# ADSORPTION OF CO$_2$ AND CH$_4$ ON METAL-CATION EXCHANGE ZEOLITE

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## ABSTRACT

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. Modification of zeolite using cation exchange 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, in which divalent cations adsorb more 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, Adsorption, Carbon dioxide, Methane

## 1.0 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. Since 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 [1].

As shown in Figure 1, exchangeable cations in NaY zeolite balance the negative charge of the aluminosilicate framework which are found within the zeolite's cavities. They are usually found at the following sites; site I, at the center of a D6R, is surrounded by an octahedron of oxygens; site I', in the sodalite cavity on the opposite side of one of the D6Rs' six-rings from site I, is close to three framework oxygens; site II', in the sodalite cage near a single six-ring (S6R) entrance to the supercage, is close to three framework oxygens; site II is in the supercage adjacent to an S6R; site III is on a twofold

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axis in the supercage, in or opposite a sodalite-unit four-ring; site III' is somewhat off site III, or much further away in the supercage but still near its inner walls, perhaps in or opposite a D6R four-ring; site IV is at the center of the supercage; finally site V is at the center of a 12-ring. Cation site IV and V are far from the zeolite framework and are not normally occupied by monoatomic cations [2].
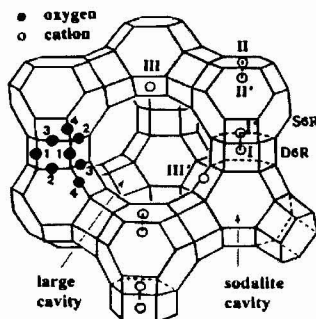


**Figure 1** Stylized drawing of the framework structure of zeolite Y [2].

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 [3]. Another study 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 [4]. Different cationic form of a given zeolite may lead to significant differences in the selective adsorption of a given gas, due to both the location and size of the interchangeable cations, which affect the local electrostatic field, and the polarization of the adsorbent. In addition, cation exchange in a zeolite produces remarkable change in zeolite properties such as thermal stability, pore size and catalytic activity.

The effects of cations are most readily revealed when zeolites with identical structure, but different cation size, charge, and concentration, are used in adsorption studies. Studies on zeolite containing polyvalent cations have shown the adsorption capacity and the heat of adsorption usually increase with increasing charge density of cations [5]. It was also suggested that a major difference between the interactions of N$_2$-Ca2+ and N$_2$-Na+ was due to the field-quadrapole interactions where specific interactions of the quadrapole with the electric field was created by cations [6]. A strong interaction was also found between divalent cations in CaX and 5A and ethylene double bond [7].

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 several types of 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. The adsorption of these gases on

zeolites and a comparison of the adsorptive behavior and properties are a great importance for the development of separation process using adsorption method. A combination of large surface area, large pore volume and electrostatic interaction between methane molecules in the electrostatic field of zeolites may enhance the adsorption of methane and carbon dioxide into the zeolites

## 2.0    EXPERIMENTAL

### 2.1    Zeolite synthesis

Zeolite 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 $100°$ 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 °C 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 °C. Before characterization, the zeolite was kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate.

### 2.2    Cation exchange

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 LiNO3 solution. The suspension was heated at 80 °C for 5 hours and the exchanged zeolite was filtered, dried in the oven at 105 °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.

### 2.3    Characterization

X-ray diffraction of  zeolite samples were characterized by X-ray Diffractometer (Bruker). The patterns were recorded using CuK☐1 radiation of ☐ = 1.5418 Å at 40 kV and 20 mA in the range of $2θ = 5° - 50°$ 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).

## 2.4    Gas adsorption

The adsorption measurement of methane and carbon dioxide gases on zeolites was measured at various pressures up to 1 bar and at temperature of 303 K 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 ($cm^3$) per unit mass (g) of adsorbent.

## 3.0    RESULTS AND DISCUSSION

### 3.1    Effect on zeolite structure

The cation exchange treatments caused some changes in the structure and properties of zeolites. 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.



