Enhancement of CO_2/CH_4 Adsorptive Selectivity by Functionalized Nano Zeolite

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ABSTRACT

In this work, we have modified a synthesized Y-type zeolite (Si/Al = 2.5), with three different amines to investigate the influence of adsorbent's surface modification on CO_2 selectivity over CH_4. The pristine and amine-functionalized NaY zeolites were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) analysis, and N_2 adsorption. The results showed that the structure of zeolite was preserved after amine modification. The adsorption capacity of CO_2 and CH_4 on these adsorbents was measured by the volumetric method at 298 K and 348 K. In comparison to CH_4, CO_2 was preferentially adsorbed on these adsorbents. the results demonstrated that incorporation of amines into zeolites structure improved significantly the selectivity towards carbon dioxide so that the optimal selectivity of CO_2 over CH_4 reached to 4.04 on zeolite modified with 2-methylaminoethanol at 348 K. Chemical interaction between adsorbate and sorbents as well as the steric effects were assessed to be the main reasons of high selective adsorption of carbon dioxide on amine-functionalized zeolites. Two of the most common adsorption models, the Langmuir and Sips isotherms, were used to correlate the experimental data of CO_2 adsorption on the adsorbents The results revealed that the amine-functionalized NaY zeolites could be a good sorbent for use in flue and natural gas separation processes.

Keywords: *Adsorptive Selectivity, Faujasite Zeolite, Separation, Amine modification.*

1. Introduction

It is widely known that during burning of traditional fuels like gasoline and diesel, large amounts of CO_2 is released into the environment which it is one of the most important issues concerning global warming. From the perspective of economic and environmental, the utilization of natural gas as fuel has several advantages such as low cost, more efficient burning, and less CO_2 emission. So, it is predicted that natural gas consumption will reach its highest level in the near future [1-3]. CH_4 is one the constituent of natural gas (usually 80–90%), but there are some contaminants like CO_2 that should be removed [4,5]. The main reasons for the removal of CO_2 from natural gas are: enhancement of the heat value of natural gas, purification of the air and reduce the global warming concern, prevention of the equipment and pipelines corrosion, and reduction the cost of natural gas transportation.

The available Carbon Capture and Sequestration (CCS) technologies for removal of CO_2 from natural

gas are amine-based absorption [6-10], cryogenic distillation [11,12], membrane and adsorption-based processes [13-15]. Owing to reaction between amines and CO_2, chemical absorption by amine solvents has high CO_2 selectivity. Nevertheless, this method suffers from some problems like high energy demand for absorbent regeneration, solvent degradation as well as transportation and storage systems damages by corrosion. Consequently, physical adsorption by porous solid materials is a promising technology because of their simplicity, low energy requirement, high efficiency, and higher selectivity in adsorptive separation processes.

Various types of microporous materials such as carbon molecular sieve [16-18], activated carbons [19,20], metal-organic frameworks (MOFs) [21-25], and zeolites [26-28], have been applied for the separation of CO_2 from CH_4. Among these adsorbents, zeolites have been more investigated because of their great potential. During the past years, much research has been conducted about pure adsorption of CO_2 and CH_4 on different zeolites [29-31], but binary adsorption of gases and adsorption separation of them on zeolites is seldom found, especially on modified and unmodified Faujasite zeolites. In this work, we have reported the CO_2 and CH_4 adsorption individually as well as CO_2/CH_4 adsorptive selectivity on pristine and amine-modified NaY zeolites. We have chosen a Y-type zeolite with relatively low Si/Al ratio, because the smaller the Si/Al ratio is, the weaker the acidity of zeolite will be, moreover for zeolite, there is an increasing tendency to polar molecules. In order to examine impact of basicity of amines on the adsorption capacity of CO_2 and CH_4, three different amines namely Diethanolamine (DEA), Tetraethylenepentamine (TEPA) and 2-methylaminoethanol (2-MAE) were selected. The properties of amine-modified NaY zeolites were characterized by SEM, XRD, FT-IR, and Brunauer–Emmet–Teller (BET). In addition, the relationship between temperature and the adsorption capacity of the adsorbents for CO_2 and CH_4 and also their selectivity has been studied.

