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Separation of $CH_4/H_2/CO_2$ Gas Mixtures Using Spherical Pellets of Deposited Zeolites on Monmorillonite

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ABSTRACT

Use of the zeolite adsorbents is one of the low-cost methods in gas purification processes. The aim of this work is to synthesize three types of zeolite/quasi-zeolite through hydrothermal technique and evaluate their performance efficiency in the hydrogen gas purification. The gas mixture contained hydrogen, carbon dioxide and methane. The results indicated that at different pressures, the adsorption of the desired gases at lower temperatures is more favorable. Although all three adsorbents had great performance, for all three adsorbents, carbon dioxide adsorption was higher than methane adsorption, and the order of efficiency was as follows: NaA>SAPO-34>BaA. However, SAPO-34 owned a more superior functioning in absorbing methane, and the performance was as follows: SAPO-34>NaA>BaA. It should be remarked that at pressures less than 300 kPa, the adsorption of the desired gases in the BaA adsorbent reached a higher value faster and shows the superb acting of this adsorbent at low pressures.

Introduction

Due to the limited resources of fossil fuels and the pollution caused by their combustion to generate energy in various industries like factories and transportation, there is an immediate demand for a clean substitution to this sort of fuel [1-3]. The distinctive features of clean fuel in common are that it does not pollute the environment and possesses no consequence on global warming by minimizing greenhouse gases (GHG) emissions [4-5]. Burning hydrogen gas as a viable energy source owns all of the earlier qualities for a clean and safe fuel [6]. The generated energy through igniting hydrogen is significant (~ 252 kJ/mol). The self-igniting temperature of hydrogen is high (~ 537 °C), lighter than conventional fuels, and rapidly rises when released into the environment [7-8]. Consequently, it can therefore be stored safely and transported in liquid form at ordinary temperatures. In most cases, hydrogen is still assumed as a reaction product and not as an alternative and recyclable fuel [9-10].

Nowadays, hydrogen is produced through a variety of prevalent methods, like natural gas reforming, partial oxidation of fossil fuels and electrolysis of water [11-13]. For example, in

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reforming of methane, produced hydrogen exists along with other gases like carbon dioxide, methane, carbon monoxide, water vapor and nitrogen [14]. To consume hydrogen as a fuel, its purity must be increased to more than 99% and the other gases must be eliminated [15]. Effective methods should be operated efficiently to reduce both the cost of purified hydrogen and to increase separation efficiency. A common method for purifying hydrogen is to use a suitable adsorbent in pressure swing adsorption (PSA) technique [16]. Up to now this approach has been applied commercially successfully, although it can be widely expanded in used adsorbents [17]. Many adsorbents like zeolites, MOFs (metal organic framework), activated carbon and polymers have been utilized in this field [18-21]. Many researchers have used composites of some adsorbents to increase gas separation performance, such as: MOF/zeolite, polymer/oxide, MOF/activated carbon, MOF/graphene and polymer/zeolite and etc. [22-24].

In a study by Delgado et al. [25], BPL activated carbon and *13X* Zeolite were utilized to purify hydrogen. The mixture contained hydrogen, methane, carbon dioxide, and carbon monoxide. The adsorption process was carried out inside a stainless-steel tube (ID. = 9 mm, 25 cm high) with the adsorbent at its center that was surrounded by two spiral tubes for preheating. The adsorption isotherms were carried out at temperatures of 25-65 °C. The ultimate outcomes demonstrated that the *13X* zeolite performed better than the *5A* zeolite and can generate a yield of 99.99% for hydrogen with a value of d 7.2 mol H_2 kg^{-1} h^{-1}, while at same condition *5A* zeolite reduced the yield by 0.09%. In another enquiry by the same researcher and his assistants [26], the purification of hydrogen from gaseous mixtures using *CaX* and *5A* zeolites was investigated in PSA method. The considerable range of adsorption temperature variations was the same as in the previous work. The results displayed that when the feed gas pressure was 3 bar, between the studied adsorbents (*4A* zeolite, *5A* zeolite, *NaX*, *AC* and *CaX* zeolites), the CaX adsorbent efficiency was superber. It also performed more effectively than *5A* zeolite with a same type used feed for hydrogen recovery testing. But in the removal of methane and carbon monoxide, the performance of *5A* zeolite was much excellence.

