

## Gas Adsorption On Modified Zeolite Adsorbent

Khairul Sozana Nor Kamarudin<sup>1</sup> Chieng Yu Yuan<sup>1</sup> Halimaton Hamdan<sup>2</sup> Hanapi Mat<sup>1</sup><sup>1</sup>Advanced Process Engineering (APEN) Research Group, Faculty of Chemical and Natural Resources Engineering,<sup>2</sup>Zeolite and Porous Material Group, Ibnu Sina Institute for Fundamental Science Studies,  
Universiti Teknologi Malaysia, 81300 Skudai, Johor.

Tel: +607-5535482, Fax: +607-5581463, Email: sozana@fkkksa.utm.my

## Abstract

Various industrial applications involving microporous material lead to synthesis of zeolite with different structural framework and properties. Even though the synthesized zeolite could expand the applications in adsorption processes, some structures are highly hydrophobic or highly hydrophilic, others are thermally unstable at temperature higher than 700 °C or adsorb at very low capacity. Therefore, their applications are limited to certain application. Thus, to overcome the problem, modifications or post synthesis treatments are introduced in order to produce modified zeolites with desired properties for specific applications. However, any modification causes some changes, thus special attention has to be paid to the texture of the zeolite because it may result in severe structural defects or variants. This paper will examine the effect of different metal cations on adsorption characteristics. The metal cations were introduced by cation exchange method. It was found that the presence of different metal cations alters the properties of zeolites and thus the adsorption characteristics. Results from gas adsorption uptake and FTIR spectra show that charge and size of metal cations could influence the gas adsorption capacity and the interaction of gas adsorbates with zeolite surface.

## Keywords:

Adsorption, modification, cation exchange, zeolite, adsorbent.

## Introduction

Crystalline zeolite consists of silicon and aluminium atoms, which are tetrahedrally coordinated by oxygen atoms. For every aluminium atom that incorporates into the framework resulting one excess negative charge which requires an equivalent amount of extra-framework cations to balance the charge. These cations exist inside the cages and channels together with intra-zeolitic water. Since the cations are not

covalently bound, it could easily be replaced by other cations [1]. The exchange of sodium ion in zeolite structural framework with other cations of different charge and molecular size, and with different quantity influences the physical and chemical properties of the zeolite. According to Hernandez-Huesca et al. [2], different cationic form may lead to significant differences in the adsorption of a given gas, due to cation's size and its location in the structural framework of the zeolite. It also affects the local electrostatic field and polarization of adsorbates. Another study by Ma [3] reported that the effect of cation on adsorption depends primarily on the size and shape of the guest molecule, the size of the cation and its location in the channel, and the interaction between cation and the guest molecule. It was also reported that the adsorption capacity of several hydrocarbons on ZSM-5 modified with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> decreases as the radius of the cation increases [4]. However, it is still unclear about adsorption characteristics on other types of zeolites.

Thus, in order to enhance the properties of zeolite, several modification methods have been used such as cation exchange, dealumination and impregnation. However, any modification causes changes in structure and properties of zeolites. Special attention has to be paid to the texture of zeolites because it may result in severe structural defects or variants. Nevertheless, cation exchange offers several advantages for modification of zeolites. It is a simple procedure and can tailor not only the pore properties of zeolites, but also surface characteristics of adsorbent. The presence of different cation changes the physicochemical properties of zeolite, thus may improve gas adsorption characteristics. Since the cations are not covalently bound, it can easily be exchanged by other cations. According to Armor [5], once the cation exchange taking place, zeolite exerts a strong, localized electrostatic field that can alter the chemistry of cations in the exchange site positions. The success however, depends on the interrelation between the zeolite structure and the gas adsorption characteristics.

Therefore, in order to control the accessibility of adsorbates, the most suitable cation need to be identified and the amount of exchanged should be monitored and controlled. Besides all the advantages, structural destruction may also occur due to the acidity of solution or the size of cation being exchanged.