2. Materials and methods
2.1 Materials
For preparation of the synthetic solution of zeolite, Sodium aluminate (Merck), Fumed silica (SiO_2 63% 200 mesh, China), sodium hydroxide (NaOH > 99.999%, Merck), and deionized water were used. DEA, TEPA and 2-MAE were obtained

from Merck and utilized for amine modification of the adsorbents. The solvent used in this work was methanol obtained from Merck. CO_2 and CH_4 gas cylinders with purity > 99.999 were used in adsorption experiments [32,33].

2.2 Synthesis of Sorbents
NaY zeolite (Si/Al = 2.5), was synthesized as reported in the previous literature [32,33]. The aluminum gel (solution 1) was prepared by dissolving 2 g sodium aluminate in 8.79 g of deionized water. For the silicone gel (solution 2) 3.665 g Fumed silica and 1.952 g sodium hydroxide were dissolved in 33.174 g of deionized water. These two solutions are mixed together in a polypropylene beaker and stirred by magnetic stirrer at ambient temperature for 72 h, and then hydrothermal crystallization was performed at 373 K for 12 h. Wet impregnation method was used for the modification of the zeolite by three different amines. First, prior to agitation NaY-zeolite powder with amine solutions, the adsorbents were soaked in methanol for 60 min. Then the soaked zeolites were dried in air and added to amine solutions with concentration of 10 wt% under agitation at ambient temperature for the desired time [33]. Eventually the modified adsorbents were filtered and dried in an oven.

2.3 Characterization
Identification of the microstructure of adsorbents was done by a powder X-ray diffractometer (Philips PW 1830 X-ray Diffraction) with Cu-Kα radiation source. The XRD patterns were obtained in the 2θ range of 5–40. In order to study the product morphology SEM (PHILIPS XL30) was used. For identifying functional groups in the surface of adsorbents, FT-IR spectra of the samples were obtained by (FT-IR DIGILAB FTS 7000 spectrometer). The specific surface area and the pore diameter of the adsorbents were obtained by N_2 adsorption–desorption isotherms at 77 K with a volumetric sorption analyzer.

2.4 Gas adsorption measurements
To evaluate the CO_2 and CH_4 adsorption capacity of adsorbents, we have used a laboratory setup based on volumetric method which has been schematically shown in Figure 1. At first, 0.5 g of adsorbent was poured into the sample cell and attached to the system. For degassing the system, the valves 6, 7, 8 and 9 were opened and

other valves were closed, then the system was vacuumed by the vacuum pump at 120 ºC for 90 min. The temperature of the adsorption system was decreased to the experiment temperature after degassing. The adsorption test was carried out by opening valves No. 1, 3, 5, 6, 7, 8 and closing other valves. The pressure drop observed during the process was the results of gas adsorption and some dead volumes in the reactor. We could exactly measure pressure reduction relevant to the gas adsorption by measuring the dead volumes via helium test [32,33].

3. Results and discussion
3.1 Adsorbent Characterization

As shown in Figure 2, the XRD pattern of the synthesized Na-Y zeolite is similar to that of the typical crystal structure of a zeolite Y [34,35]. The

diffraction peaks appearing at 2θ of 6.2º, 10.1º, 15.6º, 23.5º, 26.9º and 31.2º exhibit the synthesis of zeolite. Also can be seen, the location of diffraction peaks remains constant which reflects the fact that the structure of NaY zeolites is not affected after amine modification. However, the intensity of the peaks slightly decreases because of decrease in scattering contrast after attachment of amine groups to the pore surface [33,36]. Hence, the observed decrease in the intensity XRD peaks is probably because of filling the pore by amine groups [37].

Figure 3 shows the FT-IR spectra of adsorbents. The peaks at 1000–1100 cm^{-1} and 500-1000 cm^{-1} were associated with the asymmetric and the symmetric stretching vibrations of T-O (T= Si, Al), respectively. Also, the peak at 463 cm^{-1} is attributed to bending vibrations of T-O. The FT-IR spectra of amine-modified zeolites exhibit sharp peaks at
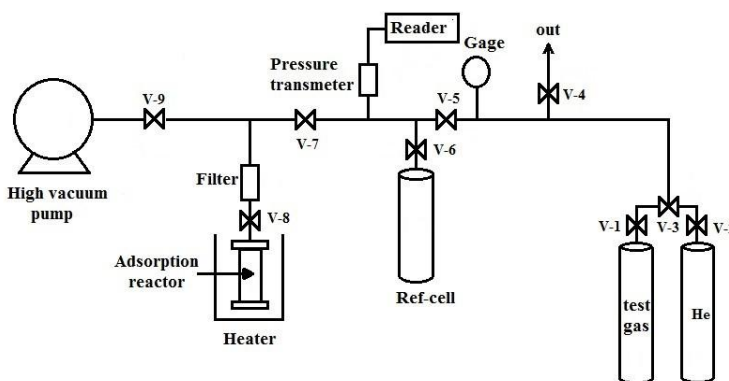

