

Gas Adsorption Characteristics of Metal Exchanged Zeolite[♦]

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ABSTRACT

Zeolites consist of alumina-silica structures of nano-sized cavities with different sizes and arrangement. In recent years, numerous studies have been conducted on the capability of zeolites as adsorbents in adsorptive gas storage (ANG) and gas separation. The adsorptive properties of zeolites depend on their structure, size, charge and distribution of cations. The effect of polyvalent cations on adsorption capacity of zeolites has been reported in the literature, which indicated that the adsorptive capacity increases with increasing charge density of the cation. The effects of metal balancing cation in zeolite structure on gas adsorption depend primarily on the size and shape of the gas molecule, the size of the cation and its location in the channel, and its interaction with the gas molecule. Zeolite modification such as cation-exchanged technique was used to determine the effect of different cation on gas adsorption characteristics. In this study, sodium cations originally present in zeolites are exchanged with other metal cations. It is observed that at very low concentration of adsorbed gas, the type of cation influences the adsorption characteristics, where divalent cations adsorb more gas than monovalent cations exchanged zeolite. At higher concentrations of adsorbed gas, the effect of cation is insignificant. However, different gases adsorb differently depending on the adsorbate-adsorbent interactions.

KEY WORDS

Zeolite, cation exchange, gas adsorption, isotherm.

INTRODUCTION

Porous materials such as zeolites, activated carbon and metal oxides can be used as adsorbents for many industrial applications such as in gas separation and adsorptive gas storage. The availability of large internal surface area and volume provide most desirable properties for these applications. Crystalline zeolite consists of aluminium and silicon atoms, which are tetrahedrally coordinated by oxygen atoms. As each aluminium atom incorporates into the framework, one excess negative charge results, which requires an equivalent amount of extra-framework cations to balance the charge. These cations exist inside the cages and channels together with intrazeolitic water. Since the cations are not covalently bound, it can easily be replaced by other cations. Once the cation exchange takes place, zeolite exerts a strong, localized electrostatic field that can alter the chemistry of cations in the exchange site positions. Hence, cations in the exchange sites are not necessarily the same as cations adsorbed (Armor, 1998). Several studies have been carried out related to gas adsorption on zeolites and modified zeolites. A study on different type of cations (Li, Na, K, Rb, and Cs) in ZSM-5 showed that the adsorption capacity decreases as the radius of the cation increases for adsorption of several hydrocarbons (Ma, 1983). Langmi *et al.*, (2003) reported that for the adsorption of hydrogen on zeolites (A, X, Y and rho), it was found that the adsorption was strongly dependent upon type of framework, type of cation (Cd and Mg) and temperature.

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Choudhary *et al.* (1994) have suggested that a major difference between the interactions of N_2-Ca^{2+} and N_2-Na^+ was due to the field-quadrupole interactions where specific interactions of the quadrupole with the electric field was created by cations. A strong interaction was also found between divalent cations in CaX and 5A and ethylene double bond (Triebe *et al.*, 1996).

The exchange of sodium ion in zeolite structural framework with other cation of different charge and molecular size, and with different quantity influences the physical and chemical properties of the zeolite. This exchange process can be carried out using cation exchange method, which allows the modification of zeolite properties at the molecular level. As a result, this method has received considerable attention recently as a method to modify the physicochemical properties of adsorbent. We have attempted to study the effect of other cations (alkali metal Group IA and the alkaline earth metal Group IIA) on physicochemical structure of zeolite and gas adsorption characteristics, which will be discussed in this paper.

MATERIALS AND METHOD

Zeolite synthesis

Sodium form of zeolite (NaY-18) was synthesized using reactant mixture with molar composition of $6.4Na_2O: 1Al_2O_3: 8SiO_2: 180H_2O$, at a crystallization temperature and time of $100^\circ C$ and 24 hours respectively. To prepare amorphous aluminosilicate gel, anhydrous sodium aluminate (Riedel-de Haën) was dissolved into sodium hydroxide (MERCK) solution and heated under rigorous stirring. Colloidal silica (Ludox, MERCK) was added into sodium hydroxide solution and heated under rigorous stirring until a clear solution appeared. Both solutions were mixed and stirred for 2 hours to obtain a homogeneous mixture, which was then transferred into a polyethylene bottle and heated at $100^\circ C$ in an oven to crystallize the zeolite. After that, the crystalline zeolite was recovered by filtration, washed with distilled water until $pH < 10$ and then dried overnight in the oven at $105^\circ C$. Before characterization, the zeolite was kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate.