Hence, for a successful application of zeolite as adsorbent, a thorough understanding of zeolite properties and gas adsorption phenomena is required. This paper will discuss several factors in relation to the physicochemical properties of zeolites that affect the adsorption of methane. The fundamental study of gas adsorption will be partly addressed with regard to the effect of different metal balancing cation on gas adsorption capacity followed by adsorbate-adsorbent interaction study using Fourier Transform Infrared (FTIR) spectroscopy technique.

## Materials and methods

### Materials

Materials used in this study are reagents obtained from various companies; NaOH from MERCK, sodium aluminate from Riedel-de Haën, colloidal silica (Ludox, 30 wt%) from Aldrich Chemical, magnesium nitrate hexahydrate and calcium nitrate tetrahydrate from MERCK, rubidium nitrate, nickel (II) nitrate hexahydrate and lithium nitrate from Fluka Chemika. All chemicals were used as received and double distilled water was used in the synthesis and preparation of nitrate solution. Methane gas (99.99 %) used for the adsorption study were obtained from Southern Industrial Gas Sdn. Bhd. and used as received.

### Zeolite synthesis

Zeolite used (Na-SZ18) was synthesized using reactant mixture with molar composition of  $6.4\text{Na}_2\text{O} : 1\text{Al}_2\text{O}_3 : 8\text{SiO}_2 : 180\text{H}_2\text{O}$ , at crystallization temperature and time of  $100^\circ\text{C}$  and 24 hours respectively. To prepare amorphous aluminosilicate gel, anhydrous sodium aluminate was dissolved into sodium hydroxide solution and heated under rigorous stirring. Colloidal silica 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  $100^\circ\text{C}$  in the oven to crystallize the zeolite. The crystalline zeolite was recovered by filtration, washed with distilled water until  $\text{pH} < 10$  and then dried overnight in the oven at  $105^\circ\text{C}$ . Before characterization, the zeolite was kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate.

### Cation exchange procedure

Synthesized zeolite (Na-SZ18) with a structural framework having Si/Al ratio of 1.53 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  $\text{LiNO}_3$  solution to obtain exchanged zeolite (LiNa-SZ18). The suspension was heated at  $80^\circ\text{C}$  for 5 hours. The exchanged zeolite was filtered, dried in the oven at  $105^\circ\text{C}$  for 12 hours, kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate. The same procedure was repeated with other cations namely rubidium, magnesium, calcium, manganese and nickel to produce exchanged zeolites which are designated as RbNa-SZ18, MgNa-SZ18, CaNa-SZ18, MnNa-SZ18, and NiNa-SZ18 respectively.

### Zeolite characterization

X-ray diffraction of zeolite samples were characterized by X-ray Diffractometer (Bruker). The patterns were recorded using  $\text{CuK}\alpha_1$  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  $0.05^\circ$  per second. The XRD results allow us to determine the sample crystallinity, unit cell parameters, and Si/Al ratio. 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.

## Results and Discussions

### Structural and physical properties

Results obtained shows that there are some changes on structural and physical properties of zeolites after cation exchanged treatment. As revealed in Figure 1, the exchange of sodium cation with metal cations of larger ionic size ( $\text{Rb}^+$  and  $\text{Ca}^{2+}$ ) results in some changes to the structural framework. The peaks are either disappeared or lower in intensities, and shift to lower angle of the spectrum. On contrary, exchanging sodium with lithium, and other transition metal ions having smaller cationic size than sodium ion results in increasing the intensities of the respective peaks. Most of the peaks shift towards higher angle indicates the shrinkages of the unit cell. Thus, it could be assumed that the extent of changes depends on the size of the cation. The bigger size cation results more changes to the zeolite samples.

Further evaluation on XRD data revealed that there are some changes to the unit cell parameter and Si/Al ratio. It is found that Si/Al ratio of LiNa-SZ18 and MnNa-SZ18 increase after cation exchange treatment. This indicates the release of Al from the zeolite framework occurred during cation exchange treatment. However, the unit cell parameter changes due to cation exchange treatment are relatively small. Based on peak intensities, it was also found that the relative crystallinity of metal exchanged zeolites experiences some changes. The intensities of LiNa-SZ18 and NiNa-SZ18 increase exceeding the based zeolite. However, others experience a decrease in relative crystallinity (Table 1).

