GAS ADSORPTION PHENOMENON IN MICROPOROUS ZEOLITE ADSORBENT

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ABSTRACT

Gas adsorption on zeolites gains remarkable attention in this new era of nanotechnology since it has industrial importance in many process industries. Efforts of chemists during the past few decades have advanced the field of synthesis and accelerated the development of zeolites with different physicochemical properties for specific application. New technologies involving gas separation, gas purification, gas storage, high temperature gas sensor, semiconductor material hold a great promise for industrial applications. In order to develop and design an efficient and economically feasible industrial adsorption process, it is important to understand the adsorption phenomena between solid and gas phases. The presence of metal cations in the extra-framework structure determines the accessibility of gas molecules into the zeolite framework. In addition, the selectivity and capacity of adsorption is also being influenced by the adsorbate-adsorbent interactions. The molecules may interact through dispersion, induction, field-quadrapole and/or repulsion forces. Hence, information on physicochemical properties of zeolites as well as the properties of adsorbent is equally important in order to understand gas adsorption phenomena in zeolite microstructures. Results of this study show that structural properties and adsorbate-adsorbent interactions affect gas adsorptive characteristics of zeolites.

Keywords: Zeolite; adsorption; microporous; cation exchange; adsorbates.

1. Introduction

Adsorption is initially viewed as a process in which adsorptive molecules (adsorbates) are transferred to, and accumulated in the interfacial layer (Sing, 1984). The interfacial layer consists of two regions, the surface layer of solid (adsorbent) and the adsorption space where molecules accumulated as adsorbates (Figure 1). Even though adsorption could be either in liquid-gas, liquid-liquid, solid-liquid or solid-gas system, but major development of adsorption processes on a large scale deals mainly with solid-gas and solid-liquid systems (Dabrowski, 2001).

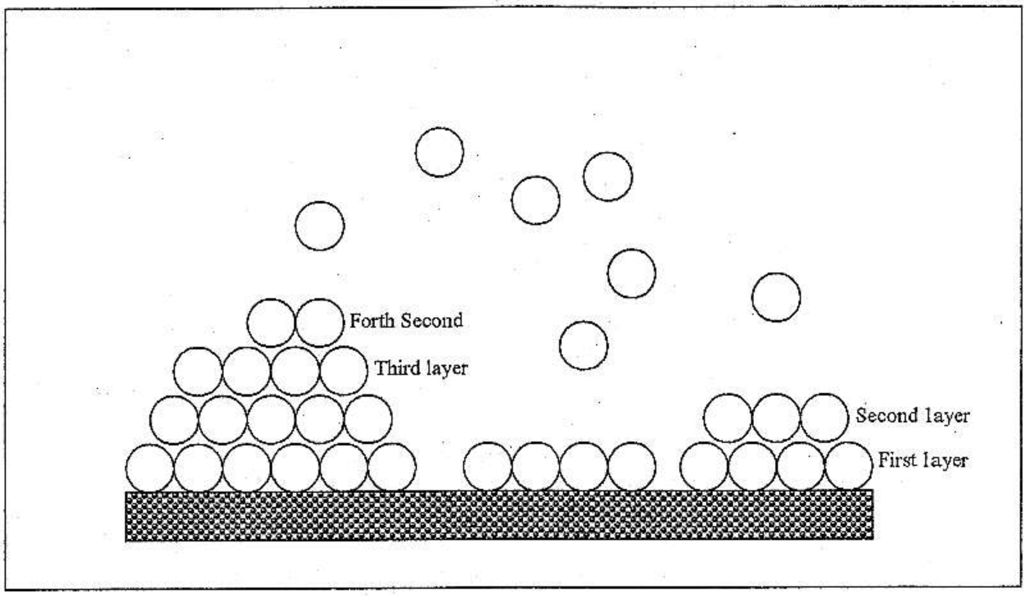

Figure 1: Schematic diagram of monolayer and multilayer adsorption.

The adsorption is generally governed by physical and chemical interactions that lead to either physical adsorption (physisorption) or chemical adsorption (chemisorption) respectively. Physical adsorption is very effective particularly at a temperature close to the critical temperature, whereas chemisorption usually occurs at much higher temperature, and can only take place on depending on types of solid surface and gas. Under favorable conditions, both processes can either occur simultaneously or alternately, and there is no sharp distinction between both mechanisms of adsorption since various intermediate cases might exist. The adsorption process is accompanied by a decrease in Gibbs free energy and entropy leading to dissipation of energy to surrounding (exothermic process) (Dabrowski, 2001).

