Adsorption of Nitrogen from Natural Gas by Clinoptilolite

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Much of world`s natural gas reserves are impure, one of the principal contaminants being nitrogen which makes it unsuitable for application and, hence, its separation is important. In this research, clinoptilolite, the most abundant natural zeolite with an open aluminosilicate framework structure and high internal surface area, was modified by ion exchange process to highly exchanged forms of cations of Na^+, K^+ and H^+. The adsorption of N_2, CH_4 and C_2H_6 on natural clinoptilolite (Cp) and on its cation-exchanged forms (Na-Cp, K-Cp and H-Cp) was studied at 25 °C. The influence of cation exchange on equilibrium adsorption of N_2 showed that selectivity decreased in the order of Cp > Na-Cp > K-Cp and H-Cp has no affinity to nitrogen.

INTRODUCTION

Noncryogenic separation of nitrogen/methane mixture from natural gas has prompted recent developments in upgrading of natural gas [1]. Zeolites are porous, crystalline, hydrated aluminosilicates of alkaline and alkaline earth cations that possess a three-dimentional structure. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra joined together in various regular arrangements through shared oxygen atoms to form an open crystal structure containing pores of molecular dimensions in to which guest molecules can penetrate. The negative charge created by the substitution of an AlO_4 tetrahedron for a SiO_4 tetrahedron is balanced by exchangeable cations (*e.g.,* Na^+, K^+, Ca^{2+}, Mg^{2+}), which are located in large structural channels and cavities throughout the structure. These cations play an important role in determining the adsorption and gas-separation properties of zeolites. These properties depend heavily on the size, charge density and distribution of cations in the porous structure.

Of more than 40 natural zeolite species known today, clinoptilolite is the most abundant in soils and sediments. The framework of clinoptilolite is formed by two parallel channels of 10-member rings (channel A) and eight-member rings (channel B) connected to a third channel C of eight-member rings [2]. The approximate channel sizes (Å) are: A, 4.4 × 7.2; B, 4.1 × 4.7; C, 4.0 × 5.5. Small hydrated cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) can easily enter the channels of clinoptilolite and compete for the major exchangeable-cation sites, designated as M(1), M(2), M(3) and M(4). The major cations are located and distributed as follow(3); M(1)is located in channel A, where $Na^+ > Ca^{2+}$; M(2) is located in channel B, where $Ca^{2+} > Na^+$; M(3) is located in channel C, where there is only K^+; and M(4) is located in channel A, where there is only Mg^{2+} [3].

Clinoptilolite has been studied or used for applications such as natural gas purification [4-8], air separation and prepurification, removal of traces of CO_2 and light hydrocarbons [9-10], flue gas and ammonia removal [11] and uptake of CO_2, CH_4, C_2H_6, N_2 and C_3H_8 [12]. Frankiewicz and Donnelly measured adsorption data for nitrogen-methane gas

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mixtures on Ca-exchanged clinoptilolite [13]. Aguilar-Armenta measured the adsorption kinetics of pure CO_2, O_2, N_2 and CH_4 on natural and cation-exchanged clinoptilolite [14]. Chao suggested the use of Mg-exchanged clinoptilolite for N_2/CH_4 separation [15]. Jayaraman measured the high pressure adsorption isotherms and diffusion rates for nitrogen and methane on cation exchanged clinoptilolites [16]. The goal of this study was separation of N_2 from natural gas by natural clinoptilolite. Natural gas is using as feed in OXO plant to produce of syntesis gas (H_2/CO) and existence of N_2 in feed is a problem.

EXPERIMENTAL

Natural clinoptilolite was prepared from the deposits located in the north of Semnan region, Iran. Natural gas containing (8.17% N_2, 85.06% CH_4 and 6.77% C_2H_6) was sampled from main line of natural gas of Arak Petrochemical Complex. X-ray powder diffraction (XRD) pattern of clinoptilolit was obtained on a Bruker D8 ADVANCE diffractometer using Cuk$_\alpha$ radiation (λ = 1.5406 Å). FTIR spectrum of the sample was obtained by a Nicolet (Magna IR550) spectrophotometer. The chemical composition of clinoptilolite and ion exchanged samples was obtained by the method explained by Maxwell [17]. A Varian (Spectr-20plus) atomic absorption spectrophotometer was used for the measurement of cations. The samples were also studied by BET N_2 adsorption method at 77.4 ºC on a high speed sorption analyzer Quantachrome (NOVA 2200). The raw clinoptilolite was crushed to 0.8-1.0 mm prior to ion exchange, heated in deionized water to remove soluble salts and dispersed in methyl iodide solution to remove heavy impurities [6].

