

METHANE ADSORPTION CHARACTERISTIC DEPENDENCY ON ZEOLITE STRUCTURES AND PROPERTIES*

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ABSTRACT

Adsorption of methane on zeolites constitutes a new area of research since it has industrial importance in process industries such as natural gas purification and adsorptive natural gas storage. In this study, the dependency of methane adsorption characteristics on zeolite structure and properties was investigated. Zeolite framework was modified by cation exchange with different alkali metals. The incorporation of metal cations into zeolite structures changes their physicochemical properties. The adsorptive behaviour of methane on zeolites was investigated at low pressures and it was found that structures and properties play important role in the adsorption of methane. Study results reveal that barium-exchanged zeolite demonstrates a high methane adsorption.

Keywords: Zeolite; structure; properties; cation exchange; adsorption; methane.

1.0 INTRODUCTION

Zeolites are potential adsorbent due to the ability of their microporous structures to adsorb molecules at relatively low pressure. They have been used extensively in industries as adsorbent for separating gases such as CH₄, NH₃, H₂S, and CO₂. Studies on methane adsorption for various molecular sieves has been carried out by Haq and Ruthven (1986a, 1986b), Yucel and Ruthven (1980), and Tezel and Apolonatos (1993). However, adsorptive capability of zeolites for non-polar molecules such as methane is not clearly explained. Their studies do not include identification of important attributes of adsorption for non-polar molecules on zeolites.

Generally, adsorption of gases on zeolites is mainly determined by two main factors, structure and physicochemical properties of adsorbent. The pore size which depends on the structure of zeolite, determines the accessibility of gas molecules into the zeolite framework. However, in certain cases it can adapt the aperture upon adsorption because of the flexibility of the framework. The degree of flexibility is a function of the framework structures in the presence of extra-framework cations and molecules (Coker *et al.*, 1998). The availability of internal space volume is another interesting characteristic of zeolites for separation/purification applications.

The selectivity and capacity of adsorption is also being influenced by the adsorbate-adsorbent interactions. This is closely related to the adsorbent chemical composition where different cationic forms of zeolites lead a significant difference in the adsorption of gases. With the presence of cations, the molecules interact through dispersion, induction, field-quadrupole and repulsion forces. It was found that the major difference between the interactions of N₂-Ca²⁺ and N₂-Na⁺ is field-quadrupole interactions. This is due to the specific interactions of the quadrupole with the electric field created by cations. Other interactions are of similar magnitude (Choudary *et al.*, 1994).

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Information on the effect of physical properties such as the type of framework structure, pore volume, pore size distribution as well as chemical properties of adsorbent (electrostatic force of cations, hydrophobicity and acidity) are both important in tailoring the effective adsorbent. This paper will describe the effects of zeolite structural parameters namely type of framework, surface area, average pore size and pore volume on methane adsorption which were obtained by zeolite structural synthesis and modifications.

2.0 EXPERIMENTAL PROCEDURE

2.1 Synthesis

Sodium forms of zeolite X (Y) were synthesized in the laboratory using reactant mixture with a molar composition of $6.4\text{Na}_2\text{O} : 1\text{Al}_2\text{O}_3 : x\text{SiO}_2 : 180\text{H}_2\text{O}$ and the hydrothermal process was carried out in a temperature range of $100 - 200^\circ\text{C}$ at different crystallization time (24 hours – 30 days). In preparing gel composition, anhydrous sodium aluminate (Riedel-de Haën) was dissolved into sodium hydroxide (MERCK) solution and heated under rigorous stirring. Ludox 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. Then, the mixture was transferred into a container (polyethylene bottle or Teflon lined autoclave) and heated in an oven at different temperatures and times for crystallization. After that, the solids were recovered by filtration, washed with distilled water until pH <10 and then dried overnight in the oven at 100°C .