Smith *et al.* (1996) reported that at relatively low pressure only few gas molecules are adsorbed, and only a fraction of the solid surface covered. As the gas pressure increases, surface coverage increases. When all sites become occupied, the adsorbed molecules are said to form a monolayer. Further increase in pressure promotes multilayer adsorption. It is also possible for multilayer adsorption to occur on certain sites of a porous surface while other sites still remain vacant. The exact nature of the adsorbate at the interface remains unclear, as whether the adsorbate remain as gas molecules with a very weak gas-solid interaction or condense on the solid surface in a liquid-like form.

Even though in gas adsorption phenomenon, surface area and pore volume of zeolite are fundamentally well-known controlling factors for adsorption, little has been known about the effect of other properties such as structural framework, pore size, solid surface properties and adsorbate properties on gas adsorption characteristics. Studies that have been carried out only produced fragmented data as some researchers only focused their studies on structural effect on gas adsorption (Kaushik *et al.*, 2002; Ackley *et al.*, 2003; Rigby *et al.*, 2004) and others highlighted the effect of adsorbates properties on gas adsorption characteristics (Tielens and Geerlings, 2001; Zhou *et al.*, 2002; Murata *et al.*, 2003; Yang, 2004).

For the successful application of zeolite as adsorbent, a thorough understanding of gas adsorption phenomena is required. Hence, the fundamental study of gas adsorption will be partly addressed in this paper with regard to the effect of structural framework and metal balancing cation on gas adsorption capacity. The interaction between adsorbates and solid surface was examined using Fourie Transform Infrared (FTIR) spectroscopy methods.

2. Materials and method

2.1 Materials

NaX (or 13X) and ZSM-5 in powder form were purchased from Zeolyst International. NaSZ-18 was synthesized using reactant mixture with molar composition of $6.4Na_2O$: $1Al_2O_3$: $12SiO_2$: $180H_2O$ (Kamarudin et al., 2004). Methane (99.99%) and carbon dioxide (99.999%) gases used for the adsorption study were obtained from Southern Industrial Gas Sdn. Bhd and used as received.

2.2 Experimental procedures

Gas adsorption measurements were carried out using thermogravimetric analyzer (Perkin Elmer, TGA7) at 323 K and 137 kPa. Initially, a sample was loaded on the sample pan and outgassed at 673K for 2 hours. The sample was then cooled and held at 323 K for adsorption to occur until it reached equilibrium. Adsorbed amounts are expressed as amount adsorbed (mmol) per unit mass (g) of an adsorbent.

Synthesized zeolite (NaSZ-18) with a Si/Al framework 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° C for 5 hours and the exchanged zeolite was filtered, dried in the oven at 105° C for 12 hours, and kept equilibrated under constant humidity in a desiccator filled with saturated ammonium nitrate. The same procedure was repeated for other cations namely lithium, magnesium, and manganese to produce metal cation exchanged zeolites which are designated as LiNaSZ-18, MgNaSZ-18, and MnNaSZ-18 respectively.

Gas-zeolite interaction was studied using the FTIR spectroscopy method. A thin self-supported wafer of each sample was prepared and outgassed (activated) in a dynamic vacuum (residual pressure < 10^{-3} mbar) for 2 hours at about 673 K placed inside the FTIR adsorption cell. The methane gas adsorbate was introduced into the adsorption cell and in-situ measurement was carried out to obtain the FTIR spectra of adsorbate-adsorbent interaction.

3. Result and discussions

3.1 Gas adsorption capacity

Zeolite frameworks contain pores, channels and cages of different dimensions and shapes. These properties may influence the amount of methane and carbon dioxide adsorb on zeolites. Adsorption capacity of samples at 137 kPa and 323 K was measured using thermogravimetric analyzer (TGA 07, Perkin Elmer). A comparison between cage-type (NaX) and channel-type (ZSM-5) structures show that cage-type structure (NaX) adsorbs more gas than the channel-type structure (Figure 2). Similar result was obtained for synthesized NaSZ-18 zeolite faujasite structure in which the supercages and sodalite cages provide bigger space for gas molecules to accumulate inside the pore (Table 1). The difference in the amount of methane and carbon dioxide adsorbed is also attributed to gas (adsorbate) structural orientation and its interaction with the solid surface.