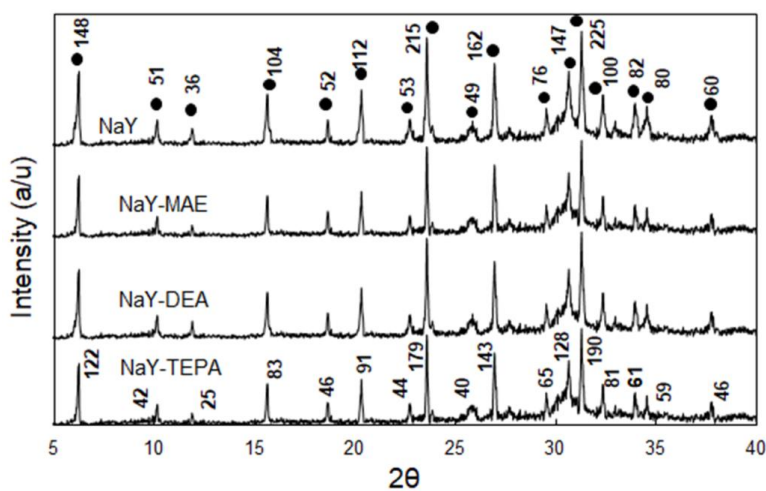Fig. 1- Schematic of volumetric system for adsorption test.

Fig. 2- XRD patterns of NaY and amine-modified NaY.

1500–1600 cm^{-1} and weak peaks at 2800–2900 cm^{-1}. The peaks at 2800- 2900 cm^{-1} indicate stretching of CH_2 from CH_2CH_2-NH_2 groups and the peaks at 1500–1600 cm^{-1} are assigned to NH_2 vibration in the primary amine group. Thus, the FT-IR spectra of amine-modified NaY zeolites prove the incorporation of amines into the channels of zeolite.

The N_2 adsorption–desorption isotherms of NaY and the amine-modified NaY at 77 K (Figure 4) are of a typical type I isotherm, which indicate the microporous feature of the adsorbents. The pore characteristics of the adsorbents are listed in Table 1. After amine-functionalization, the surface area and micropore volume of the amine-modified NaY has decreased that confirmed the occupation of the pores by the amines [33].

According to the molecular volume of the utilized amines, the surface area, pore volume and mean pore size were affected. The molecular volume of TEPA is larger than that of DEA and the molecular volume of 2-MAE is smaller than both of them. Therefore, zeolite modified with the smallest amine has the largest surface area, pore volume and mean pore size.

Figure 5 shows the SEM images of NaY zeolite and NaY - TEPA. The octahedron crystals of NaY zeolite clearly are seen from their SEM image (5a). Also, it is seen that the dimensions of the NaY zeolite crystals are smaller than 100 nm. As can be seen from Figure 5b, zeolite structure after amine midification remains unchanged.

3.2 Adsorption Measurements

CO_2 and CH_4 Adsorption isotherms of NaY zeolites before and after modification were
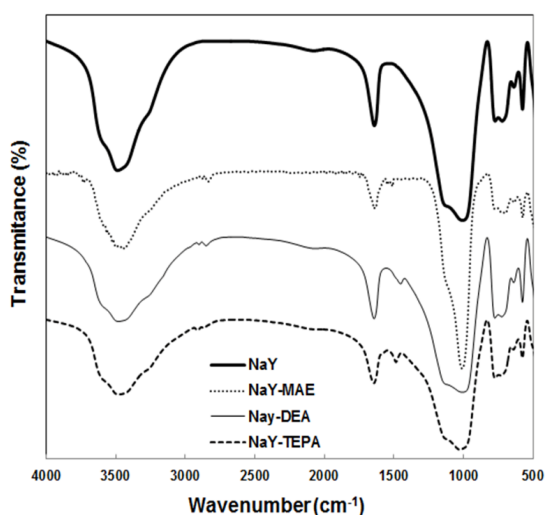

