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ORIGINAL PAPER

Study of carbon dioxide and methane equilibrium adsorption on silicoaluminophosphate-34 zeotype and T-type zeolite as adsorbent

M. Salmasi · S. Fatemi · M. Doroudian Rad · F. Jadidi

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Abstract Carbon dioxide is known as a hazardous material with acidic property that can be found as impurity in natural gas reservoirs with a broad range of 2 up to 40 %. Therefore, many efforts have been directed to remove and separate carbon dioxide from methane to prevent corrosion problems as well as improving the natural gas energy content. In this study, two molecular sieves, silicoaluminophosphate-34 (SAPO-34) zeotype and T-type zeolite, were synthesized by the hydrothermal method for the comparative study of adsorptive separation of carbon dioxide from methane. The synthesized adsorbents were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, and Brunner–Emmett–Teller techniques. These characterization tests confirmed formation of both materials with acceptable crystallinity. Both adsorbents were tested in equilibrium adsorption experiments in order to evaluate maximum capacity and adsorption affinity. Adsorption capacity of carbon dioxide and methane on SAPO-34 and zeolite T were measured in a pressure range of 0.1–2.0 MPa and temperature of 288, 298, and 308 K and fitted with the Sips and Langmuir isotherm models. The ideal selectivity of CO_2/CH_4 was determined for SAPO-34 and zeolite T at the studied pressures and temperatures, indicating that the molecular sieves can be properly used for CO_2–CH_4 separation or CO_2 capturing from natural gas.

Keywords Adsorption · Carbon dioxide · Methane · Silicoaluminophosphate-34 · T-type zeolite

Introduction

Nowadays, selective removal of carbon dioxide from methane is one of the important issues of environmental engineering. Global warming is one of the most important environmental challenges, and carbon dioxide (CO_2) has classified as a hazardous gas to the environment and public health (Pires et al. 2008). In addition, CO_2 is one of the important natural gas contaminants, which must be removed to increase the natural gas energy content and reduce its corrosive properties in natural gas storage and transportation (Baker 2002; Li et al. 2004; Delgado et al. 2006, 2007). The conventional method for removing CO_2 from methane (CH_4) in industrial applications is amine absorption, which is a toxic and noneconomic technique (Baker 2002). Recently, adsorptive methods using nanoporous materials, which are known as efficient processes, have appealed many research groups (Cichocki and Koscielniak 1999; Poshusta et al. 2000; Harlick and Tezel 2003; Delgado et al. 2006, 2007; Belmabkhout and Sayari 2009; Himeno et al. 2007; Rivera-Ramos et al. 2008; Xu et al. 2009). Molecular sieves such as zeolites and zeotypes are nanoporous materials which are finding widespread application as a catalyst and adsorbent in industrial processes (Yan et al. 2009). The small pore size, high thermal and chemical stability of zeotype, and zeolite molecular sieves make them ideal material for use in adsorption processes (Poshusta et al. 2000). The pore diameter and surface area of the absorbents are the key parameters in its adsorption capability (Rivera-Ramos et al. 2008).

Separation of CO_2 from CH_4 has been studied using various kinds of adsorbents and membranes such as X, Y,

M. Salmasi · S. Fatemi (✉) · M. Doroudian Rad · F. Jadidi
School of Chemical Engineering, College of Engineering,
University of Tehran, P.O. Box: 11365-4563, Tehran, Iran
e-mail: shfatemi@ut.ac.ir

S. Fatemi
Oil and Gas Center of Excellence, College of Engineering,
University of Tehran, P.O. Box: 11365-4563, Tehran, Iran

MCM-41, β-zeolite, ZSM-5, silicoaluminophosphate-34 (SAPO-34), and zeolite T (Poshusta et al. 2000; Rivera-Ramos et al. 2008; Cichocki and Koscielniak 1999; Xu et al. 2009; Belmabkhout and Sayari 2009; Harlick and Tezel 2003; Himeno et al. 2007; Yan et al. 2009). Harlick and Tezel (2003) obtained a CO_2/CH_4 selectivity of 1.7 at 313 K and atmospheric pressure by using ZSM-5 with a SiO_2/Al_2O_3 ratio of 280. Xu et al. (2009) studied the adsorption of pure CO_2 and CH_4 on β-zeolite, and the selectivity of carbon dioxide to methane was found 4.63 at 303 K and 1 bar. Belmabkhout and Sayari (2009) had investigated the adsorption of carbon dioxide and methane on MCM-41 at ambient temperature and high pressures. The selectivity of CO_2/CH_4 was determined around 4.5 at atmospheric pressure.