Table 1: Physical properties of zeolites.

Zeolite	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
NaX(13X)	558	0.214	16.3
ZSM-5	364	0.151	23.1
SZNa-18	794	0.299	17.8

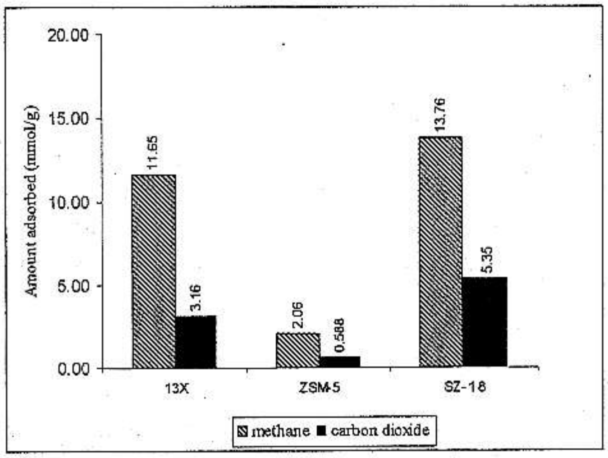

Figure 2: Gas adsorption capacity on different zeolites.

Using NaSZ-18 as a based zeolite, Na^+ ions were exchanged with different groups of cation. Again, gas adsorption capacity was determined at 323K and 137.8 kPa (20 psi). It was found that the presence of different cations in zeolite structure caused some changes to gas adsorption characteristics. The cations bring along with it a variation in a number of physical characteristics such as electrostatic potentials, electric field within the cage as well as the vacant space available for the guest within the supercage. The presence of cation with different charge and size affect the adsorptive capability of zeolite on methane and carbon dioxide since cation affect the diffusivity of gas molecules by pore blocking. However, different cation induces different bond strength between adsorbed molecule and adsorption sites. The amount of methane adsorbed on cation-exchanged zeolite increased, with different quantity. Nevertheless, carbon dioxide adsorption shows different phenomenon. The presence of magnesium ion increased the adsorptive capacity of zeolites but with the presence of lithium and manganese cations reduced the amount of carbon dioxide adsorbed. The difference is probably due to the interaction between gas molecules and the solid surface.

Thus, the cage-type zeolites (NaX and NaSz-18) proved to be a better adsorbent than channel-type zeolite. As the pore opening of the structure is twice the size of gas molecules, pore blockage is insignificant. Even though the gas molecules adsorbed at the pore opening, the other gas molecules can still diffuse through the pore window and adsorb on the inner surface of the cage. However, any deposition inside the channel-type zeolite ($pore_{ZSM-5} \approx 5.4$ Å) can affect the diffusivity and adsorptivity of gas molecules. In addition, the zig-zag channel may cause some problems as the adsorbed molecule can partially hinder the diffusion and adsorption of other molecules. The adsorption capacity of cage type zeolite can be further increased by exchanging sodium ion with other metal cations such as lithium or magnesium.

Table 2: Physical properties of metal exchanged zeolites.

Zeolite	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
NaSZ-18	794	0.300	17.8
LiNaSZ-18	874	0.330	18.1
MgNaSZ-18	829	0.313	18.0
MnNaSZ-18	694	0.267	16.5

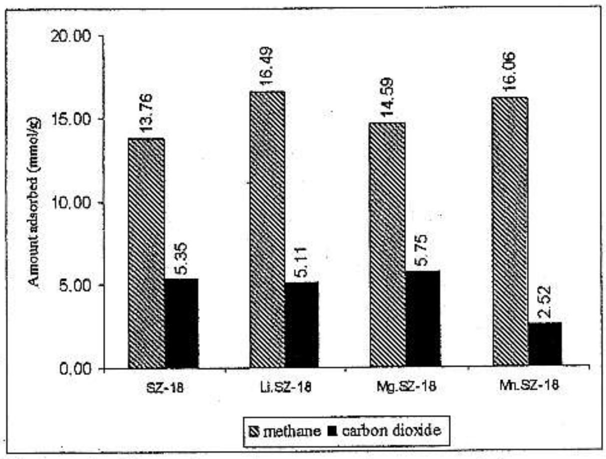

Figure 3: Gas adsorption capacity on metal exchanged zeolites.