Cation exchange procedure

Synthesized zeolite (Na-18) with a framework Si/Al ratio of 1.5 was used as based zeolite for cation exchanged experiments. The exchange process was carried out using batch method. 5 g of finely ground zeolite was dispersed in 250 mL of 0.5 M $LiNO_3$ solution. The suspension was heated at $80^\circ C$ for 5 hours and the exchanged zeolite was filtered, dried in the oven at $105^\circ C$ for 12 hours, kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate. The same procedure was repeated with other cation namely potassium, lithium, magnesium, calcium and barium. The exchanged zeolite are labeled as Li.Na-18, K.Na-18, Mg.Na-18, Ca.Na-18 and Ba.Na-18 respectively.

Zeolite characterization

X-ray diffraction of zeolite samples were characterized by X-ray Diffractometer (Bruker). The patterns were recorded using $CuK\alpha_1$ radiation of $\lambda = 1.5418 \text{ \AA}$ at 40 kV and 20 mA in the range of $2\theta = 5^\circ - 50^\circ$ at scanning speed of 0.05° per second. The XRD results allowed us to determine the sample crystallinity, unit cell parameters, and framework Si/Al. According to ASTM D3906, the total intensities of the six peaks assigned to (331), (511), (440), (533), (642), and (555) reflections were used as a comparison using commercial zeolites (NaY). The porosity of each sample was determined by measuring

nitrogen adsorption with Micromeritics ASAP 2000 at 77K. The total surface area was calculated using BET method. The external surface area and micropore volume were calculated using t-plot method. The morphology of zeolites was evaluated by scanning electron microscope (SEM).

Gas adsorption measurement

The adsorption measurement of methane and carbon dioxide gases on zeolites was measured at various pressures up to 1 bar and at temperature of 303K using volumetric adsorption analyzer (Micromeritics ASAP 2000). Each sample was activated at 400°C for a minimum of 2 hours before the adsorption measurement was carried out. Adsorbed amounts are expressed as volume adsorbed (cm³) per unit mass (g) of adsorbent.

RESULTS AND DISCUSSION

Effect on structure and properties

As reported in the literature, the cation exchange treatments could cause some changes in the structure and properties of zeolites. Thus, it is important to clarify the changes since it may affect the adsorption characteristics. Figure 1 shows SEM images of starting and cation-exchanged zeolite. Results indicate that the particle sizes and morphologies remained unchanged before and after exchange treatments. The particle size is about 1- 1.5µm.