(a)                               (b)

(c)                               (d)
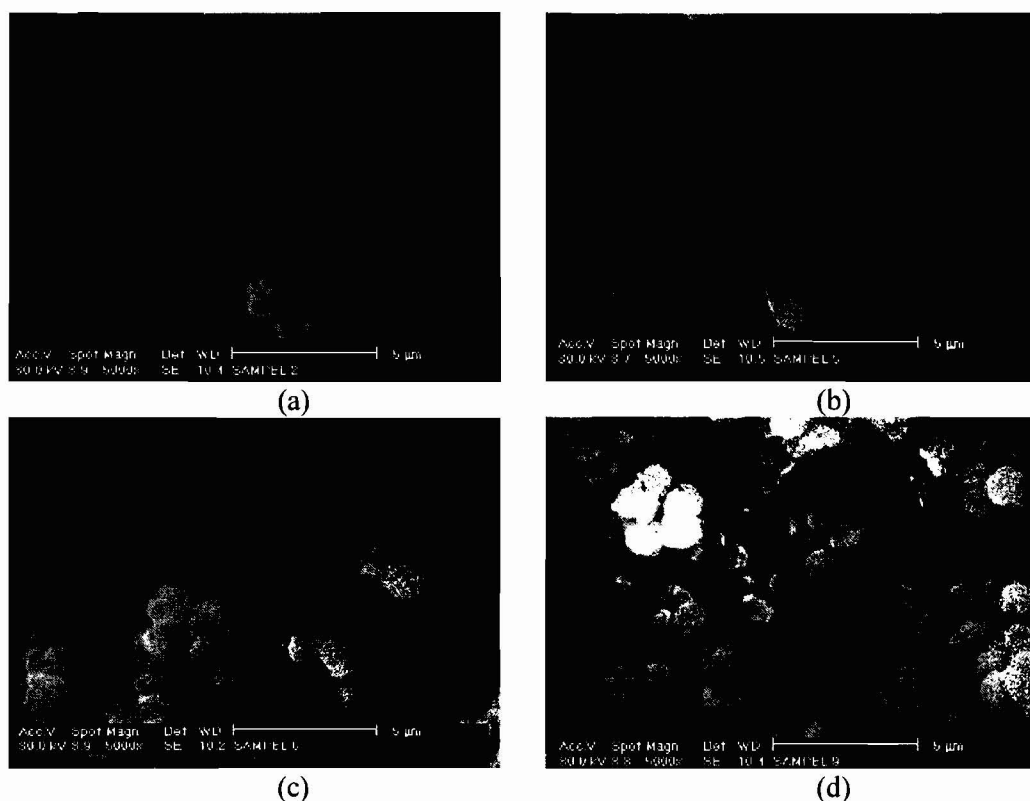
**Figure 2** Scanning electron micrograph of the products of based and modified zeolites: (a) Na-18, (b) K.Na-18, (c) Li.Na-18, and (d) Mg.Na-18.

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,

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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 (m²/g) | | Pore volume (m³/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 * Synthesized 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 $Mg^{2+}$ and $Ca^{2+}$ 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.