How the adsorbent is synthesized causes a significant effect on its structure and consequently its efficiency in the process. Consequently, one kind of adsorbent may typically exhibit different efficacy in one type of reaction with two separate synthesis methods [27]. The purpose of this investigation is to synthesize zeolite and quasi-zeolite materials such as *SAPO-34*, *NaA* and *BaA* by hydrothermal method. The porous BaA zeolite is excellent candidates in wastewater treatment. This zeolite adsorbs heavy metal ions properly. The NaA zeolite is applied for gas refinery and used for water softener. The crystal structure of SAPO-34, a micro pore zeolite, is similar to that of chabazite and has a special water absorbing capacity and bronsted acidity. This can be used as an adsorbent, catalyst and catalyst support in applications with low carbon olefin transfer, auto gas purification, MTO reactions, etc. After material synthesis and particle structure analysis using XRD, FTIR, SEM and BET tests, the most excellent types were identified in terms of porosity, size of cavities and surface to volume ratio. Afterwards, the strongest type of adsorbent was employed to purify hydrogen and separate gases such as carbon dioxide and methane from the mixture.

Materials and Methods

Zeolites Synthesis

NaA and BaA

The most fundamental step for zeolite synthesis is the gel preparation. Based on the results of Thomson and Haber's research, by applying a set of changes in time and temperature of crystallization and aging, the *NaA* zeolite was synthesized according to the following conditions. Molar ratios of raw materials were to Al_2O_3: 1.926 SiO_2: 3.165 Na_2O: 128 H_2O. Also, hydrothermal synthesis was performed according to the following details. First, 0.732 g of sodium hydroxide (NaOH, 98 wt. %, Merck) was dissolved in 80 ml of distilled water, and the resulting solution was divided into two equal volumes. Then 8.26 g of sodium aluminate (powder, >99.9%, SODIUM ALUMINATE ANHYDROUS, Sigma Aldrich) and 15.48 g sodium silicate (27 wt% SiO_2, 8 wt% Na_2O, Merck) were added to the sodium hydroxide solutions separately and mixed until clear solutions were obtained. The two solutions were added gradually together and were stirred gently to obtain a viscous gel. The gel was stirred at 60 °C for 3 h. After gel uniformization, it was transferred to autoclave for crystallization. The autoclave was properly sealed and placed in the oven at 100 °C for 20 h. Then, centrifuge was used to separate the solid from the solution. Then it was washed to remove excess ions until it was reached pH 7. Ultimately, the resultant product was dried at 200 °C (2 °C/min) for 3 h.

The *BaA* zeolite was made ready through the subsequent method by ion exchange of the *NaA* zeolite. At the start, 5 g of the *NaA* was poured into a fixed bed reactor. Next, a stream of 20% barium chloride solution 2 (anhydrous barium chloride, Beads, 99.95%, Sigma Aldrich), was passed through the particles at a flow rate of 100 ml/h at 60 °C. At the end, after washing with distilled water, the particles were returned into the fixed bed reactor, and the barium chloride solution was passed under the same conditions. This was performed three times. After rinsing, the particles were eventually left in the oven for 12 h at 100 °C for drying.

SAPO-34

According to research in the field, *SAPO-34* was synthesized with a few modifications. The following is a summary of the process. In the hydrothermal approach (based on the research of Liu et al. [35]), a gel with 1.0 Al_2O_3: 0.8 P_2O_5: 0.2 SiO_2: 2.0 DEA (diethylamine): 50 H_2O structures was formed. Ludox (AS-40, 4.5 g) and orthophosphoric acid (85%) were then added to the mixture. After carefully blending, the gel was transferred to a Teflon line autoclave and held at 200 °C for 72 h. Afterwards, the resultant solid was filtered. It was then washed with deionized water (4 times) to remove unreacted material. Eventually, the product was calcined for 3 hours at 400 ° C.

To properly use the zeolites powder in a fixed bed reactor, the synthesized zeolites were reshaped into spherical grains as follows. A muddy-like composition of 25 wt% of *Monmorillonite* (clay-Fluka) and 75 wt% zeolite was combined by adding some deionized water. The consequent compound was converted into balls of approximately 3 mm in diameter and were dried at 200 ° C for 3 h. The final shape of the three adsorbent particles is given in Fig. 1.