2.2 Modification

Sodium forms of zeolite X were cation exchanged with alkali metal by adding 5g of zeolite into a polyethylene bottle containing 250 mL of 0.5 M lithium nitrate solution. The slurries were stirred at 80°C for 5 hours in a temperature controlled water bath. The product was filtered, rinsed with distilled water, dried and kept equilibrated under constant humidity in a desiccators filled with saturated ammonium nitrate. The same procedure was repeated with other cations (KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and $\text{Ba}(\text{NO}_3)_2$).

The modified and as-synthesized samples were characterized by X-ray diffractometer (Bruker) with $\text{CuK}\alpha_1$ 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° per second. Adsorption analysis was carried out on both modified and as-synthesized zeolites using gravimetric adsorption analyzer (Micromeritics ASAP 2000). The nitrogen adsorption measurement was carried out at 77K to determine the surface area, pore volume, average pore diameter and adsorption isotherm of each sample. Methane adsorption was also carried out using the same equipment at 27°C and 1 atm to obtain adsorption isotherms. Molecular simulation on the adsorption of methane on metal-exchanged zeolites was carried out using Cerius2, MatSci. (Ver. 4.2, Accelrys Inc.).

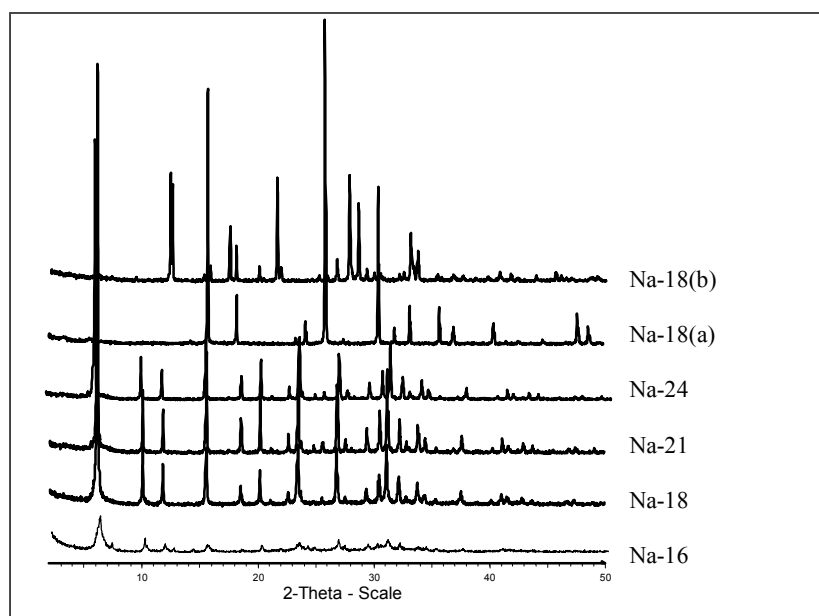
3.0 RESULTS AND DISCUSSION

As reported in literature, methane adsorption capacity on zeolite is structural dependence. The syntheses were successfully carried out under different experimental conditions to obtain different framework structures (Table 1). At 100°C , zeolite X and Y were formed, but at 200°C another phase (analcime) with similar composition was obtained. Faujasite framework transformed into gismondine as the time was extended from 24 hours to 30 days. These results show that crystallization temperature and time influence types of zeolite formed. This is due to the occurrence of successive phase transformation (Oswald's Rule) where the thermodynamically least favorable phase will crystallize first, and will be successfully replaced by more stable phases.

Table 1: Zeolite synthesis parameters and results of crystallization

Sample	SiO ₂ /Al ₂ O ₃ ratio	Crystallization temperature (°C)	Crystallization time	Phase
Na-16	4	100	24 hours	Zeolite X
Na-18	8	100	24 hours	Zeolite X
Na-21	12	100	24 hours	Zeolite Y
Na-24	20	100	24 hours	Zeolite Y
Na-18(a)	8	200	24 hours	Analcime
Na-18(b)	8	100	30 days	Gismondine

The XRD patterns of synthesized zeolites are shown in Figure 1. The crystallinity of zeolite X and Y were compared using selected peak in XRD patterns. Synthesized zeolites with different crystallinity have different physical properties (Table 2). It was found that Na-21 with the highest crystallinity has the highest surface area, pore volume but it has the lowest average pore diameter.