The purified clinoptilolite was employed in subsequent ion exchange process which was carried out with 1.0 M salt solutions at 90 °C for 72 h. After exchange, the samples were washed repeatedly with deionized water to remove the excess salt. All ion-exchanged samples were calcined at 390 °C for 12 h before adsorption measurements. Adsorption measurements were carried out at 25 °C in a stainless steel cylindrical bed with the length of 20 cm and internal diameter of 2 cm equipped with two ball valves and a pressure gauge. After equilibrium, the composition of remaining gas was

analyzed by a Varian 3800 gas chromatograph equipped with a gas sampling valve, 5A molecular sieves capillary column (25 m × 0.53 mm i.d. × 50 µm film thickness), thermal conductivity detector and helium as carrier gas. The adsorption experiments were performed at different pressures after full regeneration of adsorbent by evacuating and heating of bed.

RESULTS AND DISCUSSION

The XRD patterns of Cp sample (Fig. 1) showed that the main crystalline phases correspond to clinoptilolite. The FTIR spectrum of Cp is shown in Fig. 2. The peaks at 3600, 3440 cm^{-1} are related to stretching mode of H-O-H, the peaks at 1080 and 1150 cm^{-1} belong to antisymmetrical stretching and
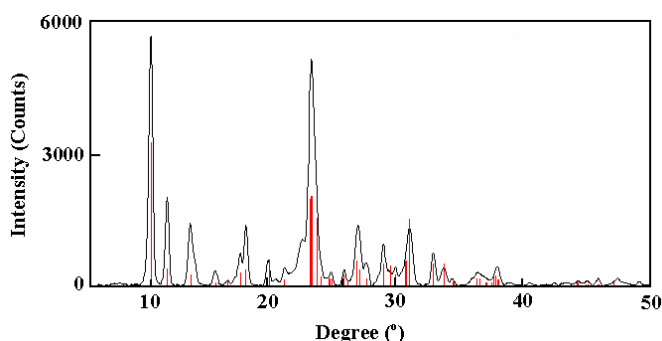
Fig. 1. X-ray powder diffraction of Cp sample and the reference Cp (vertical).
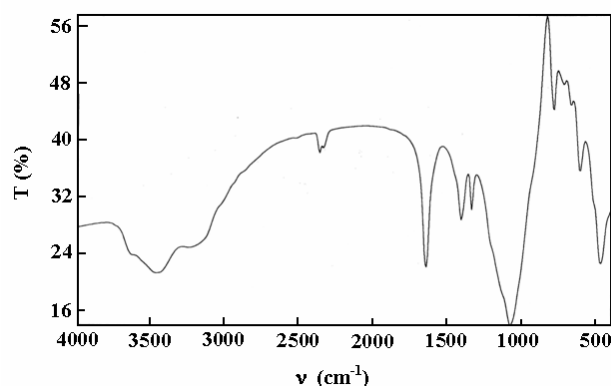
**Fig. 2.** FTIR spectrum of clinoptilolite.

peaks at 680 and 740 cm^{-1} are the symmetrical stretchings of SiO$_4$ and AlO$_4$, respectively [18].

N$_2$ adsorption isotherm of pure and modified samples has been shown in Fig. 3. The BET model described the experimental point up to p/p^o ≤ 0.4 perfectly. The total pore volume and specific surface area of the samples were calculated (Table 1). Chemical compositions of the samples are shown in Table 2. To obtain a more representative chemical composition of the bulk, the analysis was repeated 5 times for each sample, and the elements contents were averaged. The exchange was always incomplete for the studied cations.