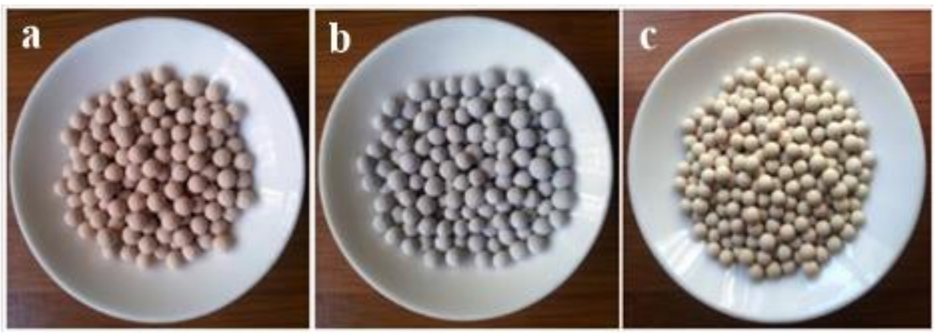

Fig. 1. The final form of synthesized zeolites, a) SAPO-34, b) BaA, c) NaA

Adsorbents Characterization

X-ray diffraction (XRD) analysis was used to investigate the crystalline structure of the adsorbent particles. The EQUINOX diffractometer (Inel Co., λ=1.5406 Å of CuKα radiation) was employed for this. The XRD patterns were determined and recorded in 5-45° (2θ) with step length of 0.05°. Scanning electron microscopy (SEM) analysis was used to survey the appearance and structure of the powders. ZEISS detector (Model Evo 18, 25 kv) was utilized for this function. X-ray fluorescence spectrometer (XRF) evaluation was operated to determine the composition and the percentage of elements in the samples. (XRF; SPECTRO X -LabPro). The BET (Brunauer, Emmett and Teller) technique was utilized to calculate the particle specific surface area. Further, the micropore volume and external surface area were also determined typically using the t-plot approach. Finally, the total pore volume was gained via applying nitrogen gas adsorption by particles at (P/P_o) = 0.99. The nitrogen adsorption and desorption of samples at 77.3 K were obtained using a Quantachrome NovaWin2 instrument.

Adsorption Process

Prior to the adsorption process, zeolites were activated to remove possible impurities in the pores. For this purpose, the particles were set into the adsorption column, and the helium gas (10 ml/min) was passed through the column at 400 °C for 1 h. The column and the particles were then cooled to ambient temperature. The features of the adsorption column were: stainless steel column, 9 mm of inner diameter, column height 62 cm and covered with Ben Marie thermal jacket with temperature adjustment accuracy of 0.1 °C. The adsorption operations were actioned at three temperatures of 5, 25 and 50 °C, at pressure range of 1-10 bar. Following settling the temperature and pressure, the inlet valve of the feed gas linked to the adsorption column was opened. The mass flow rate of each feed stream being controlled by an MFC. After the column was saturated with feed at a certain pressure, the inlet and outlet valves of the adsorbent column were closed. After a fixed period of time, samples were taken from the column exhaust gas. The sample was injected into the GC column to determine the concentration of the components. By monitoring the sub-peak levels of carbon dioxide, hydrogen and methane, the amount of each gas in the column was calculated. An outline of the system in is presented Fig. 2.

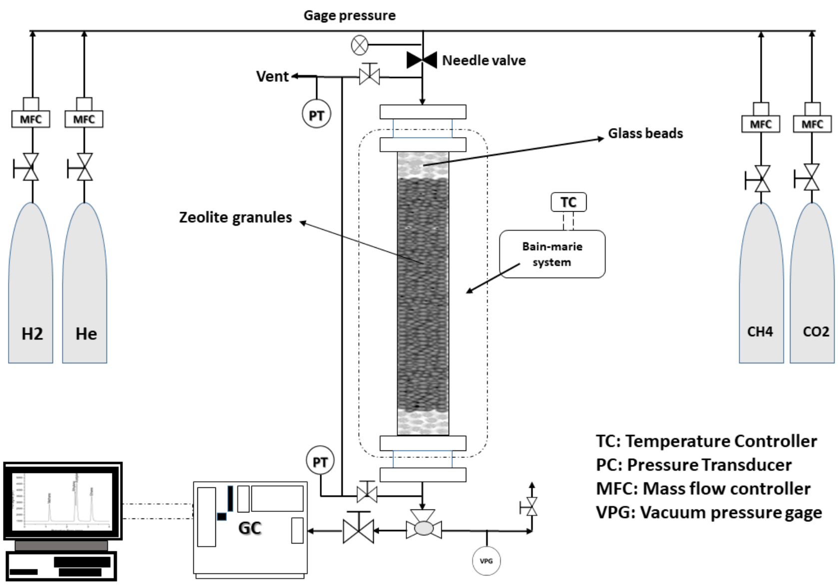

Fig. 2. Schematic graph of the adsorption apparatus

All the used gases had a purity of ≥ 99.99%. Feed gas was used at flow rate of 100 mL/min, which included the following percentages (v/v): 5% helium, 10% nitrogen, 15% carbon dioxide and 70% methane.

Theories and Calculations

According to the equilibrium adsorption information, the adsorption process can be modeled. To analysis the adsorption process, there are many models in this field, that most significant are: Langmuir, Sips, Freundlich, UNILAN and Toth. Therein research, Langmuir and Sips models were employed to study the adsorption performance. Of course, many researchers have inferred that the Sips model predicts equilibrium adsorption better than the Langmuir equation. In Eq. 1, the Sips isotherm is given:

$$q = q_m \frac{bP^n}{1 + bP^n} \tag{1}$$

where q is the quantity of adsorbed gas (mmol/g) utilizing the adsorbent at temperature T and pressure P. The value of q_m, b and n are the maximum adsorption value, dependency constant of the equation and heterogeneity constant of the process, respectively.