**Figure 1:** XRD patterns of synthesized and modified zeolites.

XRD patterns of modified zeolites are nearly the same as those of the as-synthesized crystal (Figure 2). The crystalline phases still visible but the crystallinity decreases except for lithium-exchanged zeolite. The changes are due to the size, charge, and locations of cations that lead to a rearrangement of other ions in the zeolite structure. Table 2 summarizes the properties of different zeolites. The surface area of exchanged zeolites decreases as the ionic radius of cation increases for alkali metal Group I. But for alkaline earth metal (Group II), the surface areas are relatively high even though the ionic radius of Mg²⁺ and Ca²⁺ is larger than Na⁺. This is due to the number of cations group II replacing the sodium ions in zeolite structure is less than group I that provide more space within the pore structure.

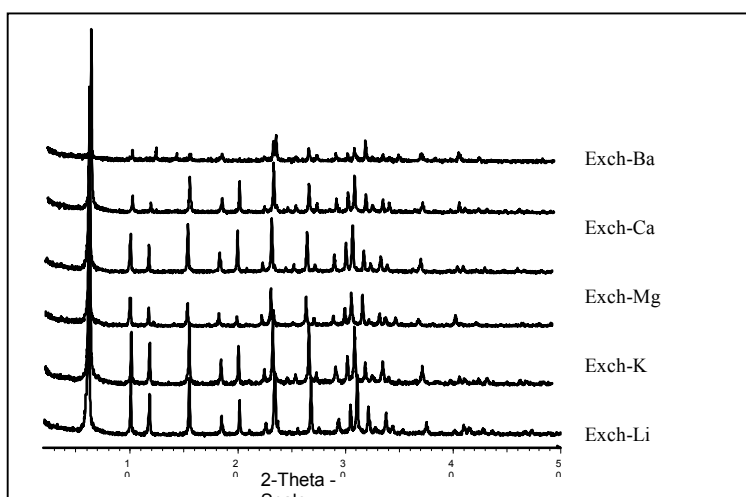


Figure 2: XRD patterns of synthesized and modified zeolites.

Table 2: Physical properties of zeolites.

Zeolite Sample	Surface area, m ² /g (Langmuir)	Pore volume, cm ³ /g	Average diameter, Å	Unit cell parameter, Å
Na-16	583.4	0.1975	29.68	24.961
Na-18	839.4	0.2996	17.75	24.863
Na-21	913.2	0.3311	15.08	24.830
Na-24	573.0	0.1997	33.65	24.780
Na-18(a)	not available	not available	not available	not calculated
Na-18(b)	16.8	0.0033	77.40	not calculated
Li- exchanged Na-18	922.9	0.3297	18.05	24.747
K-exchanged Na-18	740.9	0.2646	18.16	24.951
Mg-exchanged Na-18	871.7	0.3126	17.98	24.866
Ca-exchanged Na-18	848.2	0.3032	18.04	24.872
Ba-exchanged -18	571.2	0.2055	18.58	24.885

The amount of methane adsorbed also varies with different structures and properties of zeolite materials. Figure 3 shows the effect of faujasite structure with different pore volume, average pore diameter, and surface area on methane. Na-21 having higher pore volume and surface area but smaller average pore diameter, adsorbed more methane than other zeolite samples.