The equilibrium amounts of the components in non adsorbed gas phase and adsorbent phase at different pressures are shown in Table 3. The equilibrium content of N$_2$, CH$_4$ and C$_2$H$_6$ vs. pressure are shown in Figs. 4, 5 and 6, respectively, for Cp, Na-Cp and K-Cp samples. According to Achley [6], sodium occupies both M(1) and M(2) sites (Table 4). These sites are located at the channel intersections. Full occupancy of site M(1) and M(2) results in effective blocking of all three channels. This results in very slow diffusion rates through molecular sieving, especially for CH$_4$. Higher selectivity for N$_2$ is due to smaller kinetic diameter and higher diffusibility (Table 5) and larger interaction between N$_2$ with a quadrupole moment with electric field energy created by Na$^+$ cation in the zeolite structure. Higher quadrupole moment and polarizability (Table 5) are responsible to higher selectivity for C$_2$H$_6$ in comparison to methane.

By increasing pressure, the amount of CH$_4$ increases and competes for adsorption sites with N$_2$. The adsorption sites are engaged and smaller amounts of N$_2$ could be adsorbed and, consequently, the N$_2$ content in gas phase increases. This is because the interactions are predominantly sorbate-cation
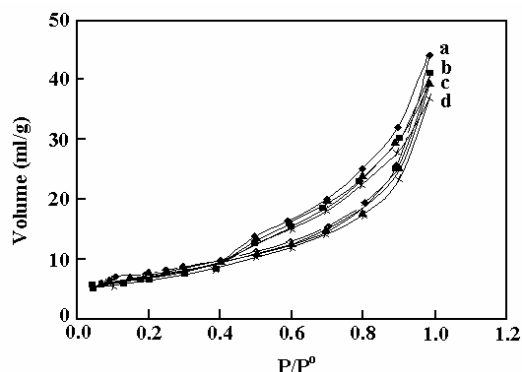
Fig. 3. Adsorption-desorption isotherm of N$_2$ (77.4 K): (a) H-Cp, (b) Cp, (c) Na-Cp and (d) K-Cp.

Table 1. Surface Area (S), Average Pore Radius (r°) and Total Pore Volume (V°)

Sample	S (m^2 g^{-1})	r° (Å)	V° (ml g^{-1})
Cp	24.43	50.48	0.0637
Na-Cp	26.19	45.86	0.0615
K-Cp	24.4	45.88	0.0574
H-Cp	26.68	49.78	0.0684

and sorbate-framework rather than sorbate-sorbate.

Figures 4, 5 and 6 also show the composition of non adsorbed gas phase on potassium clinoptilolite. Like sodium clinoptilolite, potassium clinoptilolite has selectivity for N$_2$, although slightly smaller than sodium clinoptilolite. This is due to the lower charge density of K$^+$ compared to Na$^+$ and, therefore, the lower interaction energy between K$^+$ and N$_2$. Potassium occupies site M(3) and the outer edge of A channel, which causes blocking of channel C (Table 4). This reduction

**Table 2.** Composition of Purified and Modified Clinoptilolites

	Composition (%)								Exchange (%)			
Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	K$_2$O	CaO	MgO	LOI (%)	Na	K	Ca	Mg
Cp	66.53	11.82	1.25	2.2	2.41	3.1	0.7	12.25				
Na-Cp	66.45	11.84	1.23	5.59	1.92	2.2	0.54	12.11		20.3	29	22.9
K-Cp	66.68	11.72	0.85	0.37	6.49	2.22	0.65	12.15	83.2		28.4	7.1
NH$_4$-Cp	66.52	11.78	1.17	0.75	1.82	1.41	0.63	15.86	65.9	24.5	54.5	10.1