It is also clear from the Sips equation that, when pressure is high, it tends to Langmuir and conversely, in low pressures, it tends to the Freundlich equation. It is noteworthy that utilizing MATLAB software, the constants of the Sips equation and the correlation coefficients were determined. Utilizing the constant Henrys Law, the interaction between the adsorbent and the adsorbed surface can be determined. Consequently, its determination is very important in the adsorption system. As pointed out before, at low pressures the Eq. 2 tends to the Langmuir equation (Eq. 3).

$$q = q_m \frac{bP}{1 + bP} \tag{2}$$

$$\lim_{P \to 0} \left(\frac{q}{P}\right) = bq_m = K_H \tag{3}$$

As indicated in Eq. 3, the amount of adsorption at pressures near zero tends to a constant value that is popularly known as Henry's Law constant. In Eq. 2, if the $(1/q)$ is plotted versus $(1/P)$, the b and q_m can be easily obtained. As well, the Henry's constant relation with temperature is described via the Van't Hoff equation, shown below (Eq. 4):

$$\ln\left(\frac{K_H}{K_{H_o}}\right) = \frac{-\Delta H}{RT} \tag{4}$$

In Eq. 4, ΔH (J/mol) presents the amount of heat or adsorption energy. K_{H_0} is the parameter of the van't Hoff equation, T absolute temperature and R represents the global constant of gases. At a certain temperature, the subsequent fraction can be used to compare the adsorption equilibrium selectivity ($S_{1,2}$) for the two types of gas (Eq. 5):

$$S_{1,2} = \left(\frac{K_{H,1}}{K_{H,2}}\right) \tag{5}$$

in which, the numerator and denominator of the fraction refer to the Henry's constants for gases 1 and 2 respectively.

Result and Discussion

Characterization of Adsorbents

In order to determine the crystalline phase of the particles, XRD analysis was done. The outcomes of the XRD evaluation are demonstrated in Fig. 3.

Most zeolites have large single units, and consequently in their diffraction pattern, some reflections are viewed at small diffraction angles. This especially overlaps the reflected rays when the zeolite mixture is existent.

In the case of *NaA* zeolite by other investigators, they have found characteristic peaks at (2θ): 7.2, 10.3, 12.6, 16.2, 21.8, 24, 26.2, 27.2, 30, 30,9, 31.1, 32.6, 33.4 and 34.3 that are consistent with those obtained in this study. As well, for the pattern obtained of the *SAPO-34* zeolite, it corresponds with to the structures detected in the references, indicating a cubic crystalline arrangement.

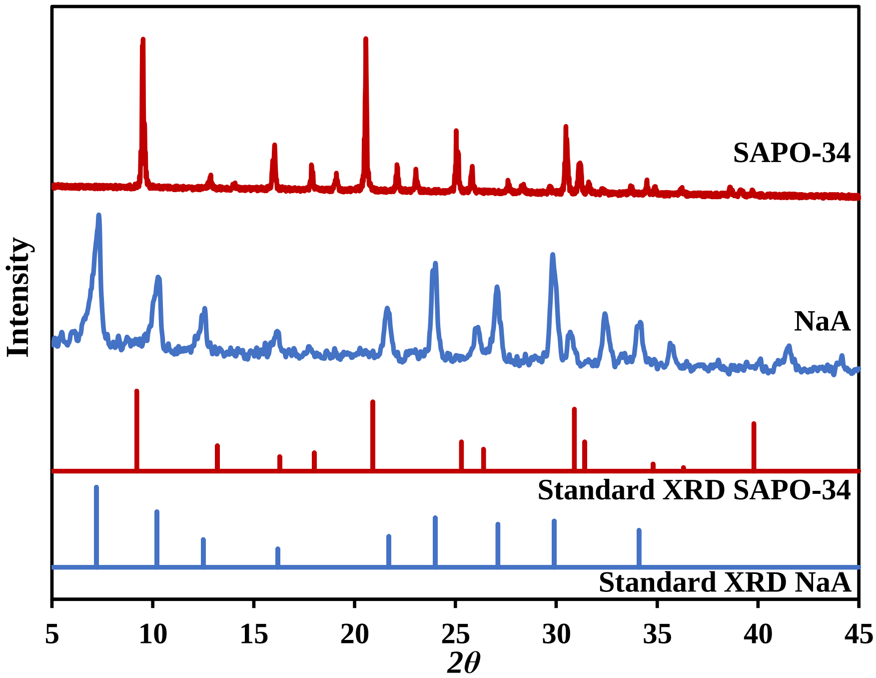

Fig. 3. XRD patterns of the adsorbents

The SEM images displayed in Fig. 4 also confirm the results of the XRD test because the cubic structures of the zeolites are properly recognizable. As Fig. 4 clearly shows, most *SAPO-34* and *NaA* adsorbent particles present a cubic crystalline appearance with oblique edges. But their chief difference is in particle largeness and *SAPO-34* crystals are in the range of about 200 to 500 nm, and *NaA*-crystals with a finer dimension are less than 200 nm in size.