However, the XRD spectra (Figure 1) proved that the structures were not completely collapse or formed amorphous phase. The shifted or the absence of peaks only indicates that the crystalline structures experience some degree of defects or crystalline imperfection. It could be associated to the size of cation which is larger than sodium ion, thus alters the lattice of the respective exchanged zeolite. However, our observations also reveal that exchanging sodium ions with  $\text{Li}^+$  (Group IA) and  $\text{Mg}^{2+}$  (Group IIA) ions results in some improvement on the total surface area of exchanged zeolites.

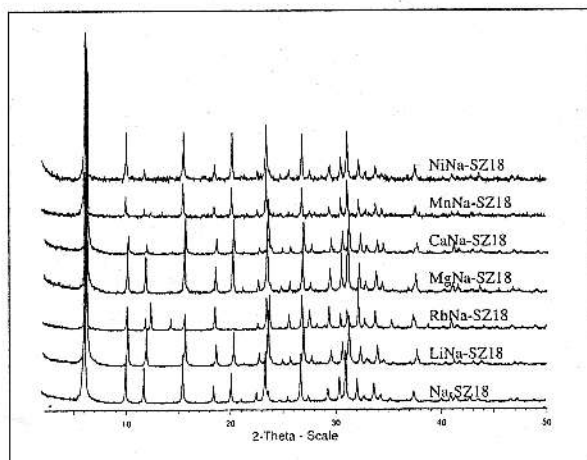


Figure 1: XRD patterns of metal exchanged zeolites.

In overall, the structural changes in zeolites are quite complex. Although sodium can be easily replaced from the zeolite framework by cation exchange method, our results show that the size and type of cation replacing sodium ion affect the crystallinity and the porosity of the structure. In principle, exchanging sodium with divalent cations results in two sodium cations being replaced from the extra-framework. Hence, the pore opening would become larger with the presence of the divalent cations. However, as the atomic number of increases, so does the cationic radius, and

again the surface area and pore volume decreases. In addition, the location of the cation in the structural framework may or may not influence the adsorbate to diffuse into the interior cages. These might explain the reason why the RbNa-SZ18 experiences a great loss in term of surface area and pore volume. However, the destruction of zeolite structure may not solely due replacement of cations. The experimental condition may also contribute to the destruction on zeolite structure, and thus the microporosity the zeolites. However, with appropriate selection of cation and controlled experimental condition, the properties of adsorbent could be improved.

Table 1: Structural properties of metal exchanged zeolites.

Zeolite	Cell parameter (Å)	Si/Al ratio	Relative crystallinity (%)
Na-SZ18	24.85	1.5	100
LiNa-SZ18	24.75	2.0	106
RbNa-SZ18	24.88	1.6	52
MgCa-SZ18	24.85	1.5	100
CaNa-SZ18	24.85	1.5	72
MnNa-SZ18	24.75	2.0	71
NiNa-SZ18	24.85	1.5	101

Table 2: Physical properties of metal exchanged zeolites.

Zeolite	BET Surface area ( $\text{m}^2/\text{g}$ )	Micropore volume ( $\text{cm}^3/\text{g}$ )	Average pore diam. ( $\text{cm}^3/\text{g}$ )
Na-SZ18	813.6	0.299	1.78
LiNa-SZ18	894.8	0.301	1.80
RbNa-SZ18	569.8	0.215	1.51
MgNa-SZ18	845.9	0.313	1.80
CaNa-SZ18	821.5	0.303	1.80
MnNa-SZ18	710.0	0.267	1.86
NiNa-SZ18	574.9	0.210	2.12