Table 3. Equilibrium Values of Components in Gas and Sorbent Phase

Sample	P (bar)	N_2 (mmol)		CH_4 (mmol)		C_2H_6 (mmol)	
		Gas	Sorbent	Gas	Sorbent	Gas	Sorbent
Purified	4	0.11	1.92	25.22	12.16	0.35	1.22
	6	0.25	3.71	42.22	13.85	0.68	1.68
	8	0.39	3.82	61.25	13.51	1.02	2.12
	10	0.85	4.28	80.38	13.07	1.48	2.45
	12	0.91	5.24	100.52	11.64	1.84	2.87
	15	1.25	6.43	130.09	10.09	2.73	3.16
Na-Cp	4	0.22	1.83	25.05	12.33	0.28	1.29
	6	0.39	2.69	40.14	15.93	0.47	1.89
	9	0.91	3.72	69.33	14.78	0.86	2.68
	12	1.83	4.32	97.47	14.67	1.22	3.51
	14	2.36	4.82	117.17	13.66	1.57	3.93
K-Cp	6	0.84	2.24	29.91	26.17	0.26	2.11
	7	0.93	2.66	36.82	28.61	0.25	2.52
	8	1.15	2.95	45.87	28.89	0.18	2.69
	10	1.34	3.79	64.11	29.35	0.16	3.77
	12	1.69	4.46	85.31	26.84	0.14	4.57
	15	2.12	5.57	115.63	24.55	0.15	5.74
H-Cp	6	3.62	0.54	37.31	18.77	0.08	2.28
	8	4.31	0.21	54.43	20.33	0.16	2.98
	11	6.33	0.68	83.62	19.91	0.28	6.21
	15	8.52	0.83	123.48	16.72	0.31	5.59
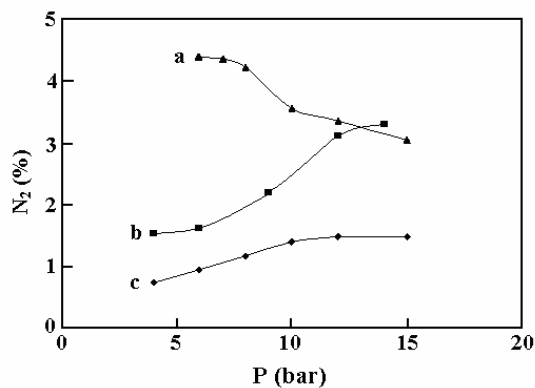
Fig. 4. Nitrogen content of the gas after equilibrium with the sample: (a) K-Cp, (b) Na-Cp and (c) Cp.
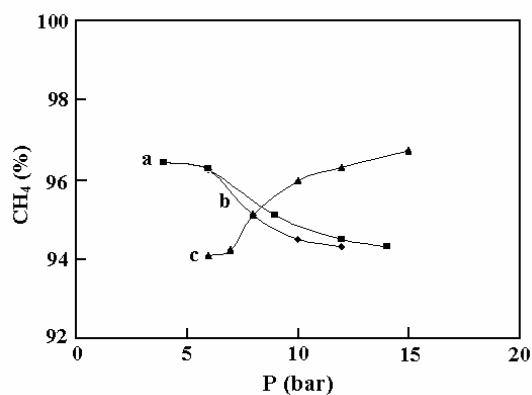
Fig. 5. Methane content of the gas after equilibrium with the sample: (a) Na-Cp, (b) Cp and (c) K-Cp.
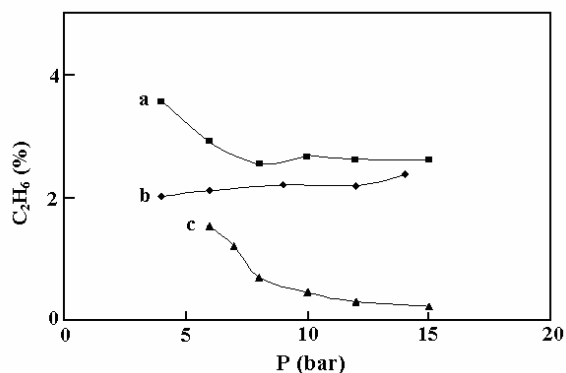
Fig. 6. Ethane content of the gas after equilibrium with the sample: (a) Na-Cp, (b) Cp and (c) K-Cp.

Table 4. Channel Blockage Matrix for Clinoptilolite [7]

Site	Channel A		Channel B		Channel C	
	CH_4	N_2	CH_4	N_2	CH_4	N_2
M(1)/M(2)	pb[b]	pb	b[a]	b	pb	pb
M(3)	o[c]	o	o	o	b	b
M(4)	pb	pb	o	o	o	o

[a]Blocked. [b]Partially blocked. [c]Open

Table 5. Physical Constants of Gases [19]

|	σ (Å)[a]	μ (Å^3)[b]	α (Å^3)[c]
N_2	3.64	0.31	1.4
CH_4	3.8		2.6
C_2H_6	3.8	0.27	3.9

