallinity, crystallization time should be adjusted in it’s relevant optimum value [43, 44]. Also, this zeolite synthesis is favored by low synthesis temperatures as it observed in sample S₃.

3.2.3. The alkalinity

Another affecting parameter in the FAU type zeolite synthesis is its synthesis solution’s alkalinity level as defined by OH⁻/Si or Na₂O/H₂O ratio, where the resultant zeolite crystallinity increases as this factor increases to higher values. The synthesis solution’s high alkalinity is favored for the 13X zeolite formation, however, it should be limited to an optimum value since Si and Al sources’ solubilities increase at very high synthesis solution
alkalinities and silicate anions polymerization degree also decreases while polysilicate and aluminate anions polymerization accelerates. Consequently, the synthesis solution alkalinity increment reduces induction and nucleation periods and speeds up the zeolite crystallization [35]. However, very high alkalinity level result in the gel’s silica solubility increment where in turn result in the gel lower supersaturation. The synthesis gel supersaturation is important for the zeolite crystals’ nucleation and growth then the zeolite crystallinity decreases at low aluminous silicate content. Passing over the optimum 13X zeolite synthesis solution alkalinity result in the formed zeolite dissolution where act as a aluminous silicate precursor and FUA zeolite transformation to the NaP zeolite [38, 41]. This behavior was also observed in figure 2 (sample S2) and figure 3 (sample S1). Reduction in the synthesis solution alkalinity prevents the nucleation process as is observed in figure 3 (sample S4).

3.2.4. The water content

$\text{H}_2\text{O}$ as the synthesis solution solvent in hydrothermally synthesized zeolites can change their other parameters’ range of effectiveness. The water content impact is evaluated in term of the zeolite synthesis solution’s $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar. The synthesis solution $\text{H}_2\text{O}$ content is a key factor for the solutions’ reactants concentration tuning in order to affect the zeolite crystals growth. Generally, the gel saturation/supersaturation is important for the zeolite crystals growth increment and consequently large zeolite crystals formation. On the other hand, the synthesis solution water content reduction results in its $\text{pH}$ increment and pure sodalite formation as can observed for S2 and S8 samples in figure 3 [45].

SEM images of the optimum crystals obtained in the Plackett—Burman method results (as observed for sample S1 in figure 2 and sample S5 in figure 3) are shown in figures 4 and 5, respectively, in two different magnifications. As it is clearly observed in these images, the 13X crystals were successfully formed [46] and their particles mean size were estimated using Image J software as 1.03 and 0.59 $\mu$m, respectively.

As the Taguchi experimental design results revealed, the sample S5 condition in table 6 is optimum where the 13X zeolite powder was successfully formed and then the sample’s gel composition, as $\text{Al}_2\text{O}_3$: 5.4$\text{SiO}_2$: 13$\text{Na}_2\text{O}$: 840$\text{H}_2\text{O}$, was employed as the optimized 13X zeolite powder’s synthesis solution for the zeolite membranes preparation. The selected affecting variables on the 13X membrane preparation are crystallization temperature, synthesis time, and coated layer number as shown in table 9.

3.3. Effects of synthesis parameters on the prepared zeolite membranes

Selected variables of the coated layers number and the crystallization temperature and time impacts on the zeolite membranes preparation and their pure $\text{H}_2$ and $\text{CO}_2$ gas permeances and ideal $\text{H}_2$/CO$_2$ selectivities were investigated and their results were discussed in the following paragraphs.

3.3.1. Effect of coating layers number on the zeolite membranes separation performance

Cross-sectional and surface SEM images of the 13X single layer coated zeolite membrane with the optimum synthesis gel composition prepared at 80 $^\circ$C for 16 h is shown in figure 6. As is observed, the 13X zeolite crystals grew uniformly on the support surface at allocated enough the synthesis time and temperature. As shown in figures 7 and 8, one of the most important affecting parameters on the zeolitic membranes separation.
performance enchantment is the coated zeolite layers number on the supports top surfaces. In order to enhance the previously top single layer zeolite coated supports, it was seeded again by 13X zeolite particles and placed into the autoclave previously filled with the optimum gel composition for the second zeolite layer coating. The third zeolite layers was also hydrothermally coated as same as the second layer on the previously twice coated membranes to cover non-selective defects, cracks or voids (if any) on the single or double layer zeolite coated membranes' surfaces. As the coated zeolites layers number increased, the defects, cavities and voids between zeolite crystals were filled with newly grew zeolite layer and the membrane gas separation performance improved, i.e. its ideal selectivity increased while its permeance reduced. The membrane ability to separate two gaseous component is often characterized in terms of ideal selectivity ($\alpha_{A/B}$) which is the ratio of permeabilities or permeances of the two gases. Due to the three zeolite layer coated membranes' higher ideal H$_2$/CO$_2$ selectivity, here after impact (s) of the synthesis zeolite time and temperature on the three layer coated zeolite membranes were investigated and discussed in the following paragraphs.

### 3.3.2. The synthesis temperature effect(s) on the membranes separation performance

All researchers have paid a particular attention to different zeolites crystallization temperature due to its strong impact on the zeolite membranes' crystallinity, size and their purity, i.e. phase content [47, 48]. The desired 13X zeolite phase only can be obtained within the specific temperature range as was found in the range of 80 °C–100 °C in the current study. The zeolite synthesis temperature impact on the prepared 13X zeolite membranes’ H$_2$ and CO$_2$ permeances are shown in figure 9. As it can be observed, increment in the synthesis temperature from 80 to 90 °C resulted in the membrane’s gaseous penetrants permeances enhancement where can be attributed to the larger 13X zeolite crystals formation on the supports' surface at higher synthesis temperature [37].