The results of the XRF test, the percentages composition of the zeolites are presented in Table 1. Also, in Table 2 gives the BET test results. XRF results confirm the synthesis of all three adsorbents. Comparison of these results proves complete ion exchange from sodium to barium.

The specific surface area of the adsorbent particles, the volume of the micropores, and other related properties were determined by the *T*-plot approach. The results are consistent with many of the published findings in this field.

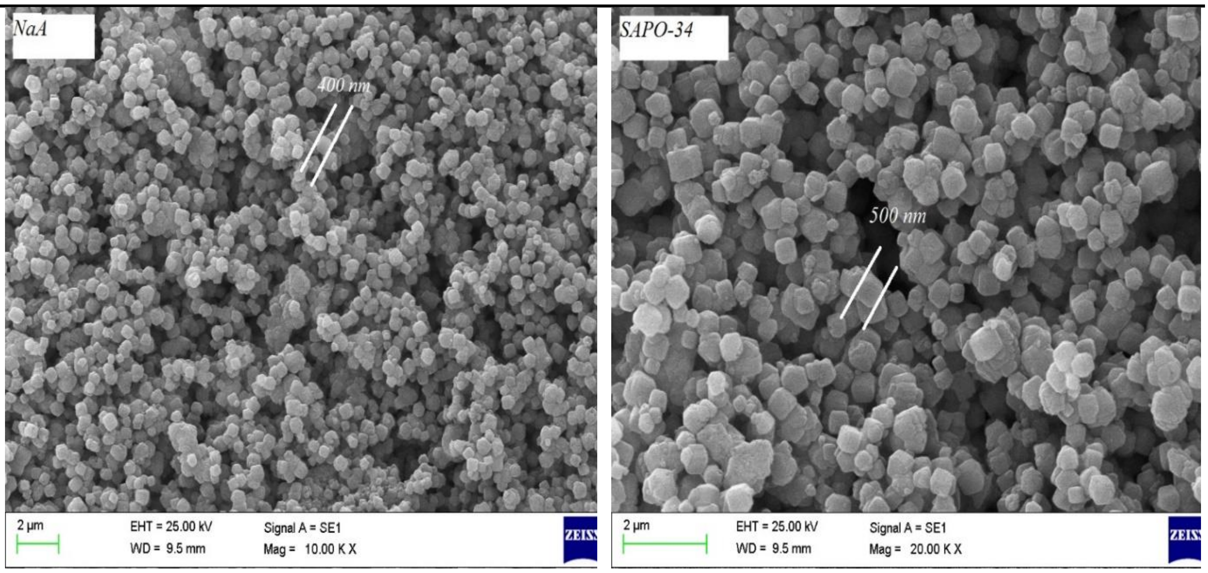

Fig. 4. SEM images of the zeolites

Table 1. Results of XRF analysis (chemical compositions)

Sample	SiO2	Al2O3	Na2O	TiO2	Fe2O3	MgO	CaO	K2O	P2O5	BaO
NaA	36.61	29.04	24.13	0.26	1.42	0.86	1.52	1.39	0.11	0.01
SAPO-34	14.71	49.06	1.69	0.02	0.06	0.03	0.05	0.04	34.32	0.05
BaA	32.89	23.65	0.12	0.31	1.33	0.78	1.02	0.98	0.09	34.21

Table 2. The textural characteristics of synthesized adsorbents

Sample	BET surface area (m^2/g)	Microspores volume (cm^3/g)	External surface area (m^2/g)	Pores volume (cm^3/g)
NaA	232.4	0.11	41	0.15
SAPO-34	402.2	0.19	45	0.23
BaA	211.8	0.09	40	0.12

Evaluation of the Adsorption Performance for Pure Components

The isotherm diagrams for the adsorption of the three gases: methane, hydrogen and carbon dioxide on the three synthesized zeolites are displayed in Fig. 5. Each diagram shows the adsorption isotherm for a certain gas and zeolite at three temperatures. The pressure is also varied from 1 to 1000 kPa. In Fig. 5, each row is for certain zeolite and each column is for a gas.