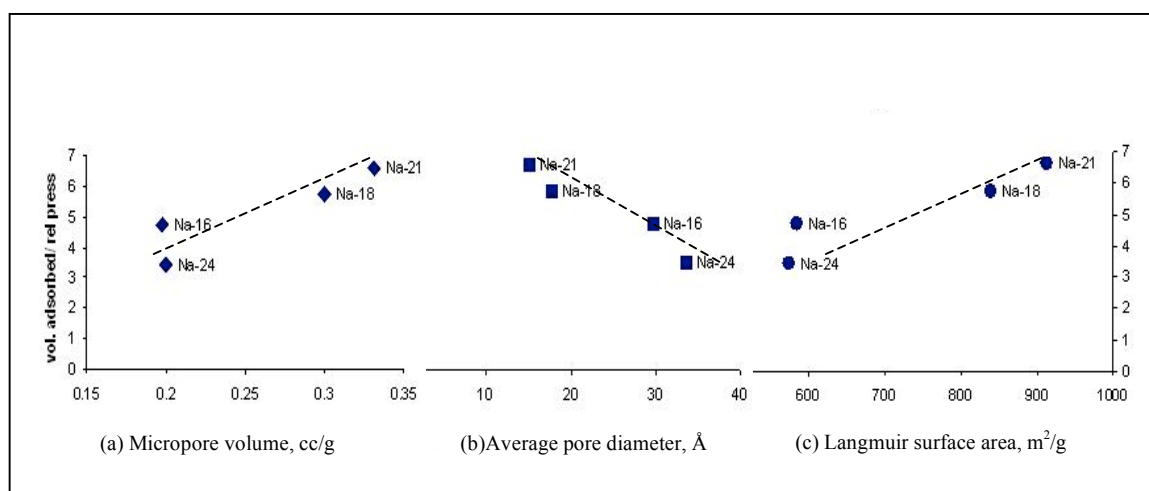


Figure 3: The effect of physical properties of zeolite on methane adsorption.

In addition to zeolite structures, cations also play an important role in the adsorption of methane. By carrying out cation exchange procedure, sodium ions were replaced by different types of metal ion. Figure 4 shows the effect of cation exchange on methane adsorptivity. Even though quantitative amount of cations replacing sodium is not yet determined, zeolite sample (Na-18) that was exchanged with several types of cation show some variations in properties and methane adsorptions. It was found that Na-18 adsorbed $4.305 \text{ cm}^3/\text{g}$ (STP) of methane. However, when cation exchanged was carried out, the amount of methane adsorbed increases to $10.58 \text{ cm}^3/\text{g}$ (STP). For alkali metals Group I and II, adsorption increases as the atomic number of metal increased (Ba-18 and K-18). But in general, alkali metals Group II adsorbed more than Group I. The dashed and solid lines represent the effect of cations from top to bottom and from left to right of the Periodic Tables (Figure 4). Evidently, this shows that for non-polar molecules such as methane, the adsorption characteristic is not of the same pattern as those with polar molecule (N_2) (Kamarudin *et al.*, 2003).