The crystals' nucleation and also growth are strongly affected by the synthesis temperature. The pre-crystal nuclei number and the crystal growth rate are decreased and increased, respectively, as the synthesis temperature increases. As crystal growth rate increased, larger crystals in size are formed and integrated faster as the membrane selective layer over the seeded support. Faster crystals integration is obtained in the compensate of lower average zeolite crystals density, i.e., more defective regions such as nonselective cracks or voids are appeared in the faster formed zeolitic membrane layer [40, 49].

As the synthesis temperature more increased from 90 to 100 °C, much larger crystals were formed resulted in larger zeolite defects appearance on the membrane zeolite selective layer. Coarser formed zeolite crystals led to
improved higher porous and rougher coated zeolite layer, i.e. less top layer compactness and uniformity as more defect/crack appearance in the coated top zeolite layer. At the lower synthesis temperatures (i.e. 80 °C), a dense, uniform and smooth surface crystalline top zeolite layer was formed [40, 50]. Based on the tradeoff between gaseous penetrants’ permeance through the membranes and their ideal selectivities, the zeolite synthesis temperature of 80 °C was selected and applied for further investigation hereafter to prepare the optimum zeolite membrane in separation performance point of view.

3.3.3. The synthesis time effect(s) on the membranes separation performance
Synthesis time is also another strongly affecting parameter on the zeolite membrane preparation. Synthesis time impact on the prepared zeolite membrane’s H₂ and CO₂ permeances at various operating temperatures are shown in figure 10. Synthesis time of 8 h was not found enough proper for the 13X zeolitic top layer formation on the support’s surface as it was formed as a very thin zeolite layer, resulted in its high permeability and low
selectivity. As observed, increasing the zeolite synthesis time from 8 to 12 h for all the synthesized membranes, resulted in the zeolite layer thickness increment and its integration on the membrane support surface as a dominant phenomenon occurred at 12 h synthesis time. The zeolite layer, which determines gas penetration behavior of the membrane, was formed properly at 12 h synthesis time and uniformly covered the support surface resulted in the reduced membrane gas penetration. Meanwhile there were still non zeolitic/amorphous regions kept the membrane’s selectivity low [49].

At the synthesis time higher than 12 h, gaseous penetrants permeabilities increase due to increased porosity of the formed zeolite layer as the larger crystals are formed and the selective zeolite layer crystallinity and porosity enhance as well. At the zeolite top layer, non-zeolite cavities are covered by larger zeolite crystals, and thus the

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**Figure 7.** Effect of coated zeolite layer number on the 13X zeolite membrane’s ideal \( \text{H}_2/\text{CO}_2 \) selectivity.

**Figure 8.** Effect of coated zeolite layer number on the 13X zeolite membrane’s \( \text{H}_2 \) permeance.
membranes selectivities enhance and penetrants permeabilities also increase due to the more porous selective layer. Since, higher selectivity of the membrane is favored with its higher permeance, the 16 h synthesis time with high ideal H₂/CO₂ selectivity and also acceptable penetrants permeances (although it is lower than that of the 8 h synthesized zeolite membrane) was selected as the best membrane synthesis time [49].

Figure 11 indicates synthesis temperature’s impact on ideal H₂/CO₂ selectivities of the zeolite membrane’s at various synthesis times. The membrane selectivity decreased as the synthesis temperature increased from 80 to 100 °C. As the synthesis temperature increased up to 100 °C, more non-zeolite cavities or defects were appeared in the coated top zeolite layer on the support, led to the membranes’ lower selectivities. However, the membrane ideal selectivity increment at the crystallization temperature till 80 °C can be attributed to the 13X zeolite layer complete growth on the seeded supports. Also, as figure 11 reveals, as the synthesis time prolonged from 8 to
16 h, the prepared membrane ideal selectivity improves. Therefore, the best permeances of the prepared 13X zeolite membranes was obtained a synthesis temperature of 80 °C for a 16 h.

4. Conclusion

Some affective variables on the 13X zeolite powders synthesis were evaluated by the Plackett—Burman experimental design method and, they were ranked based on their effectiveness. After selecting the most affective synthesis variables, the 13X zeolite powders were synthesized by the Taguchi experimental design method’s L9 orthogonal array. Effects of different synthesis parameters, including the synthesis solution SiO2/Al2O3 molar ratio, water content as H2O/Al2O3 molar ratio and, alkalinity as Na2O/Al2O3 molar ratio and, also the crystallization temperature on the 13X zeolite powder formation were also investigated. The characterization analysis results indicated that the zeolite crystals synthesized with the synthesis solution composition of 5.4SiO2:Al2O3: 13Na2O: 840H2O at 80 °C for 16 h has the highest 13X zeolite crystallinity degree of ~100%. The synthesis temperature was found as the most effective synthesis parameter on the 13X zeolite powder, after that, the 13X zeolite powder crystallinity was greatly affected by the synthesis solution alkalinity and the third parameter was found as the synthesis solution’s SiO2/Al2O3 ratio. Finally, the synthesis solution water content had the lowest impact on the 13X zeolite crystallization.

As the 13X zeolite powder synthesis temperature increased, the crystal nucleation and growth rate increased and larger crystals were formed. Synthesis time and temperature and zeolite coated layers numbers effects were also investigated on the 13X zeolite membrane’s H2 and CO2 permeances and ideal H2/CO2 selectivities. Finally the optimum 13X zeolite membrane’s H2 permeance as 2.88 cm³ cm⁻² Pa s and ideal H2/CO2 selectivity as 4.72 were obtained at three coated zeolite layer number (i.e. the complete growth of 13X zeolite layer) on the membrane support at 80 °C for 16 h.

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