### Gas adsorption

As discussed earlier, the presence of cation by means of cation exchange method causes some changes to the structure and physicochemical properties of the zeolites. When  $\text{Na}^+$  ions were exchanged with the cations, new physical and chemical environment within the structural framework such as electrostatic potentials, electric field within the cage, as well as the vacant space available for the

adsorbate molecule within the supercage would change accordingly depending on the exchanged cations. As shown in Figure 2, by exchanging  $\text{Na}^+$  with  $\text{Li}^+$  results in high methane adsorption capacity. Higher adsorption capacity was also observed for  $\text{MgNa-SZ18}$ ,  $\text{MnNa-SZ18}$ , and  $\text{NiNa-SZ18}$ . However, the adsorption capacity of  $\text{RbNa-SZ18}$  and  $\text{CaNa-SZ18}$  is lower than the based zeolite ( $\text{Na-SZ18}$ ). In both cases, the introduction of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  improves the adsorption capacity of methane. Both exchanged zeolites have higher surface area than the based zeolite. However, our results on  $\text{MnNa-SZ18}$  and  $\text{NiNa-SZ18}$  show that the surface area and pore volume are not the only determining factor for high adsorption capacity of non-polar molecules such as methane. Even though the surface area and pore volume of  $\text{MnNa-SZ18}$  and  $\text{NiNa-SZ18}$  are relatively lower than  $\text{Na-SZ18}$  (based zeolite), but their adsorption capacity are higher than the based zeolite. Hence, apart from surface area and pore volume, there are other factors that could influence the adsorption capacity of zeolites. In this case, the presence of those cations could be the reason for higher adsorption capacity.

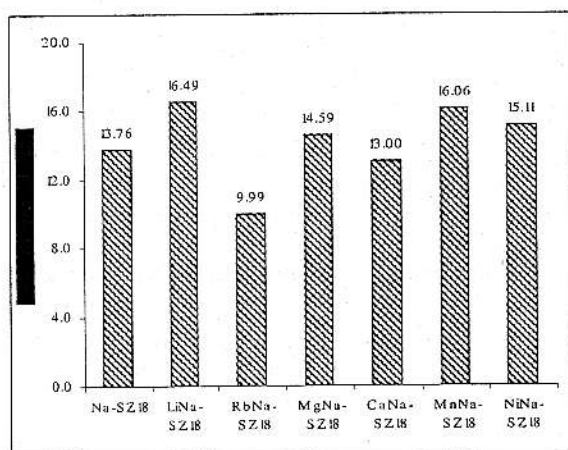


Figure 2: Methane adsorption capacity at 323 K and 137 kPa.

The adsorption behavior of metal exchanged zeolites was further investigated in term of gas diffusion and adsorption rate. As reported by Yeh and Yang [6], diffusion in metal exchanged zeolites has been the subject of many discussions since it might involve blocked pores and covered adsorption sites. However, the used of faujasite type zeolite ( $\text{Na-SZ18}$ ) could reduce the possibility of pore blocking since the pore opening of this type of zeolite is large enough to avoid any blockage to occur. Thus, the presence of larger cation such as  $\text{Rb}^+$  would not significantly affect the diffusivities of the adsorbate molecules since the kinetic diameter of methane (3.8 Å) is smaller than the typical pore opening of faujasite type zeolites (7.4 Å).

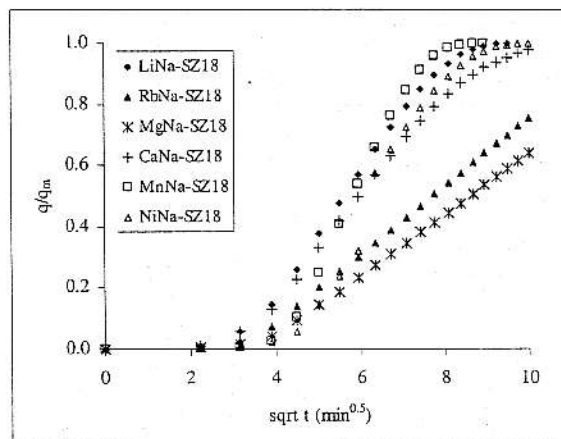


Figure 3: Fractional uptake curve of methane on metal exchanged zeolites.