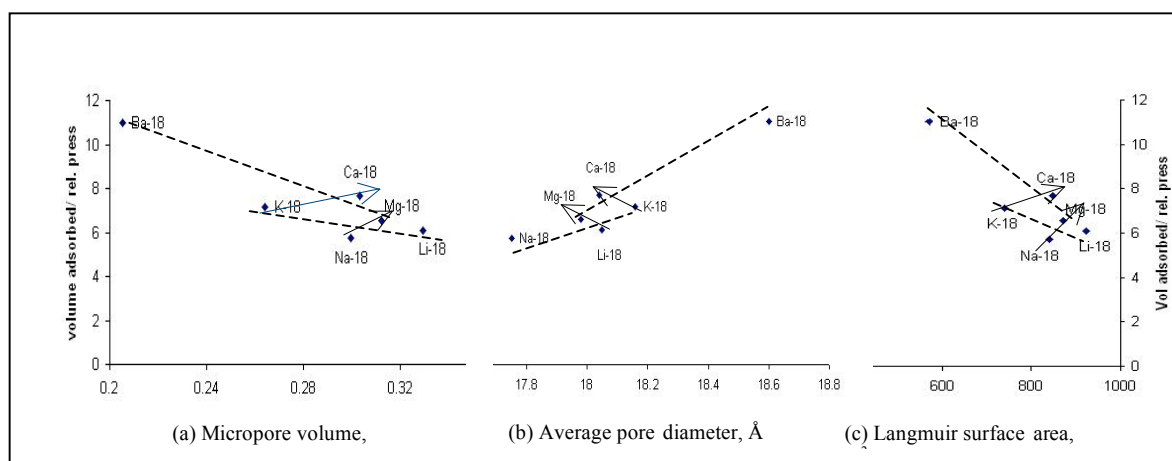


Figure 4: The effect of cations on methane adsorption.

As shown in Figure 4, barium-exchanged zeolite adsorbed more methane than magnesium-exchanged zeolite even though the surface area and micropore volume of barium-exchanged zeolite is lower. At low pressure, the charge and size of cations have stronger influence than the surface area and micropore volume of zeolites. Molecular simulations also prove that by exchanging sodium with other cations, the amount of methane adsorbed increased even though the results are not the same pattern as the experimental results. Table 3 shows results of exchanging 80 % of sodium with different cations, where the amount of methane adsorbed into exchanged-FAU are higher than Na-FAU zeolite. The presence of other cations increased the electrostatic field within the zeolite cavities. This may influence the amount of methane adsorbed onto zeolite surface.

Table 3: Quantitative amount of methane adsorbed on different cation exchanged zeolites

Cations in faujasite structure	Methane adsorbed @ 1 atm , 300K (cm ³ /g)
Na-FAU	11.1
Na-Li-FAU	15.38
Na-Ca-FAU	17.78
Na-Ba-FAU	14.44

CONCLUSION

Structure and physicochemical properties of zeolites influence methane adsorption. In term of structure, zeolite X and Y with faujasite structure have pore openings that permit the diffusion of methane. With open cage type framework, zeolite X and Y are more capable to adsorb methane than gismondine and analcime. Furthermore, the pore volume and surface area are increased by exchanging zeolite with lithium and decreased when exchanged with barium. But, barium-exchanged zeolite adsorbed more methane than other metal-exchanged zeolites. The results suggest that framework structure and type of cation not only affect the physical properties of zeolites but it also affect the adsorption capacity of methane. This implies that methane adsorption characteristics depend on zeolite structures and properties.

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REFERENCES

- Choudary N. V., Jasra R. V., Bhat S. G. T., “*Adsorption of binary mixture of N₂, O₂, and Ar in zeolite NaCaX*” in Weikamp J., Karge H. G., Pfeifer H., Holderich W. (Eds.), *Zeolites and Related Microporous Materials: State of Art. Studies in Surface Science and Catalysis. Vol.84*, Elsevier Science (1994).
- Coker E. N., Roelofsen D. P., Barrer R. M, Jansen J. C., Van Bekkum H., “*Sorption of bulky aromatic molecules in to zeolite NaX*” *Microporous and Mesoporous Materials* 22, 261 – 268 (1998).
- Haq N. and Ruthven D. M., “*Chromatographic study of sorption and diffusion in 4A zeolite*” *J Colloid Interface Science* 112 (1) 154 – 163 (1986a).
- Haq N. and Ruthven D. M., “*Chromatographic study of sorption and diffusion in 5A zeolite*” *J Colloid Interface Science* 112 (1) 164 – 169 (1986b).
- Kamarudin K. S., Hamdan H., Mat H., *Unpublished data* (2003).
- Tezel F. H. and Apolonatos G., “*Chromatography study of adsorption for N₂, CO, and CH₄ in molecular sieve zeolites*” *Gas Separation Purification* 7(1) 11 – 17 (1993).
- Yucel H. and Ruthven D. M., “*Diffusion in 4A zeolite: study of the effect of crystal size*” *J C S Faraday I* 76, 60 -70 (1980).