In this research, two types of molecular sieves (SAPO-34 and T-type zeolite) were nominated due to their ability of CO_2 separation from CH_4. SAPO-34, as a kind of zeotype material, is a cage-type molecular sieve with framework structure similar to the naturally occurring chabazite zeolite (Lee et al. 2007). Chabazite structure has a three-dimensional pore system with ellipsoidal cages interconnected via 8-membered ring windows with pore apertures of 0.38 nm × 0.38 nm (Djieugoue et al. 2000; Denayer et al. 2008; Yan et al. 2009). This geometry allows molecules, such as CO_2, with kinetic diameter of 0.33 nm to easily diffuse through the crystal structure (Rivera-Ramos et al. 2008). Another proposed molecular sieve for CO_2 adsorption is T-type zeolite, which belongs to the offretite–erionite intergrowth family of zeolites. The frameworks of offretite and erionite are different but closely related (Yang and Evmiridis 1996). Stacking faults of these two types of zeolites not only in their synthetic samples but also in natural forms usually have been observed (Breck and Acara 1960). T-type zeolite framework often shows the same properties as erionite, especially in adsorption experiments (Mougenel and Kessler 1991). Small pores of T-type zeolite, 0.36 nm × 0.48 nm, allow the selective separation of different mixtures such as CO_2 from CH_4 (Ceckiewicz 1980; Mirfendereski et al. 2008; Cui et al. 2004a, b).

Various studies dealing with SAPO-34 zeotype and T zeolite, especially in the field of membrane applications, are reported in the literature; however, studies about their application in the adsorption process are rarely found. As mentioned in the literature, there are some reports for separation of CO_2 from N_2 and separation of CO_2 from CH_4 by T zeolite and SAPO-34 membrane; however, there is not found any literature about separation of CO_2 from the flue gas. The ideal selectivities for CO_2/N_2 and CO_2/CH_4 have been found as 31 and 266, respectively, at 343 K for T zeolite membrane (Qi and Henson 1998; Poshusta et al. 2000; Cui et al. 2004a, b; Rivera-Ramos et al. 2008). Cui et al. (2004a, b) reported CO_2/CH_4 selectivity of about 3.6 on the T zeolite at 298 K and pressure of 0.1 MPa. Li et al. (2004) studied separation of CO_2/CH_4 by SAPO-34 membranes, and the best CO_2/CH_4 separation selectivity was found to be 67 at 297 K. Sr^{2+}-SAPO-34 adsorbent was the best option for CO_2 removal from CH_4 mixture, especially at low concentrations. This kind of adsorbent was capable of removing as much as 2.8 wt% at a CO_2 partial pressure of 3–10 atm at room temperature (Rivera-Ramos et al. 2008). To design and produce an appropriate adsorbent for capturing CO_2 and acidic gases from natural gas, a comparison between SAPO-34 and T-type zeolite is required that has not been found in the literature. In the present work, SAPO-34 zeotype and T-type zeolite are synthesized by the hydrothermal method, and their adsorptive properties are evaluated and compared in various pressures and temperatures. The evaluated properties can be used for design of the cyclic adsorption processes such as pressure swing adsorption, for selective separation of CO_2 from natural gas at a wide range of pressure around normal temperatures (Li et al. 2004).