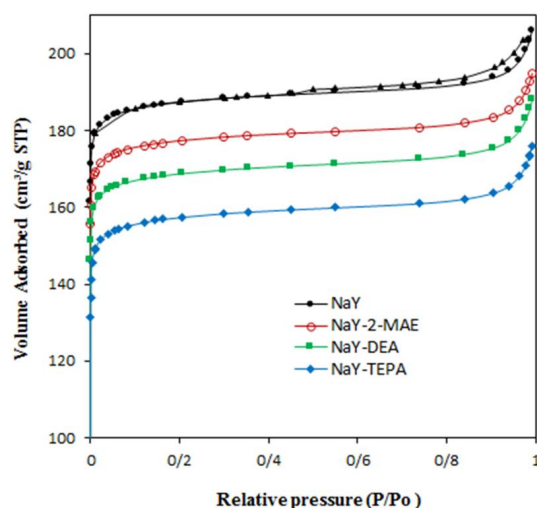Fig. 3- FTIR spectra of NaY and amine-modified NaY.

Fig. 4- N$_2$ adsorption-desorption isotherms of NaY and amine-modified NaY.

Table 1- Structural properties of NaY and the amine-modified NaY

Adsorbent	S_{BET} (m^{2}g^{-1})	Pore volume (cm^{3}g^{-1})	Mean pore diameter (Å)
NaY zeolite	212	0.213	7.0
NaY-2-MAE	191	0.172	6.21
NaY-DEA	183	0.161	5.98
NaY-TEPA	172	0.148	5.64

measured at 298 K and 348 K (Figures 6 and 7). The pure component selectivity for the CH_4 and CO_2 were obtained from their adsorption isotherms. By applying Equation 1, the adsorption selectivity of gas 1 over gas 2 can be calculated [32,38], where V_1 and V_2 are the volumes of the adsorbed gases at certain pressure and temperature, respectively.

$$A_{1/2} = V_1/V_{2\,(P,T)} \qquad \text{(eq. 1)}$$

At both temperatures, adsorption capacity of the adsorbents for CO_2 is greater than CH_4 (Figures 6 and 7). As can be seen in Table 2, after the modification with amines, the adsorption capacity of both gases decreased at 298 K. At 348 K the CO_2 adsorption capacity increased whereas the adsorption capacity of CH_4 decreased consequently, adsorption selectivity CO_2/CH_4 enhanced at high temperature (Table 3).

At the ambient temperature, the dominant

mechanism for the gases adsorption on NaY zeolite and amine modified zeolites is physisorption. According to the molecular volume of the utilized amines, the adsorption capacity of the gases is justified. As noted, the largest surface area, pore volume and mean pore size are related to zeolite that modified with the smallest amine, so the modified zeolite with the smallest amine has the highest CO_2 absorption capacity.

In the case of methane, the polarity of amines justifies the adsorption capacity of CH_4. The hydroxyl groups in the 2-MAE and DEA amines cause a large polarization in the zeolite network and reduce the CH_4 gas absorption capacity.

At high temperatures, the dominant mechanism is chemisorption. The reaction between the amine groups with the CO_2 molecules caused the higher adsorption capacity CO_2 to CH_4 on amine-modified zeolite NaY samples. The chemical reactions occurred between amine groups and CO_2 produce
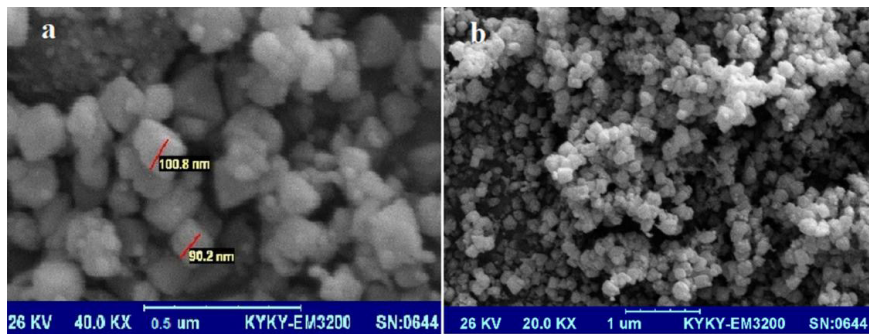