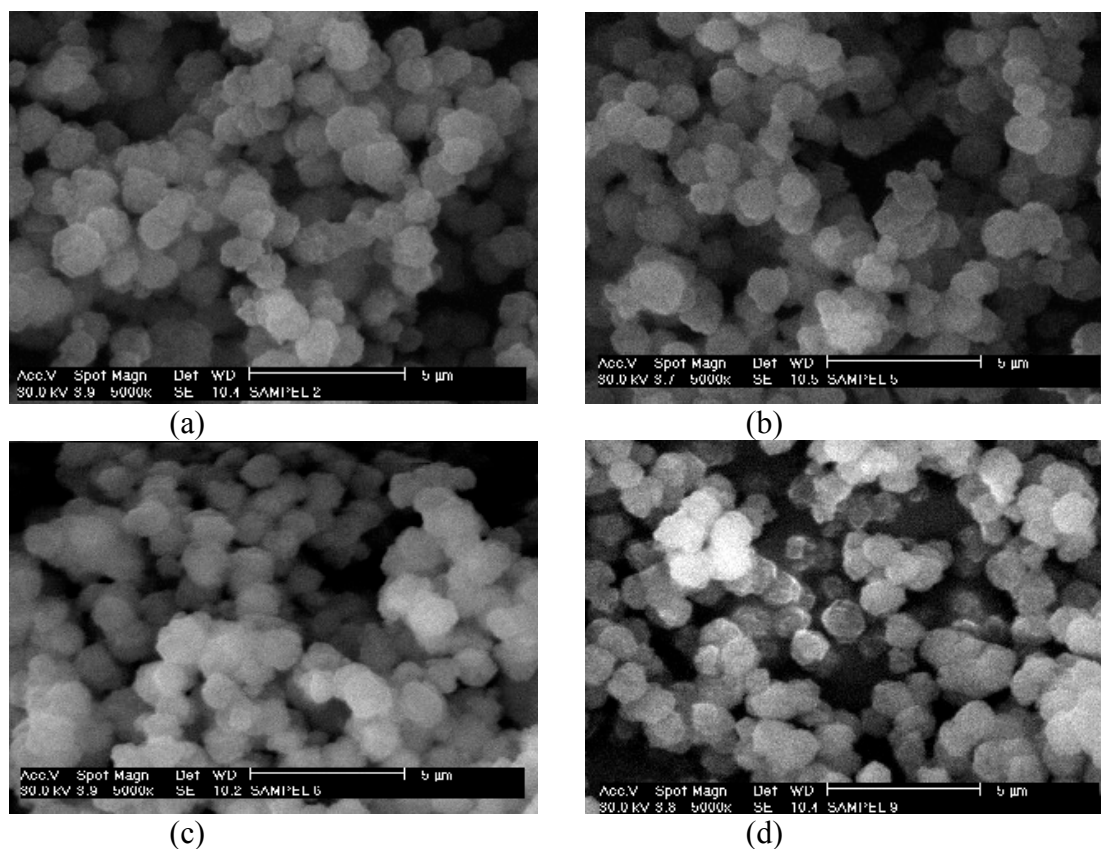


Figure 1: Scanning electron micrograph of the products of based and modified zeolites: (a) Na-18, (b) K.Na-18, (c) Li.Na-18, and (d) Mg.Na-18.

Table 1 summarizes the changes in Si/Al, crystallinity, and porosity of zeolites. It was found that the changes in crystallinity for exchanged zeolite for Group IA are relatively small. However, the exchange with alkaline metal Group IIA results in lower crystallinity of zeolites (Ba.Na-18, Mg.Na-18 and Ca.Na-18). The framework Si/Al of exchanged zeolites decreased after the treatment except for Li-exchanged zeolite, indicating that extraction of Al from the zeolite framework occurred during the exchange treatments.

Table 1: Physicochemical properties of modified zeolites.

Zeolite	Framework Si/Al	Relative crystallinity (%)	Surface area (m ² /g)		Pore volume (m ³ /g)	
			Micropore	External	Micropore	Mesopore/ Macropore
NaY #	2.6	100	809.5	10.6	0.3042	0.0240
Na-18*	1.5	76	793.8	19.7	0.2996	0.0615
Li.Na-18	2.0	81	874.4	20.4	0.3297	0.0740
K.Na-18	1.2	40	702.1	17.2	0.2646	0.0620
Mg.Ca-18	1.5	76	828.8	17.1	0.3127	0.0676
Ca.Na-18	1.5	55	804.0	17.4	0.3032	0.0673
Ba.Na-18	1.4	6	542.2	11.7	0.2055	0.0518

Commercial zeolite * Based zeolite

Figure 2 show typical adsorption profiles of microporous structures (Type 1), even after cation exchange treatments. The surface area and pore volume (Table 1) calculated from nitrogen adsorption isotherms show a decrease as the ionic radius of cation increases for alkali metal Group I. The decrease is due to the destruction of zeolite framework as revealed by XRD patterns and degree of crystallinity. But for alkaline earth metal (Group II), the surface areas of Na-18 exchanged with Mg²⁺ and Ca²⁺ are relatively high even though the ionic radius is larger than Na⁺. Since the number of cations from Group II which replaced the sodium ions in the zeolite structure is less than those from Group I, there is more space for nitrogen to adsorb on the zeolite surface. The results probably show an increase in mesopore volume which reflects the formation of meso and macropores for all type of exchanged zeolites.