Materials and methods

Adsorption apparatus

The adsorption apparatus presented in Fig. 1 was set up to measure the equilibrium amount of adsorbed carbon dioxide and methane at three temperatures (288, 298, and 308 K) and various operating gauge pressures (0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0 MPa). Helium was used as carrier gas to measure the void fractions. During each experiment, the temperature of reference and adsorption vessels was kept constant by a circulation bath. A pressure transducer was used to monitor the pressure from the beginning to the end of each experiment. Degassing of the adsorbent was performed under vacuum and high temperature (358 K for 3 h). In order to determine the adsorption capacity, about 2.2 g of adsorbents was placed in the adsorption cell. After pretreatment of the adsorbent, the adsorption test started at an initial pressure and a fixed temperature, to approach to the equilibrium state. The adsorbed amount was calculated by measuring the initial pressure and pressure after equilibrium condition. The detailed illustration of the experimental setup is explained elsewhere (Rasoolzadeh et al. 2008).

Synthesis of adsorbent

Synthesis of SAPO-34 zeotype

SAPO-34 is a zeotype molecular sieve composed of Al, P, and Si elements. Silicoaluminophosphate gel was

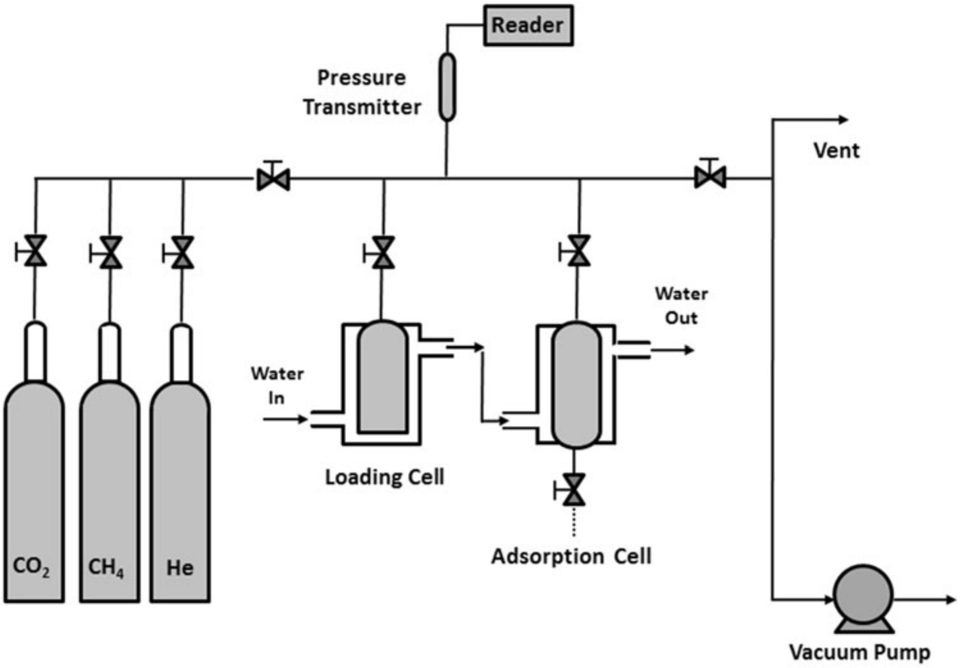

Fig. 1 Schematic of adsorption apparatus

prepared from a gel composition of Al_2O_3: P_2O_5: 0.6 SiO_2: 1 TEAOH: 1 morpholine: 60 H_2O. The synthesis procedure followed for gel preparation is described as following. Firstly, aluminum isopropoxide (AIP, Merck) was dissolved in a mixture of orthophosphoric acid (85 wt% H_3PO_4, Merck) and deionized water to form aluminum sol. Mixture of colloidal silica (40 wt% SiO_2, Aldrich) and template was added to aluminum sol. In present work, tetraethylammonium hydroxide (35 wt% aqueous solution of TEAOH, Aldrich) and morpholine (Merck) were used as the organic templates. The resulting gel was aged at room temperature for 24 h. After the aging period, the gel was transferred into a Teflon autoclave and crystallized at 458 K for 48 h. The synthesized material was recovered by centrifugation, washed several times, and then dried at 373 K. Final product was then calcined at 873 K for 5 h.