By comparing all graphs with the reference isotherms defined in IUPAC classification, can be found that all of them follow the Type-1 adsorption isotherm [28]. The adsorption curves obviously illustrate the adsorption power of the adsorbent. The steeper slope at lower pressures shows that with slight increase in pressure, the maximum adsorption can be achieved. So, for all the adsorbents, the CO_2 adsorption capacity was higher than the other two gases, and also the *BaA* zeolite performed better and the CO_2 adsorption at very high pressures is slightly higher in *NaA* zeolite. The surfaces of the adsorbents have the cations, and the better adsorption of CO_2 can be attributed to its stronger quadrupole moment with the adsorbents surface rather than to the other two gases [29-30]. The unit cell structure of the *BaA* and *NaA* zeolites are composed of eight sodalities cages that are attached to double four-membered loops, but *SAPO-34* owns the different structure that shaped from duplicate 6-rings. As well as the pore sizes of these zeolites are equal to 3.9, 3.6 and 3.7 nm for NaA, BaA and SAPO-34 respectively. From all the diagrams in Fig. 5, the obvious consequence is that accompanied by temperature increasing, the maximum adsorption capacity and equilibrium time decreases. Due to the increase in particles kinetic energy, so the desorption process precedes the adsorption [31]. The adsorption data for temperature of 278 K were fitted on two isotherm equations of Sips and Langmuir. In this way, the stability of the equations was gained to determine the heterogeneity of the adsorbents. These outcomes are reported in Tables 3 and 4.

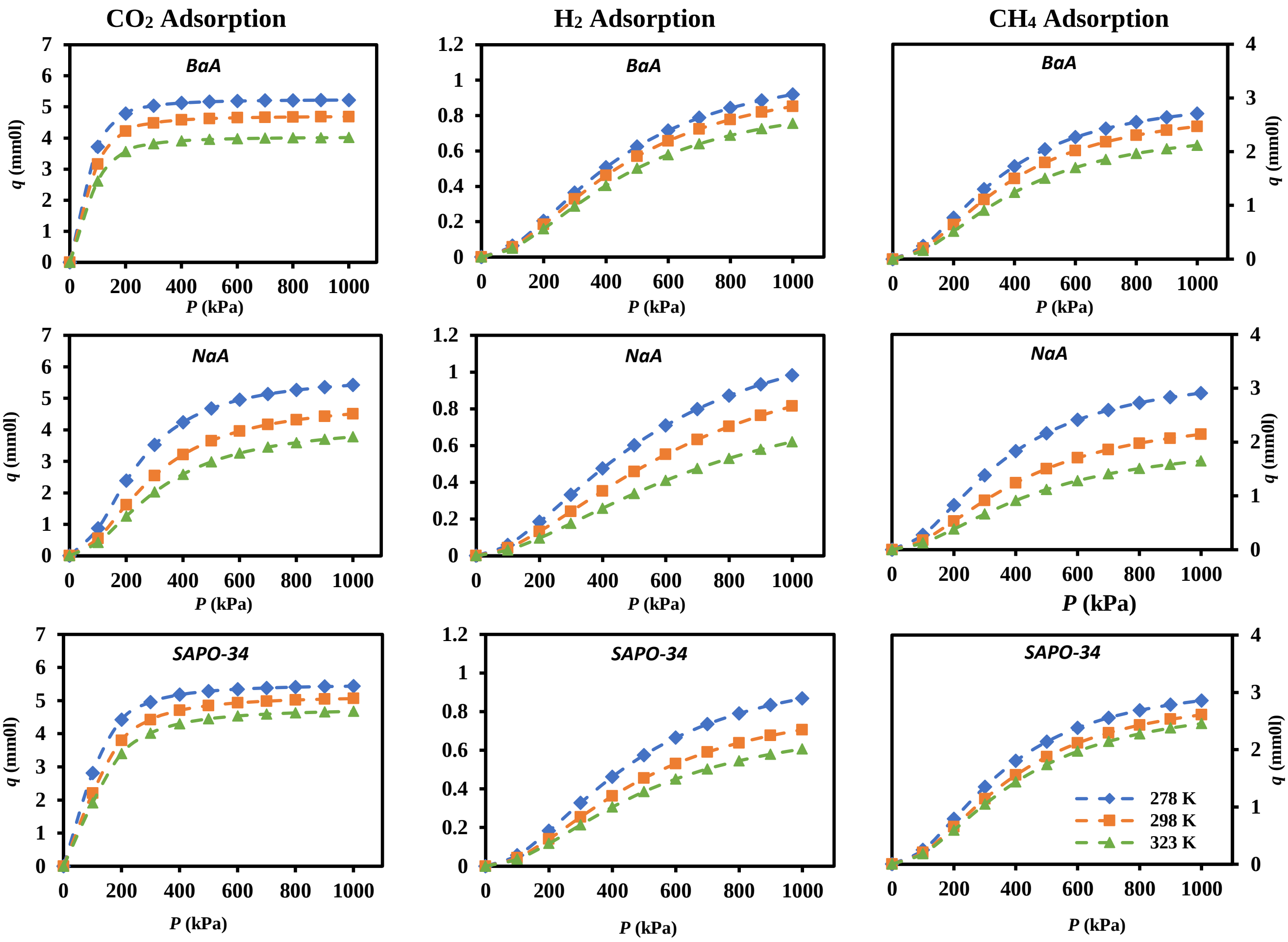

Fig. 5. CH_4, H_2 and CO_2 adsorption isotherms 278, 298 and 323 K for three adsorbents