Adsorption equilibrium

The N₂ adsorption for synthesized (Na-18) and commercial zeolite (NaY) samples at 77K are typical of type I isotherms with relatively small external surface. The adsorption-desorption results show that the isotherms almost overlap with small hysteresis, indicating that the zeolite samples possess open and uniform microporous system. It is observed that a significant amount of nitrogen was already adsorbed on zeolites at very low pressures. The abrupt increase of nitrogen adsorption at relatively low pressure also indicates the ability of N₂ to penetrate freely into the micropores. The adsorption isotherm of N₂ approaches plateau at P/P₀ = 0.25 (Figure 2a). Adsorption of exchanged zeolites also follow type I isotherm (Figure 2b).

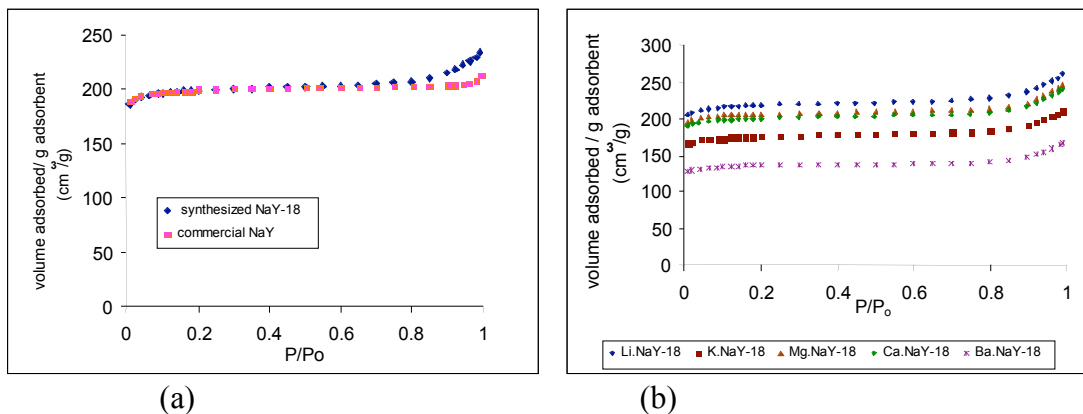


Figure 2. Adsorption isotherms of nitrogen at 77K: (a) Synthesized Na-18, commercial NaY, and (b) Exchanged zeolites.

The influence of cation on gas adsorption was investigated using alkali and alkaline earth metal exchanged zeolites for pressures up to 1 bar at 303K. The presence of cation alters the electrostatic field within the zeolite cavities and hence, influences the amount of CH₄ and CO₂ adsorbed on zeolite surface. CH₄ adsorption is far from saturation and will generally saturate at higher pressure. The presence of other cations in zeolite structure alters the adsorption characteristics. CH₄ and CO₂ adsorptions show different patterns toward different group of cations. In CH₄ adsorption, the amount of gas adsorbed increases as the atomic number increased even though the surface area and pore volume decrease. At pressure below 1 bar, the charge and size of cations have stronger influence on gas adsorption than the surface area and micropore volume. The result also show that after cation exchange treatment, zeolites with divalent metal cations adsorbed more gas than monovalent cation exchanged zeolite. This is due to stronger adsorptive centers of divalent cations in zeolites. But this condition only applies for CO₂ at relative pressure (P/P₀) less than 0.1.

The CO₂ adsorption isotherms of modified zeolites show an abrupt increase of CO₂ adsorption but the linear adsorption for CH₄ over pressure ranges understudy. This indicates that CO₂ has greater affinity to adsorb than CH₄ even though the kinetic diameter of CH₄ (3.8 Å) and CO₂ (3.3 Å) are comparable and smaller enough and could pass through the pore opening of zeolites (≈ 7.4 Å). The CO₂ adsorbs at least 10 times greater than CH₄. The specific interaction of quadrupole of CO₂ molecule with electric field created by cation is likely the reason for higher adsorption of CO₂. These results also proved that, non-polar molecules such as CH₄ has lower adsorption affinity towards zeolites.