Synthesis of T-type zeolite

T zeolite which is composed of Al and Si elements was prepared by mixing sodium hydroxide (98 wt%, Merck), potassium hydroxide (85 wt%, Merck), sodium aluminate (54 wt% Al_2O_3, 41 wt% Na_2O, Riedel-de Haen), colloidal silica (40 wt% SiO_2, Aldrich), and distilled water. The molar composition of the initial gel was SiO_2: 0.05 Al_2O_3: 0.26 Na_2O: 0.09 K_2O: 14 H_2O. T-type zeolite gel was prepared by dissolving the potassium hydroxide and sodium hydroxide in distilled water, then slowly adding sodium aluminate and colloidal silica. Then, the mixture was stirred for 1 day to ensure homogeneity. The resulting gel was placed in a Teflon lined autoclave and kept at 378 K in an oven for 7 days. The white solid product was washed with distilled water and then dried at 483 K.

Characterizations

X-ray diffraction (XRD) pattern of powdered adsorbents was obtained on a powder X-ray diffractometer (Bruker D8) using CuKα radiation ($\lambda = 1.54$ Å). The morphology of adsorbents was confirmed using a Philips XL30 scanning electron microscope (SEM). The chemical composition of the adsorbents was determined by Oxford 2538 scanning electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer. Brunner–Emmett–Teller (BET) surface area was measured using nitrogen adsorption/desorption isotherms determined at 77 K by a Micromeritic ASAP 2010 analyzer.

Results and discussion

Characterization

XRD pattern of SAPO-34 and zeolite T is shown in Fig. 2. According to the XRD patterns, the position of peaks of both synthesized adsorbents is similar to those SAPO-34 and zeolite T reported in the literature (Lok and Patton 1984; Zhou et al. 2009).

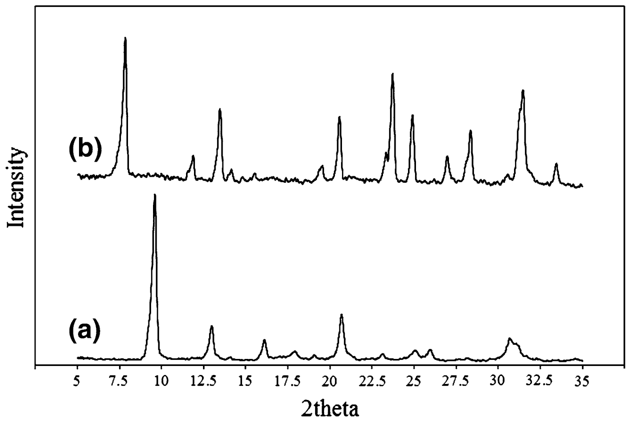

Fig. 2 XRD pattern of adsorbent: (*a*) SAPO-34 and (*b*) zeolite T

Figure 3 shows the SEM images of SAPO-34 and zeolite T. As shown, SAPO-34 and T-type zeolite have formed in cubic and rod-shaped crystals, respectively.

The composition and the BET surface area of each absorbent are given in Table 1. The BET sur'face area of synthesized SAPO-34 and zeolite T was determined 502 and 352 m^2/g, respectively.

Adsorption process

Adsorption isotherm

Equilibrium data of the adsorbed CO_2 and CH_4 were measured by the volumetric method. The equilibrium adsorption data of CO_2 and CH_4 were well fitted with Sips (Langmuir–Freundlich) model, which exhibited better presentation of experimental data than the other models in the studied ranges of pressure and temperature. The general form of Sips model can be observed as Eq. (1) (Do 1998).

$$q = q_{\mathrm{m}} \frac{(bp)^{\frac{1}{n}}}{1 + (bp)^{\frac{1}{n}}} \tag{1}$$

Table 1 Composition of absorbents

Absorbent	BET surface area (m^2/g)	Composition (mol%)				
		Na	K	Al	P	Si
SAPO-34 zeotype	502	–	–	0.58	0.29	0.12
T-type zeolite	352	0.03	0.21	0.14	–	0.61