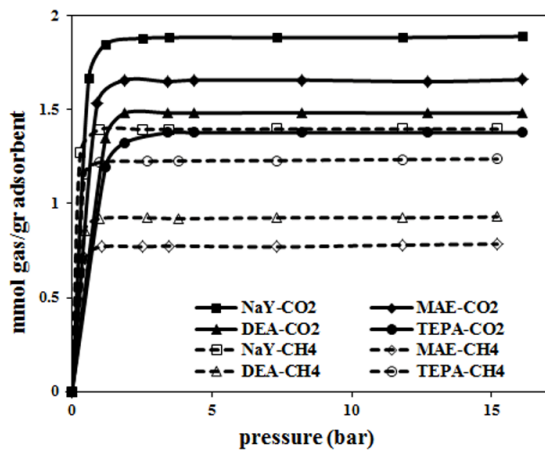Fig. 5- SEM images of (a): NaY zeolite and (b): NaY - TEPA.

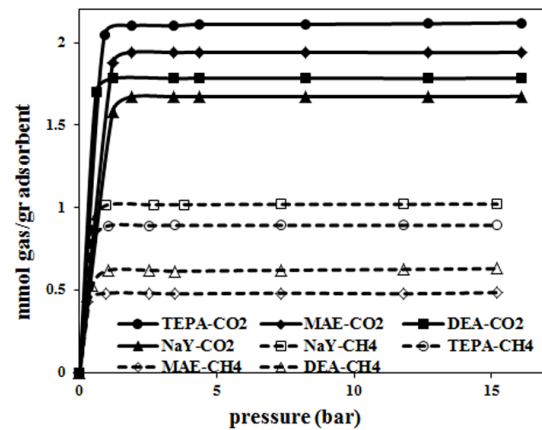Fig. 6- CO_2 and CH_4 adsorption isotherms of unmodified and amine-modified NaY zeolite at 298 K.

Fig. 7- CO_2 and CH_4 adsorption isotherms of unmodified and amine-modified NaY zeolite at 348 K.

the carbamate species according to Equation 2 [33]:

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^- \qquad (eq. 2)$$

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad (eq. 3)$$

TEPA has high chemical absorption capacity due to having 5 amine groups. At high temperatures, due to increased molecular movement, the number of collisions per unit time increases, therefore, it shows the higher CO_2 adsorption capacity. Both NaY-DEA and NaY-2-MAE have an amine group, but in NaY-2-MAE because of the lower steric hindrance of the methyl group, the CO_2 adsorption capacity is higher. In the case of CH_4, because no chemical reaction exists between gas molecules and amine groups, therefore the CH_4 adsorption capacity at high temperatures also decreases.

The reaction between the amine groups with the CO_2 molecules and steric effect caused the higher adsorption capacity CO_2 to CH_4 on amine-modified zeolite NaY samples. The kinetic diameter of CH_4 and CO_2 is 3.80 and 3.30 A°, respectively. Incorporation of amines decreases the pore diameter of zeolite NaY (Table 1) consequently, the decrease in pore diameter has a less influence on the adsorption capacity of CO_2 than that of CH_4. Therefore, the selectivity of CO_2 over CH_4 increases after amine modification of the zeolite NaY.

In order to correlation of the experimental data of CO_2 adsorption on NaY zeolites before and after modification, the Langmuir and Sips adsorption models [39,40] were utilized. Table 4. Shows the values of model parameters.

Langmuir isotherm corresponded to homogeneous adsorbent surfaces is shown by Equation 4 [41]:

Table 2- Adsorption capacity of CO_2 and CH_4 on pristine and modified zeolites at 298 K and 348 K

Adsorbent	gas adsorption capacity (mg.g^{-1})			
	CO$_2$		CH$_4$	
	298 K	348 K	298 K	348 K
NaY	82.8	73.5	22.3	16.2
NaY-TEPA	60.6	92.9	19.5	14.2
NaY-MAE	72.9	85.4	12.3	7.7
Nay-DEA	65.2	78.0	14.7	9.0

Table 3- Pure component equilibrium selectivity for CO_2 and CH_4 on adsorbents at 298 K and 348 K

Adsorbent	Pure component equilibrium selectivity (CO$_2$/CH$_4$)	
	298 K	348 K
NaY	1.34	1.65
NaY- TEPA	1.13	2.37
NaY-MAE	2.16	4.04
Nay-DEA	1.61	2.87

$$q = q_m \frac{bP}{(1+bP)} \qquad \text{(eq. 4)}$$

Where q_m is the maximum amount of gas adsorbed (mmol g^{-1}), q and b (KPa^{-1}) are the adsorbed capacity (mmol g^{-1}) at equilibrium pressure P and the Langmuir constant, respectively.