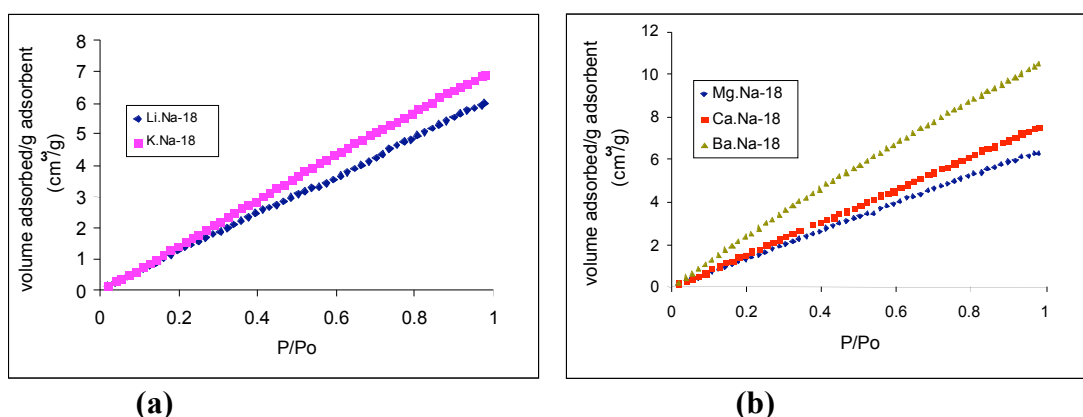


Figure 3. CH₄ adsorption isotherms at 29°C: (a) alkali metal exchanged zeolites and (b) alkaline earth metal exchanged zeolite.

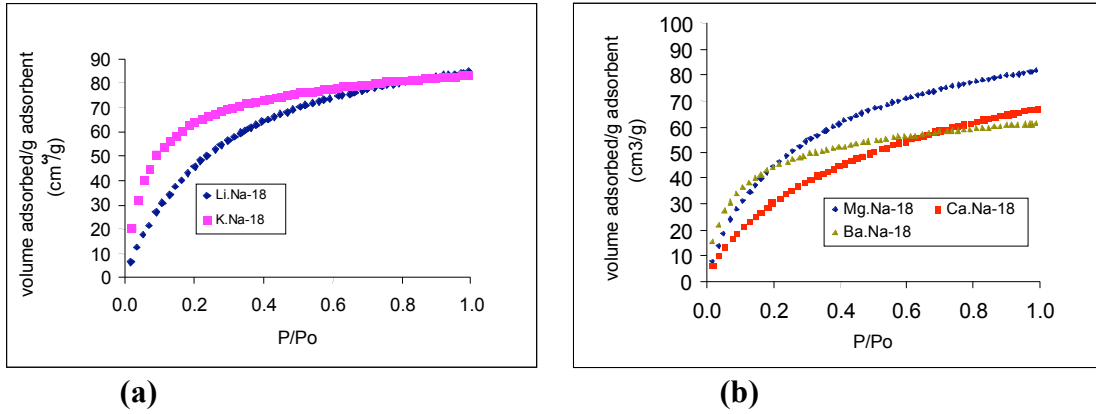


Figure 4. CO₂ adsorption isotherms at 29°C: (a) alkali metal exchanged zeolite and (b) alkaline earth metal exchanged zeolite.