This study also shows that different cations change the properties of zeolite and adsorptive characteristics of gas adsorption. The presence of lithium and magnesium cations increases the surface area of and pore volume of zeolites (Table 2) but the surface area and pore volume of manganese exchanged zeolite is reduced. Similar phenomenon was observed on the average pore diameter of cation exchanged zeolite. But the adsorption does not directly depend on the surface area and pore volume for both methane and carbon dioxide. Thus, the adsorption of gases also depends on the size and the charge of cations.

3.2 Gas – zeolite interactions

In gas adsorption, the number of molecules attracted to a solid surface depends on the extent of interaction between the gas (adsorbates) and the solid (adsorbent) which determine the mechanism of adsorption either monolayer, multilayer or volume filling in micropore space of porous material such as zeolites.

Figure 4 shows the FTIR spectra of CH_4 adsorbed on cage-type (NaX and NaSZ-18) and channel-type (ZSM-5) zeolites. A sharp band around 3000 cm^{-1} is assigned to the ν_3 (antisymmetric) of adsorbed methane. A weak band in the spectra around 2900 cm^{-1} is assigned to ν_1 (symmetric) band induced by interaction with the adsorption site. According to Yoshida et al. (2000), the band was very weak, and the integrated intensity ratio of ν_1 band to ν_3 was about 1/40. Another band at around 1300 cm^{-1} is assigned to the ν_4 bending mode of methane. Yang et al. (2001) have proposed in their study that the interaction between methane and the wall of zeolite structure is not based on the active sites but more likely due to the confinement effect. This explained the reason why peaks that assigned to ν_3 and ν_4 can only be observed in NaX and NaSZ-18 zeolites (cage-type structure) but no specific peak can be assigned to ZSM-5 spectra (Figure 4). The adsorption on ZSM-5 occurs at very low capacity, and the interaction between the surface and gas molecule is too weak to be detected in the FTIR spectra region.

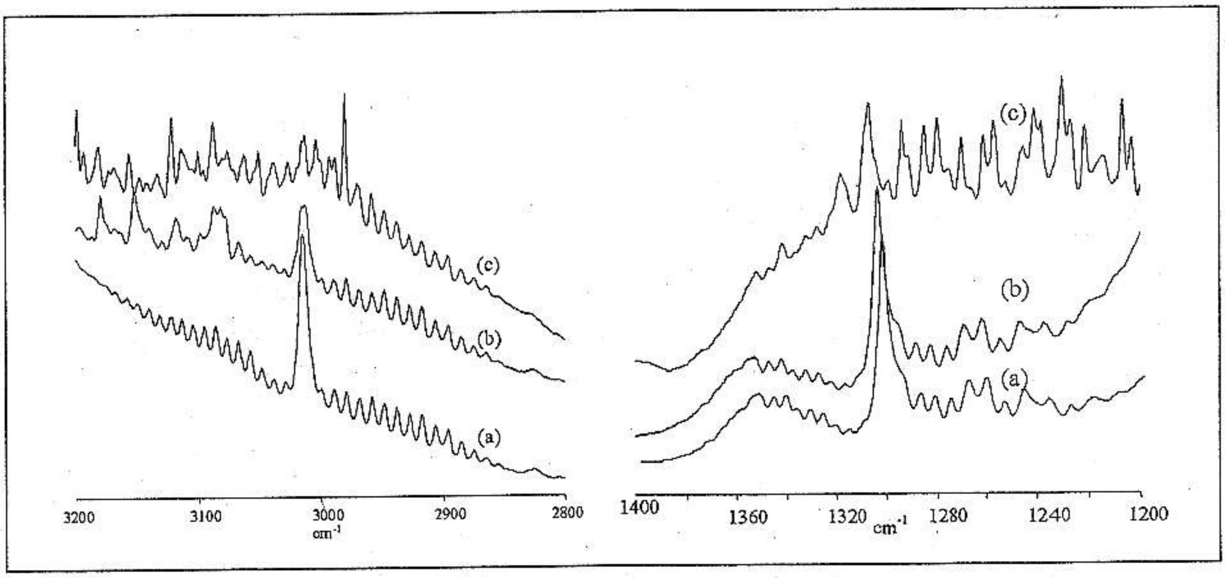

Figure 4: FTIR spectra of CH_4 adsorbed on different zeolites at 323 K and 137.8 kPa: (a) NaSZ-18, (b) NaX, and (c) ZSM-5.