In this equation, p is the equilibrium pressure and q_{m}, b, and n are the maximum adsorption capacity, the adsorption equilibrium constant, and the parameter indicating the heterogeneity of the system, respectively. The fitting parameters (q_{m}, b and n) of isotherm equations are temperature dependent and define as Eqs. (2), (3), and (4), respectively (Do 1998).

$$q_{\mathrm{m}} = q_{\mathrm{m}0} \exp\left[\chi\left(1 - \frac{T_0}{T}\right)\right] \tag{2}$$

$$b = b_0 \exp\left[\frac{\Delta H_{\mathrm{ads}}}{RT_0}\left(\frac{T_0}{T} - 1\right)\right] \tag{3}$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1 - \frac{T_0}{T}\right) \tag{4}$$

In above equations, $q_{\mathrm{m}0}$, b_0, n_0, and χ are the constants of the temperature dependent equations. T_0 is the reference temperature which is equal to 288 K as the lowest temperature in our experiments.

The unknown parameters of Sips model were determined by the direct search method of Nelder–Mead simplex to minimize sum of squared difference of actual and model equilibrium adsorption. The correlated parameters of fitted isotherms are listed in Table 2. The heterogeneity parameter of CH_4 has been obtained equal to one ($n = 1$) which present a Langmuir model behavior of CH_4 isotherm. It is concluded that methane adsorption system is a homogenous energetic sites with one layer adsorption. The heterogeneity parameter of CO_2 adsorption was calculated

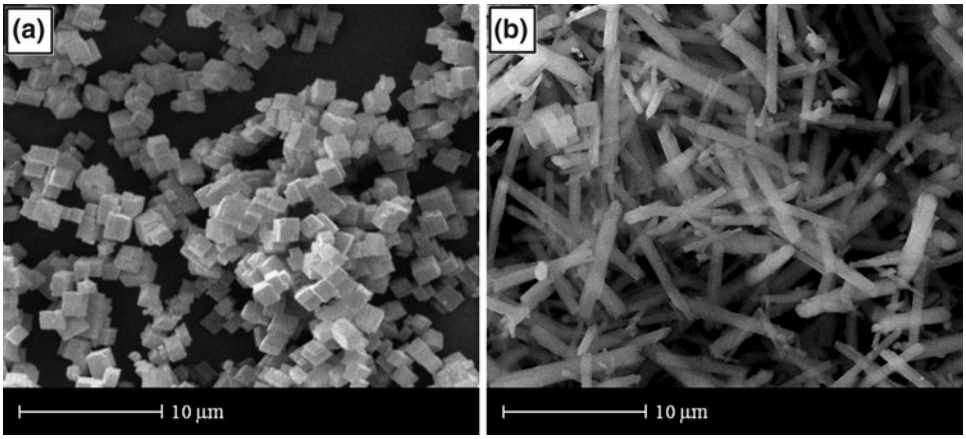

Fig. 3 SEM photo of adsorbent: **a** SAPO-34 and **b** zeolite T

as two ($n = 2$), and this reveals a heterogeneous system for CO_2 adsorption on the sites of SAPO-34 and zeolite T adsorbents.

The single-gas adsorption isotherms of CO_2 and CH_4 for SAPO-34 and zeolite T obtained at 288, 298, and 308 K, when the gas operating gauge pressure was varied from 0.1 to 2.0 MPa, are shown in Figs. 4 and 5. Adsorption isotherms for both adsorbents show that at the same process conditions, same pressure, and temperature, CO_2 adsorbed significantly more than CH_4. This phenomenon can be regarded to the difference between molecular size of CO_2 and CH_4 as well as quadrupole property of CO_2 compared to CH_4. Because of the difference in kinetic diameter of CO_2, 0.33 nm, and CH_4, 0.38 nm, CO_2 would pass through the molecular sieves pore mouths, whereas it might be difficult for CH_4, especially at the lower pressures (Huesca et al. 1999). In addition, high quadrupole moment of CO_2 against CH_4 led to higher affinity of adsorbent surface for CO_2. The slope of CO_2 isotherm changes dramatically at low pressures, whereas at higher pressures, the adsorption capacity increases only slightly with pressure. The results in Table 2 reveal that the model parameters, q_m and b, increase by temperature decreasing, which is in agreement with above results. It needs to be emphasized that all calculated model parameters for CO_2 are more than that of CH_4.