In order to elucidate further, the adsorption data was fitted using the existing thermodynamic models. The simplest model that relates between the amount of gas adsorbed and gas phase pressure is given by the linear equation, Henry's law for adsorption that is only valid for dilute system

$$\theta = kP \quad (1)$$

Another model that is commonly used is the Langmuir model, which signifies that adsorption takes place on an energetically uniform surface without any interaction between adsorbed molecules. The equilibrium relation is given as

$$\theta = \frac{q}{q_m} = \frac{Bp}{1 + Bp} \quad \text{or} \quad p = \frac{1}{B} \left(\frac{\theta}{1 - \theta} \right) \quad (2)$$

where B and θ are the equilibrium constant and fraction of monolayer coverage respectively. When the amount adsorbed is far smaller compared with the adsorption capacity, the equation is reduced to Henry type of equation. As reported by Choudhary and Mayadevi (1996), gas adsorption can also be described using the Freundlich model, which has two constants; α and β that often successfully correlate experimental data for low and intermediate values of θ .

$$\theta = \alpha P^\beta \quad (3)$$

The applicability of the Freundlich is limited only for adsorption below the saturation concentration. This is due to the fact that the model gives no limit of adsorption capacity, making the amount adsorbed goes to infinity when the pressure increases.

The CH₄ adsorption data fits very well with Henry's equation that indicates that adsorption occurs in a dilute form. This is further verified by the Freundlich model, where β values are close to unity (Table 2), and the equation reduces to a linear form (Henry's type of equation). The experimental data also shows that CO₂ adsorption is higher than CH₄. Therefore, Henry's equation can only be applied at extremely low concentration of CO₂, which is basically at very low adsorption pressure. At adsorption pressure below 1 bar, CO₂ adsorption can be well described by Langmuir and Freundlich models. The estimated values of the model constants of the best fitting adsorption isotherm for CH₄ and CO₂ are presented in Tables 2 and 3.

It was observed that at extremely low concentration of adsorbed gas the presence of cation plays an important role in gas adsorption. Surface area and pore volume do not influence the adsorption of the gas. With the presence of K⁺ and Ba²⁺ in zeolite replacing sodium ions, equilibrium constant for CH₄ is higher than zeolite exchanged with Li⁺ and Mg²⁺. A strong interaction between divalent cation and adsorbate is indicated by adsorption equilibrium constants (k and α) of Ba.Na-18 in Table 2. Similarly, this adsorption behavior was also observed for CO₂ at extremely low pressure. As the adsorb gas

concentration increases, the influence of cation gradually reduces and the effect of pore volume becomes more profound.

Table 2. Model constants calculated from the best fitting of CH₄ adsorption isotherm.

Zeolite	Henry constant	Freundlich constants	
	k	α	β
Na-18*	7.456	7.509	1.009
Li.Na-18	6.085	6.132	1.011
K.Na-18	7.140	7.272	1.029
Mg.Na-18	6.551	6.554	0.993
Ca.Na-18	7.684	7.695	0.999
Ba.Na-18	11.003	11.002	0.965

*Based zeolite

Table 3. Model constants calculated from the best fitting of CO₂ adsorption isotherm.

Zeolite	Langmuir constants		Freundlich constants	
	B	q_m	α	β
Na-18*	10.22	108.69	114.54	0.3594
Li.Na-18	3.76	106.38	97.05	0.5509
K.Na-18	17.00	84.03	89.51	0.2662
Mg.Na-18	4.56	95.23	91.84	0.5203
Ca.Na-18	4.87	68.49	72.30	0.5687
Ba.Na-18	18.56	59.88	65.34	0.2901

*Based zeolite

CONCLUSIONS

Physicochemical properties of zeolite change when the sodium in zeolite framework was exchanged by other metal cations. From the adsorption isotherm obtained, adsorption was affected by the presence of metal cations at very low concentration of gases. CH₄ adsorb in much smaller quantities than CO₂ due to the fact that there is a strong specific interactions between adsorbate and the electric field created by the structural cations in zeolites framework. Therefore at low concentration, the equilibrium constant depends on adsorbate and cation properties. However, when the concentration of gases increases, the effect of cation sites is no longer significant. The pore volume will determine the amount of gases that can accumulate in the pores. Isotherm models can be used to describe the adsorption of CH₄ and CO₂ adsorption. Henry equation was found to be successful at very low concentration, whereas Langmuir and Freundlich equations was better suited to fit at higher concentration of gas adsorption.

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