#### Diffusional time constant

Based on the data obtained from fractional uptake curve and the assumption that adsorption occurred on isothermal single-component and solely controlled by micropore diffusion, the diffusional time constant could be determined. Diffusional time constants ( $D/r^2$ ) of methane at 137 kPa and 323K are shown in Table 3. According to Olson et al. [7], diffusional time constant does not depend only on temperature but also the physical and chemical properties of adsorbates. In addition, high apparent time constants are due to the strong interaction affinity between adsorbates and adsorbent [8]. The results show that the presence of cation affects the diffusional time constant ( $D/r^2$ ), and in several metal exchanged zeolites, the values are higher than the based zeolite ( $\text{Na-SZ18}$ ). In this study, the adsorption methane were carried out at constant temperature and pressure, therefore it is important to recognized that the diffusional constants do not solely provide evidence for the effect of the single parameter, but it is rather the combination of several parameters such as structural, physical and chemical properties of adsorbents, and adsorbates.

Table 3: Diffusional time constant of methane at 323 K and 137 kPa.

Zeolite	Diffusional time constant, $D/r^2 \times 10^5$ (sec <sup>-1</sup> )
Na-SZ18	4.01
LiNa-SZ18	6.80
RbNa-SZ18	2.31
MgNa-SZ18	1.84
CaNa-SZ18	5.27
MnNa-SZ18	13.52
NiNa-SZ1	6.31



### Initial adsorption rate

Initial adsorption rate of gases was determined from the dynamic experimental data in order to understand the kinetics of gas adsorption of different metal cation exchanged zeolites (Table 4). Large pore opening and pore volume might be the reason for high initial adsorption rate of methane. Again, this result provides further evidence on the effect of cation on methane adsorption capacity of MnNa-SZ18. Even though the sample has relatively lower crystallinity and surface area than the based zeolite, the result shows that the initial adsorption rate is relatively higher than the based zeolite. Hence, this result also indicates that presence of cation could enhance the adsorptive properties of the adsorbents even though the structural properties of the adsorbent itself decreases.

**Table 4: Initial adsorption rate of metal exchanged zeolites.**

Zeolite	Initial adsorption rate $\times 10^6$ (mmol/sec)
Na-SZ18	3.57
LiNa-SZ18	5.35
RbNa-SZ18	1.48
MgNa-SZ18	1.93
CaNa-SZ18	3.31
MnNa-SZ18	5.86
NiNa-SZ1	4.40

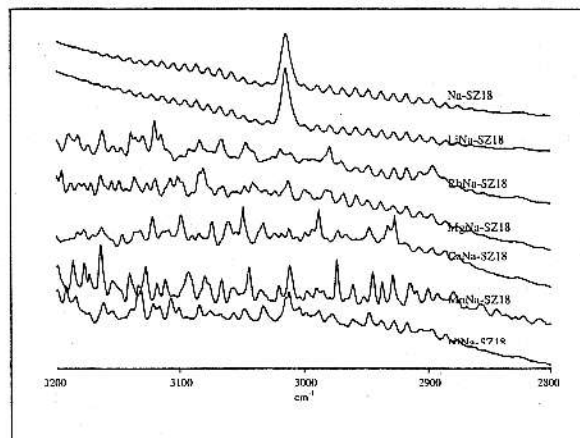
### Gas-zeolite interaction

In order to elucidate the effect of different cations on methane zeolite interaction, the FTIR measurements were carried out using Na-SZ18 as a based zeolite. Although unique identification of the adsorption spectra is difficult to performed, some peaks could attribute to specific bonds resulting from the adsorbate and adsorbent interactions. FTIR spectra of methane adsorbed on zeolites could be observed in the region between 3200 – 1200  $\text{cm}^{-1}$ . Two peaks appeared in the region around 3020  $\text{cm}^{-1}$  and 1306  $\text{cm}^{-1}$  that assigned to asymmetric band ( $\nu_3$ ) and symmetric band ( $\nu_4$ ) respectively [9].