Comparison of Figs. 4 and 5 illustrates that SAPO-34 adsorbed more amount of both components, CO_2 and CH_4, in contrast to zeolite T. In the case of CH_4, the higher adsorption capacity of SAPO-34 against zeolite T can be interpreted with respect to the kinetic diameter of CH_4 and pore size of the adsorbents. The higher adsorption capacity of CO_2 in SAPO-34 may arise from higher surface area of SAPO-34 in contrast to zeolite T. In addition, the more polarity of SAPO-34 in comparison with T-type zeolite, due to lower Si/Al ratio, excels in CO_2 adsorption for SAPO-34.

The heat of CO_2 and CH_4 adsorption, ΔH_{ads}, was estimated using the Clausius–Clapeyron equation, which is expressed by Eq. (5) (Do 1998).

Table 2 The calculated isotherms parameters at each temperature

Absorbent	Component	Model	Temperature (K)	q_m (mol/kg)	$b \times 0.1$ (MPa^{-1})	n	AARD
SAPO-34	CO_2	Sips	308	4.92	0.52	2	0.048
			298	5.49	0.54	2	0.035
			288	5.99	0.57	2	0.028
	CH_4	Langmuir	308	2.68	0.09	1	0.089
			298	2.72	0.12	1	0.085
			288	2.88	0.16	1	0.079
Zeolite T	CO_2	Sips	308	3.42	1.01	2	0.026
			298	3.56	1.12	2	0.027
			288	3.66	1.31	2	0.024
	CH_4	Langmuir	308	1.36	0.29	1	0.034
			298	1.56	0.31	1	0.041
			288	1.68	0.34	1	0.040