Table 3. Sips constants for considered gases and adsorbents at 278 K

Sips Parameters	Adsorbed Gas								
	CH_4			**H_2**			**CO_2**		
	NaA	SAPO-34	BaA	NaA	SAPO-34	BaA	NaA	SAPO-34	BaA
qm (mmol/g)	3.340	3.231	3.054	1.320	1.070	1.115	5.722	5.490	5.238
n	1.8803	1.9633	1.9561	1.7893	1.8912	1.8891	1.9981	1.9872	2.1105
K (kPa-1)	1.54E-5	9.81E-6	1.49E-3	1.24E-5	9.14E-6	1.01E-5	1.80E-5	1.11E-4	1.46E-4
R2	0.992	0.997	0.987	0.972	0.991	0.979	0.998	0.999	0.988

Table 4. Langmuir constants for considered gases and adsorbents at 278 K

Langmuir Parameters	Adsorbed Gas								
	CH_4			**H_2**			**CO_2**		
	NaA	SAPO-34	BaA	NaA	SAPO-34	BaA	NaA	SAPO-34	BaA
qm (mmol/g)	3.340	3.231	3.054	1.320	1.070	1.115	5.722	5.490	5.238
b (kPa-1)	4.94E-4	6.57E-4	4.87E-4	4.61E-4	3.49E-4	4.12E-4	7.0E-4	1.021E-3	5.64E-4
R2	0.989	0.907	0.987	0.959	0.993	0.991	0.964	0.918	0.907

In Eq.'s 1 and 2, the constants of isotherms are explained previously. Also, the responses of the equations are adsorption (dependent variable) in mmol/g that were obtained at different pressures as an independent variable.

Evaluation of Gas Selectivity and Henry's Constant

Another criterion for determining the intensity of the adsorption force between the adsorbent and the adsorbate was to find the Henry's constant applying the Langmuir equation. Bigger values of this constant indicate a better interaction between the two adsorption factors [32]. The mentioned values are given in Table 5.

As well, utilizing the Henry's constants ratios, the selectivities for gases were calculated and are given in the last two columns of Table 5. This result that the selectivity for carbon dioxide is greater than hydrogen, confirms its better adsorption by the adsorbents. Carefully in Henry's constants for all samples, a decreasing trend is observed with increasing temperature. In the field of gas separation and purification, Henry's constants and selectivity are particularly important. And with the help of these specifications, the best adsorbent can be preferred for the process [33]. As a direct result of the Van't functional Hoff equation, the $ln(K_H)$ was carefully plotted against $1/T$ and is displayed in Fig. 6 for each zeolite.

Table 5. Henry's constants of CH_4, H_2 and CO_2 and alteration of equilibrium selectivity of CO_2/CH_4 and H_2/CH_4 on the adsorbents

Adsorbent	Temp. (K)	KH (mmol. g−1. kPa^{-1})			KH(CO2)/ KH(CH4)	KH(H2)/ KH(CH4)
		CH4	H2	CO2		
NaA	278	0.0016	0.0005	0.0007	2.4276	0.3688
	298	0.0012	0.0054	0.0026	2.2183	0.4605
	323	0.0008	0.0004	0.0018	2.1323	0.4749
SAPO-34	278	0.0021	0.0004	0.0056	2.6405	0.1759
	298	0.0017	0.0003	0.0041	2.4707	0.1822
	323	0.0014	0.0026	0.0034	2.4274	0.1862
BaA	278	0.0015	0.0004	0.0029	1.9863	0.3089
	298	0.0012	0.0004	0.0023	1.9412	0.3197
	323	0.0009	0.0003	0.0017	1.8923	0.3262

An additional proof for deciding the intensity and strength of adsorption connecting the adsorbent and the adsorbate is to find the heat of adsorption. The larger the value of this parameter, the higher the adsorption quality [34]. The desired results of these calculations are reported in Table 6. As can be seen from the results in Table 6, the highest and the lowest heat of adsorption are related to carbon dioxide and hydrogen, respectively on the *SAPO-34* adsorbent.