The Sips isotherm is the combined formula of Langmuir and Freundlich equations which is given by the Equation 5:

Table 4- Langmuir and Sips isotherm parameters for the adsorption of CO_2 on NaY zeolite and amine-modified zeolites

adsorbent	Langmuir				Sips					T***
	q_m*	b**	R^2	ARE%	q_m	b	n	R^2	ARE%	
NaY	1.91	0.160	0.998	1.323	1.88	0.035	0.368	0.999	0.529	298
	1.69	0.133	0.999	1.257	1.67	0.011	0.114	0.999	0. 041	348
NaY-TEPA	1.41	0.056	0.997	1.798	1.38	0.016	0.334	0.999	0.152	298
	2.12	0.326	0.999	0.141	2.11	0.074	0.552	0.999	0.062	348
NaY-MAE	1.68	0.141	0.998	1.024	1.65	0.010	0.041	0.999	0.452	298
	1.95	0.265	0.999	1.192	1.94	0.013	0.068	0.999	0.067	348
NaY-DEA	1.51	0.098	0.997	1.342	1.51	0.097	0.986	0.997	1.342	298
	1.79	0.370	0.999	1.932	1.79	0.433	1.04	0.997	0.976	348

* (mmol.g^{-1}), **(bar)$^{-1}$, ***(K)

Table 5- The CO_2 adsorption capacity in different porous materials

Adsorbent	gas adsorption capacity (mg.g^{-1})	condition	References
Zeolite 13X	37.33	348K	[43]
13X/MEA	48.64	348K	[43]
MCM-48-PEHA-DEA	22.44	298K	[44]
SAOP-43	47.08	298K	[45]
ZSM-5	47.52	313K	[45]
NaY zeolite	82.80	298K	This study
NaY zeolite	73.51	348K	This study
NaY-TEPA	92.90	348K	This study
NaY-2-MAE	85.42	348K	This study
NaY-DEA	78.00	348K	This study

$$q = q_m \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \qquad \text{(eq. 5)}$$

Where q (mmolg^{-1}) an q$_m$ are the amount of gas adsorbed at equilibrium pressure of P and the maximum adsorption capacity, respectively. The n and b (KPa^{-1}) are heterogeneity parameter and the adsorption equilibrium constant, respectively. The b parameter shows the adsorbate affinity for surface of adsorbent [42].

An error function based on the average percent deviation calculated was utilized in order to estimation of the fitting accuracy of the proposed model for the experimental data (Equation 6) [32].

$$ARE\% = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_i^{exp} - q_i^{cal}}{q_i^{exp}} \right| \qquad \text{(eq. 6)}$$

Where ARE (%) and N are the average percent deviation and the number of data points available in the adsorption equilibrium isotherms, respectively. q^{exp} and q^{cal} are the experimental and calculated amounts adsorbed (mmol g^{-1}), respectively.

According to the data of table 4, the Sips isotherm has the high correlation coefficients ($R^2 > 0.99$) and an average percent deviation value of less than 2% therefore it is the best model for adsorbents and presents the excellent agreement between the experimental data and the model parameters, which indicated the heterogeneous nature of the adsorbents surface [32].

Table 5 shows a comparison between the CO_2 adsorption capacity obtained in this study and the values of other literature. The CO_2 adsorption capacity of the adsorbents of this study under similar conditions is higher than that of other porous materials. It is concluded that amine-modified NaY zeolites are the suitable materials for CO_2 capture from gas mixtures.

4. Conclusion

In this work, NaY Zeolite was modified with two different amines. The adsorbents are characterized by XRD, BET and FT-IR methods. The incorporation of amines did not deteriorate the structure of NaY Zeolite. Gas adsorption capacity was measured by the volumetric method at 298K and 348 K. Between the two adsorbates (i.e. CO_2 and CH_4), CO_2 was preferentially adsorbed on the adsorbents. The incorporation of amines improved the selectivity of CO_2/CH_4, and the optimum selectivity of CO_2/CH_4 could reach as high as 4.04 on NaY-MAE. Such high adsorption selectivity can be attributed to chemical adsorbate-adsorbent interaction as well as steric effect.

Acknowledgment

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