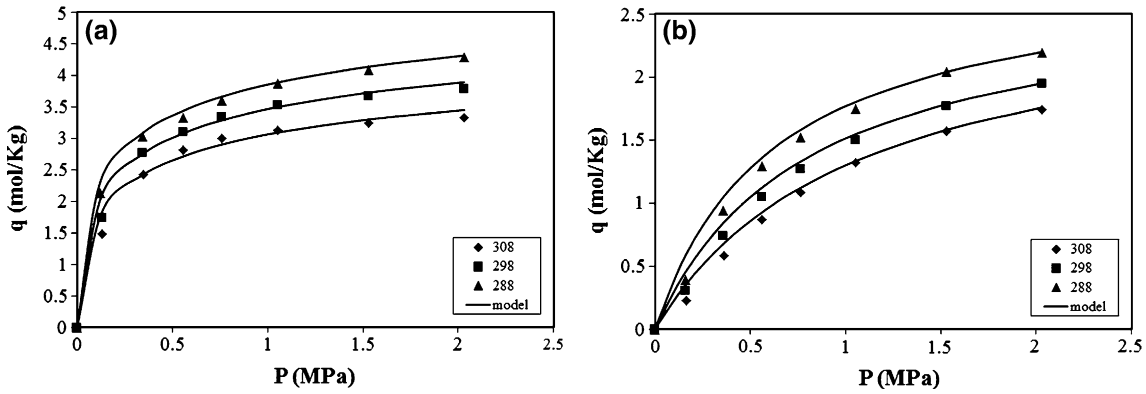

Fig. 4 Adsorption isotherm of **a** CO_2 and **b** CH_4 for SAPO-34 zeotype

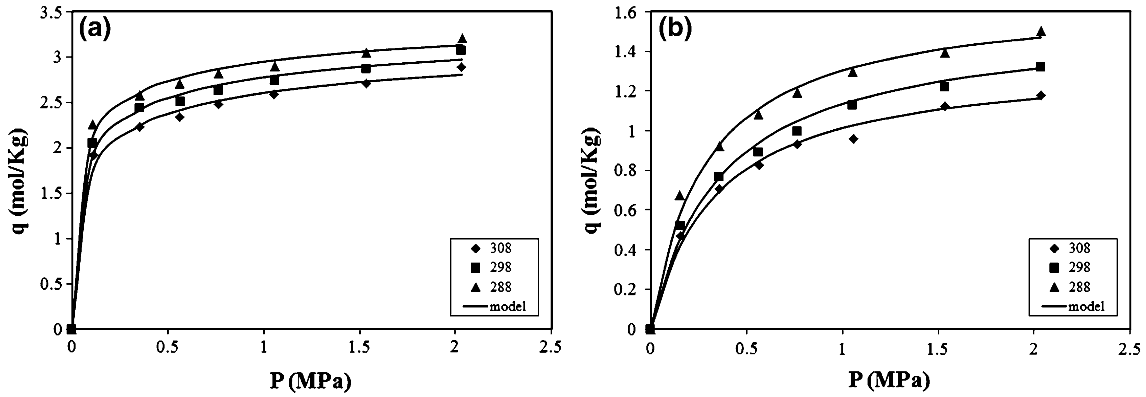

Fig. 5 Adsorption isotherm of **a** CO_2 and **b** CH_4 for zeolite T

Table 3 Heat of adsorption for SAPO-34 and zeolite T

Adsorbed gas	SAPO-34	*T*
CO_2	39.38	33.62
CH_4	24.44	22.30

$$\Delta H_{\text{ads}} = R\frac{\partial \ln P}{\partial(1/T)}\bigg|_q \tag{5}$$

It was obtained by plotting ln *P* versus reciprocal of temperature. The value of ΔH_{ads} is correlated with adsorption type, physical, or chemical adsorption. In addition, estimated value of ΔH_{ads} is significant with respect to adsorbent regeneration. The heat of CO_2 and CH_4 adsorption on both adsorbents is reported in Table 3.

As shown, the resulted heats of adsorption estimated by Clausius–Clapeyron equation are in the range of physical adsorption. The values founded for CO_2 are significantly higher than CH_4, which can be explained in terms of smaller molecular size of CO_2 against CH_4 and stronger interaction of CO_2 with adsorbent surface in comparison with CH_4.

Adsorption selectivity

The single-component isotherm is a tool for calculating the ideal selectivity of the adsorbent for carbon dioxide against methane. Various adsorbed amounts at different pressures and temperatures are now available from the equilibrium model to find the ideal selectivity of CO_2 over CH_4 using the Eq. (6) (Hosseinpour et al. 2011).

$$\text{Adsorption selectivity} = \frac{q_{\text{eq,CO}_2}/P_{\text{eq,CO}_2}}{q_{\text{eq,CH}_4}/P_{\text{eq,CH}_4}} \tag{6}$$