The $N_2$ 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 $N_2$ to penetrate freely into the micropores. The adsorption isotherm of $N_2$ approaches plateau at $P/P_o = 0.25$ (Figure 2a). Adsorption of exchanged zeolites also follow type I isotherm (Figure 2b).
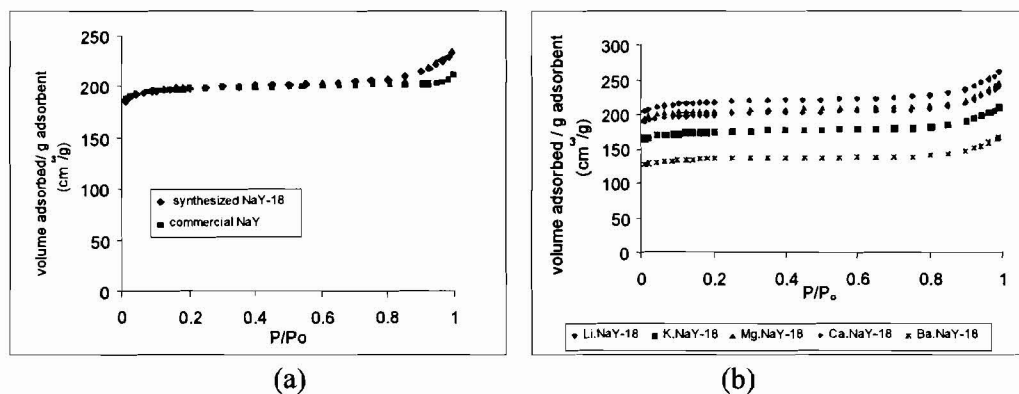
**Figure 2** Adsorption isotherms of nitrogen at 77K: (a) Synthesized Na-18, commercial NaY, and (b) Exchanged zeolites.

The influence of cation on gas adsorption was investigated using alkali and alkaline earth metal exchanged zeolites for pressures up to 1 bar at 303 K. The presence of cation alters the electrostatic field within the zeolite cavities and hence, influences the amount of $CH_4$ and $CO_2$ adsorbed on zeolite surface. $CH_4$ adsorption is far from saturation and will generally saturate at higher pressure. The presence of other cations in zeolite structure alters the adsorption characteristics. $CH_4$ and $CO_2$ adsorptions show different patterns toward different group of cations. In $CH_4$ 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 $CO_2$ at relative pressure ($P/P_o$) less than 0.1.

The $CO_2$ adsorption isotherms of modified zeolites show an abrupt increase of $CO_2$ adsorption but the linear adsorption for $CH_4$ over pressure ranges understudy. This indicates that $CO_2$ has greater affinity to adsorb than $CH_4$ even though the kinetic diameter of $CH_4$ (3.8 Å) and $CO_2$ (3.3 Å) are comparable and smaller enough and could pass through the pore opening of zeolites ($\approx$ 7.4 Å). The $CO_2$ adsorbs at least 10 times greater than $CH_4$. The specific interaction of quadrapole of $CO_2$ molecule with electric field created by cation is likely the reason for higher adsorption of $CO_2$. These results also proved that, non-polar molecules such as $CH_4$ has lower adsorption affinity towards zeolites.
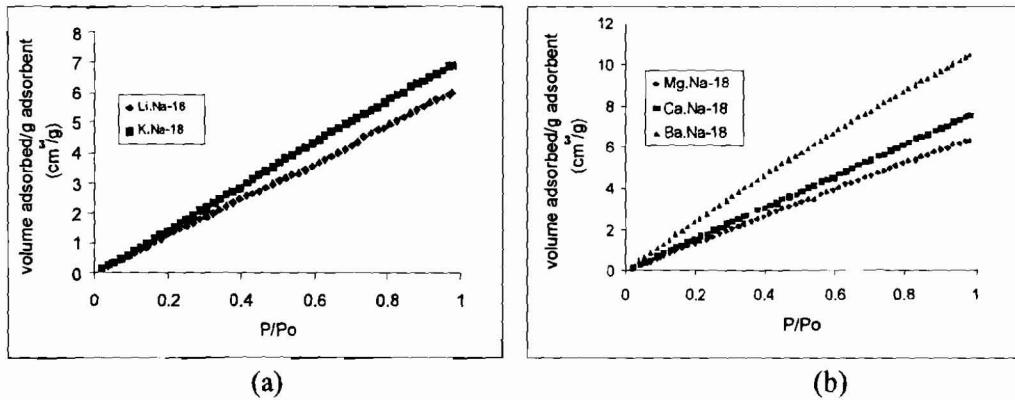
**Figure 3** $CH_4$ adsorption isotherms at 29°C: (a) alkali metal exchanged zeolites and (b) alkaline earth metal exchanged zeolite.
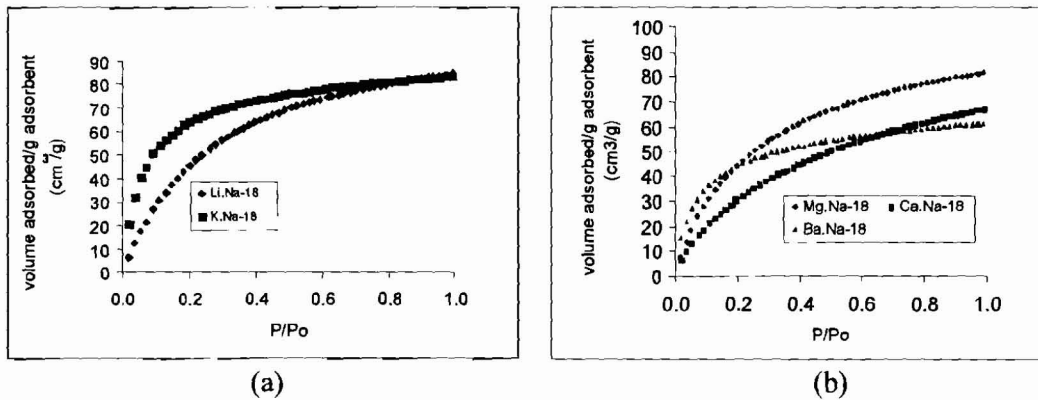