According to Yamazaki et al. [10], a peak around 3015  $\text{cm}^{-1}$  ( $\nu_3$  band) is a result of free rotation of the adsorbed molecules around a single axis normal to the adsorbent surface. Figure 4 shows that a sharp peak ( $\nu_3$  band) is clearly visible as methane interacts with LiNa-SZ18 zeolite. However, for other zeolite samples,  $\nu_3$  band is shifting, decreasing intensity and having low intensity peaks on the both side of the  $\nu_3$  band. This is probably due the presence of more than one cation in zeolites after the cation exchange treatment that results in the existence of non-symmetrical electrostatic field of different strengths. In other words,

surface heterogeneity could be the reason for the presence of several peaks in the region around 3015  $\text{cm}^{-1}$ .

Another peak around 1300  $\text{cm}^{-1}$  that is assigned to  $\nu_4$  band is clearly visible in all metal exchanged zeolites (Figures 5). The spectra indicate that the presence of larger cation size results in broader peak with relatively less intensity. In addition, the presence of  $\text{Mn}^{2+}$  ions results the peak splitting into two. This might be due to the fact that when the cation exchange takes place, the electrostatic field of the zeolite surface changes according to the properties of the exchanged cation. However, as reported by Barbosa et al. [11], the difference in structural position could also affect on the extent of interaction between metal cation present and the adsorbate. The location of cation in the structural framework would determine the extent of exposure of the cation to adsorbate. Thus, it also explains the reason of different intensities and peak areas for different type of cation exchanged zeolites.



**Figure 4: FTIR spectra ( $\nu_3$ ) of methane adsorbed on metal exchanged zeolites.**

In addition, the frequencies of the bands shift to lower frequency resulted from methane interaction with the cations. It was also found that the peak of the divalent cation exchanged zeolites shift more than the monovalent cation exchanged zeolites. The larger shift due to strong interaction between the cation and the adsorbate. However, the peak areas also represent relatively the amount of methane adsorbed to the adsorption sites. A large quantity of  $\text{Li}^+$  cations that act as adsorption sites might be the reason for the large peak area obtained around  $\nu_3$  band. On the other hand, even though the quantity of divalent cation might be low, it could attract more adsorbates than monovalent cation due to larger electrostatic field gradient. Hence, the concentration of adsorbates would be higher at the

adsorption sites. Both conditions would result in larger peak areas.

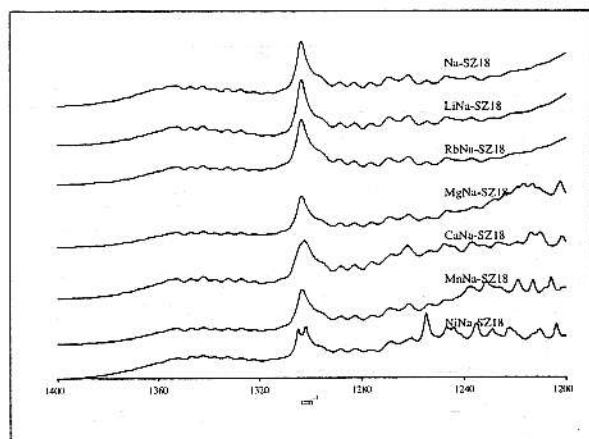


Figure 5: FTIR spectra ( $\nu_4$ ) of methane adsorbed on metal exchanged zeolites.

## Conclusions

This study shows that the presence of different cation changes the structural and physical properties of zeolites. After cation exchange, the presence of faujasite structure could be the basis for reasonably high adsorption capacity for the modified samples. In addition, it also proved that surface area is not the only determining factor controlling methane adsorption. In fact, the presence of cation could also influence the adsorptive characteristics of zeolite adsorbent. Hence, this study shows that the selection of metal cation is crucial in engineering the suitable adsorbent for gas adsorption system.

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