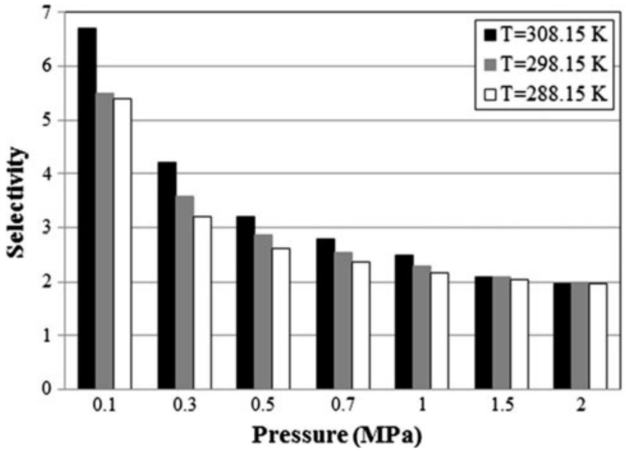

Fig. 6 Selectivity of CO_2/CH_4 for SAPO-34 zeotype

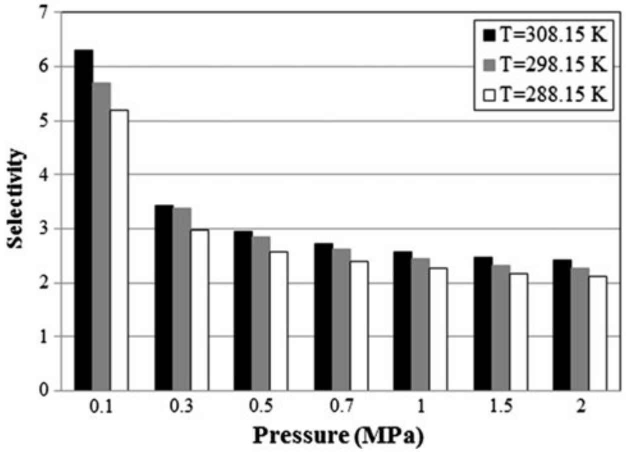

Fig. 7 Selectivity of CO_2/CH_4 for T-type zeolite

Figures 6 and 7 exhibit the selectivity of CO_2 over CH_4 at three temperatures for the two adsorbents. It is evident that the selectivity of CO_2 over CH_4 decreases with the increase of equilibrium pressure. Significant variations in adsorption selectivity were observed in the range of pressure between 0.1 and 0.5 MPa. At the higher pressures, variation of selectivity was not pronounced. The highest selectivity values for both adsorbents were obtained at the atmospheric pressure. This phenomenon can be due to the higher adsorption amount of CO_2 compared to CH_4 at the atmospheric pressure. On the other hand, the selectivity of CO_2 against CH_4 rises by increasing temperature. It is according to the higher adsorbent affinity toward CO_2 compared with CH_4. In general, the higher adsorption capacity of CO_2 can be explained by its smaller molecular size and the interaction of quadrupole moment of CO_2 with the surface of adsorbents, whereas CH_4 with no dipole moment and larger molecular size do not show any significant attraction to the pores and surface of the adsorbents at low pressures, and only at high pressures by creating induced polarity and London forces shows weak interaction with the adsorbents surface. Such differences between CO_2 and CH_4 adsorptive properties resulted to stronger effect of temperature on CH_4 adsorption and desorption compared with CO_2. Therefore, as it can be seen in Figs. 6 and 7, temperature increase resulted to the higher selectivities, because the adsorption amount of CH_4 decreases more effectively than CO_2 at higher temperatures.

Conclusion

In this research, synthesis of two nano-structured materials, SAPO-34 and zeolite T, was conducted successfully for CO_2 separation from natural gas. The performance of those materials was studied for adsorptive separation of CO_2 from CH_4 in a volumetric setup. The equilibrium adsorption tests were carried out and modeled at temperatures of 288, 298, and 308 K and pressures of 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0 MPa. The isotherm data were fitted on Sips model for CO_2 and Langmuir model for CH_4 adsorption with good agreement between model and experiments. The ideal selectivity of CO_2/CH_4 was determined for both adsorbents at various pressures and temperatures. The selectivity of the adsorbents toward CO_2 was more than six times higher than CH_4 and this revealed the applicability of the both adsorbents for efficient separation of CO_2 from CH_4 at normal pressure and temperature. The produced materials with their good CO_2 adsorption affinity would be appropriate candidates for dynamic adsorption processes. It should be noted that comparison between SAPO-34 and T-type zeolite has shown more ability of SAPO-34 for selective adsorption of CO_2; however, there was not much significant difference between the selectivity of the studied adsorbents.

Acknowledgments This work has been carried out in Adsorption Process Lab in the School of Chemical Engineering of University of Tehran.

Nomenclature

q	Adsorption capacity (mol/kg)
q_m	Maximum adsorption capacity (mol/kg)
q_{eq}	Equilibrium adsorbed amount (mol/kg)
p	Pressure (MPa)
p_{eq}	Equilibrium pressure (MPa)
b	Adsorption equilibrium constant (MPa^{-1})
T	Temperature (K)
T_0	Minimum experimental temperature (K)
n	Parameter indicating the heterogeneity of the system
R	Gas constant (kJ/mol K)
ΔH_{ads}	Heat of adsorption (kJ/mol)

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