Table 6. Pre-exponential factors and heat of adsorption for studied gas on the adsorbents

Adsorbent	KHo (mmol. g^{-1}.kPa^{-1})			-ΔH (kJ/mol)		
	CH4	H2	CO2	CH4	H2	CO2
NaA	1.035E-5	1.015E-4	6.52E-6	1.4169	0.5056	1.7882
SAPO-34	5.784E-5	1.780E-5	5.717E-5	1.0036	0.8515	1.2761
BaA	5.049E-5	2.640E-5	7.190E-5	0.9469	0.8021	1.0420

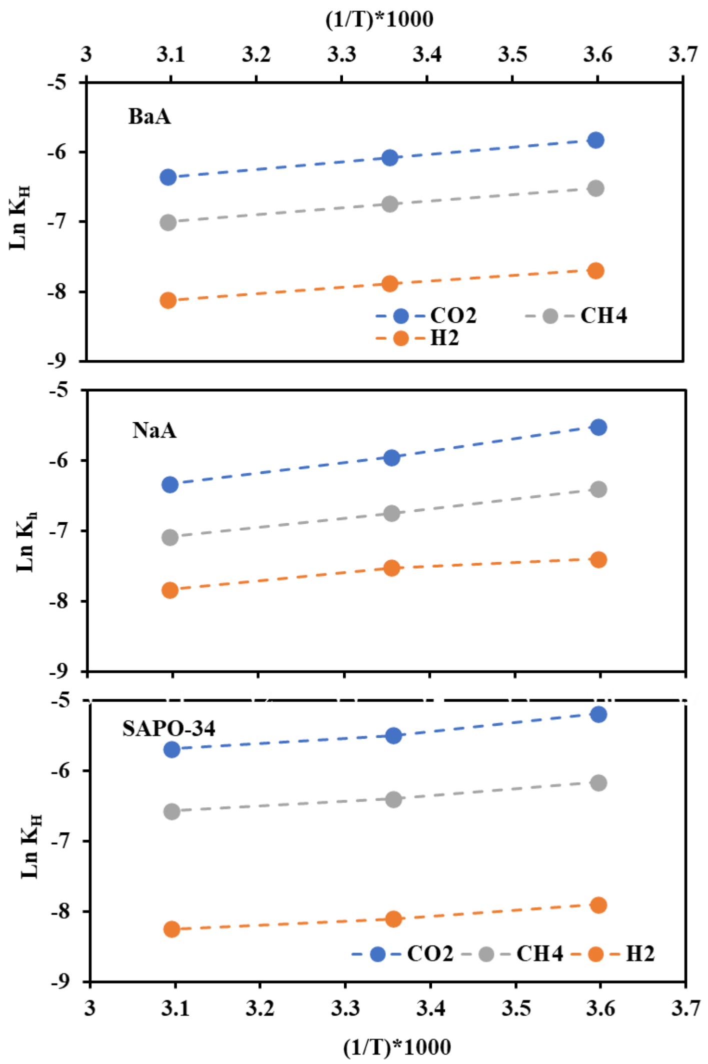

Fig. 6. Ln (K_H) against of (1/*T*) for adsorption of CO_2, N_2 and CH_4 on the adsorbents

Conclusions

In this investigation, in order to purify natural gas, adsorption onto zeolite adsorbents was utilized. For this purpose, three types of adsorbents were synthesized, identified and used in the adsorption process. The adsorption process was such that with pressure variations from low to 1,000 kPa and at three temperatures (278, 293 and 323 K) the equilibrium adsorption isotherms were analyzed. The studied gas contained CH_4, H_2 and CO_2. All the studied adsorbents had excellent carbon dioxide uptake and separation performance which owned the greatest potential in terms of *NaA* and *SAPO-34* uptake. It should be noted that although *BaA* zeolite had a little difference in maximum adsorption, its isotherm was kinetically superior. *BaA* zeolite possessed the highest adsorption at lower pressures than the other two zeolites, one of its advantages. Two isotherms of Langmuir and Sips were employed to investigate the adsorption procedure. The adsorption data were fitted to the equations, and the parameters of the equations were determined. The results of two-isotherm parameter analysis confirmed the maximum carbon dioxide uptake on *NaA* and *SAPO-34*. The constants obtained from Henry's law for different temperatures and different adsorbents were obtained and compared. As the results showed, the selectivity of carbon dioxide to methane was higher than that of hydrogen to methane for all three adsorbents at 278 K. The selectivity of carbon dioxide to methane for the three adsorbents *NaA*, *SAPO-34* and *BaA* were: 2.4, 2.6 and 1.99 respectively. The selectivity ratio for hydrogen to methane for the three adsorbents was: 0.37, 0.17 and 0.31 for *NaA*, *SAPO-34* and *BaA* respectively.

In other words, the absorption capacity of the two adsorbents *NaA* and *SAPO-34* is high, but the adsorption performance on *BaA* is also excellent, which may increase the adsorption capacity by changing BaA synthesis procedure.

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