**Figure 4** $CO_2$ adsorption isotherms at 29°C: (a) alkali metal exchanged zeolite and (b) alkaline earth metal exchanged zeolite.

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

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

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

$$\theta = \frac{q}{q_{m}} = \frac{Bp}{1+Bp} \quad \text{or} \quad p = \frac{1}{B}(\frac{\theta}{1-\theta}) \qquad (2)$$

where $B$ and $\theta$ 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, gas adsorption can also be described using the Freundlich model, which has two constants; $\alpha$ and $\beta$ that often successfully correlate experimental data for low and intermediate values of $\theta$ [8]. 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.

$$\theta = \alpha P^{\beta} \qquad (3)$$

The $CH_4$ 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 $\beta$ 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 $CO_2$ adsorption is higher than $CH_4$. Therefore, Henry's equation can only be applied at extremely low concentration of $CO_2$, which is basically at very low adsorption pressure. At adsorption pressure below 1 bar, $CO_2$ adsorption can be well described by Langmuir and Freundlich models. The estimated values of the model constants of the best fitting adsorption isotherm for $CH_4$ and $CO_2$ are presented in Tables 2 and 3.

**Table 2** Model constants calculated from the best fitting of $CH_4$ adsorption isotherm.

| Zeolite | Henry constant $k$ | Freundlich constants $\alpha$ | $\beta$ |
|---|---|---|---|
| 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 $CO_2$ adsorption isotherm.

| Zeolite | Langmuir constants $B$ | $q_m$ | Freundlich constants $\alpha$ | $\beta$ |
|---|---|---|---|---|
| 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

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 $Ba^{2+}$ in zeolite replacing sodium ions, equilibrium constant for $CH_4$ is higher than zeolite exchanged with $Li^+$ and $Mg^{2+}$. A strong interaction between divalent cation and adsorbate is indicated by adsorption equilibrium constants ($k$ and $\alpha$) of Ba.Na-18 in Table 2. Similarly, this adsorption behavior was also observed for $CO_2$ 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.

## 4.0 CONCLUSIONS

Gas adsorption was affected by the presence of metal cations in zeolite at a very low concentration of gases. $CH_4$ adsorb in much smaller quantities than $CO_2$ due to the fact that there is a specific interactions between adsorbate and the electric field created by the structural cations in zeolites framework. 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 was used to describe the adsorption of $CH_4$ and $CO_2$ adsorption. Henry equation successfully fits at very low concentration, whereas Langmuir and Freundlich equations was better suited to fit at higher concentration of gas adsorption.

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