[a]Kinetic diameter. [b]Quadropolar moment. [c]Polarizability.

in pore blocking also allows the access for methane and ethane with larger kinetic diameters (Table 5), causing the equilibrium selectivity for methane and ethane to be higher than that for the case of sodium clinoptilolite. In K-Cp sample, channels A and B are open and, therefore, the increase in pressure of feed gas causes more N_2 adsorption. This also attribute to faster diffusion of N_2 in comparison to CH_4.
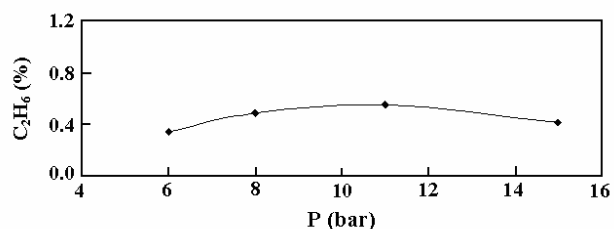
The purified clinoptilolite is a complex, naturally occurring zeolite containing many cations (*i.e.*, Na^+, K^+, Mg^{2+}, Ca^{2+} and small amount of Fe^{3+}) located in different cationic sites in varying proportions. Hence, in purified clinoptilolite, the
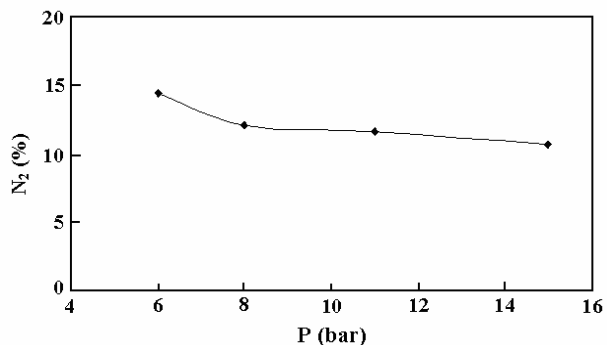
Fig. 7. Nitrogen content of the gas after equilibrium with H-Cp.
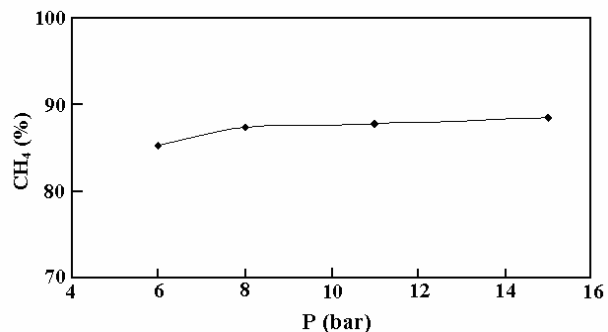
Fig. 8. Methane content of the gas after equilibrium with H-Cp.

Fig. 9. Ethane content of the gas after equilibrium with H-Cp.

influence of cation sites on equilibrium adsorption is not straightforward. The composition of gas phase on purified clinoptilolite showed that the zeolite has excellent selectivity for N_2. Indeed, the purified clinoptilolite shows an average behavior of all cationic forms of clinoptilolite.

The H-Cp was prepared by ion exchange with ammonium chloride solution. Figures 7, 8 and 9 show the N_2, CH_4 and

C$_2$H$_6$ content on H-Cp, respectively. H-Cp shows a very good equilibrium selectivity for CH$_4$; hence, H-Cp could be used for the separation of methane/nitrogen mixtures and methane could be obtained as a desorption product [16]. H$^+$ is a very small cation with very high charge density, causing more open pores of zeolite and, therefore, the channel blockage factor decreased so that larger and more polarizable molecules as methane and ethane can easily diffuse and adsorb properly. The larger polarizability of CH$_4$ compared to that of N$_2$ may even offset the quadrupole moment interaction effect of N$_2$ so that CH$_4$ heat of adsorption can be larger than that of N$_2$.

CONCLUSIONS

Sodium and potassium exchanged and purified form samples of clinoptilolite were found to be suitable for adsorption of N$_2$ and hydrogen form for CH$_4$ adsorption. Based upon the results of this study, the purified clinoptilolite could be used for N$_2$ adsorption without any modification.

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