The effects of cation on the adsorption of methane are further examined by exchanging Na^+ in SZ-18 with different types of cations namely Li^+, Mg^{2+} and Mn^{3+}. This study shows that the presence of different cations change methane-zeolite interactions and thus adsorption mechanism. Figure 5 shows that v_3 band that assigned to asymmetric stretching of methane can be detected in LiNaSZ-18 zeolites but the peaks cannot be clearly seen for MgNaSZ-18 and MnNaSZ-18. However, v_4 that is assigned to bending mode of methane can be detected in all samples. Therefore, the presence of peaks does not reflect the adsorptive capacity of zeolites but rather indicate the interaction between adsorbate-adsorbent at the active sites. The stronger the interaction, the higher the peak could be observed.

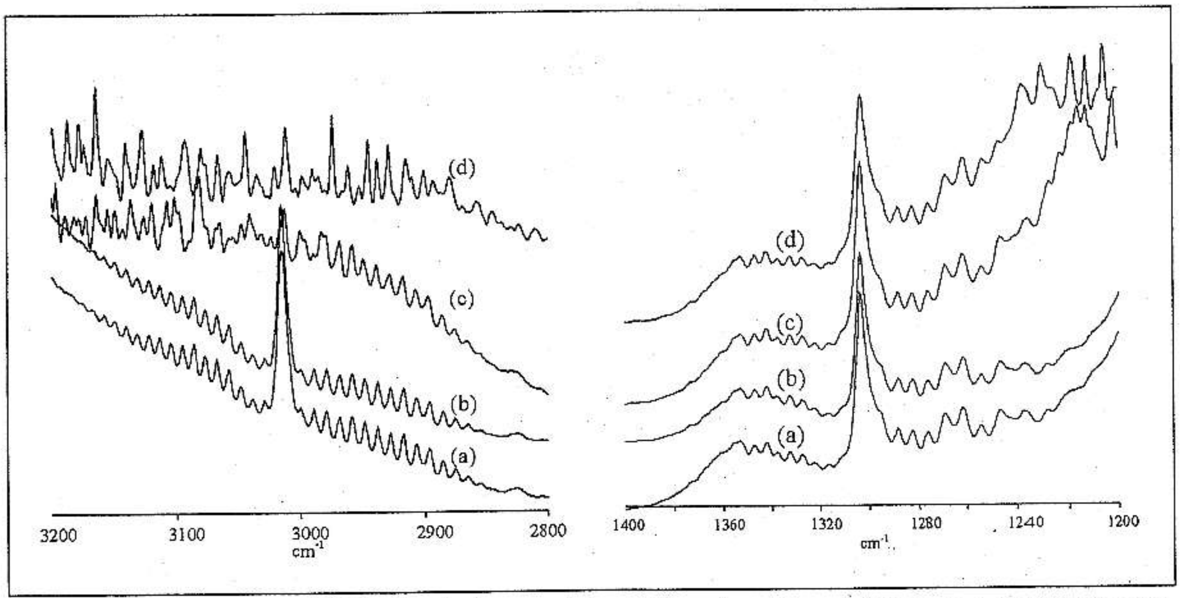

Figure 5: FTIR spectra of CH_4 adsorbed on metal exchanged zeolites at 323 K and 137.8 kPa: (a) NaSZ-18, (b) LiNaSZ-18, (c) MgNaSZ-18, and (d) MnNaSZ-18.

In the case of CO_2, as shown in Figures 6 and 7, peaks appear in two regions, 2350 – 2370 cm^{-1} and 1500 – 1700 cm^{-1}. Peak in a region of 2350 – 2370 cm^{-1} denotes ν_3 band, the physisorbed undissociated molecular CO_2 species. Another peak corresponding to chemisorbed species that appear in the region of 1500 – 1700 cm^{-1}. This is typically correspond to CO_2 molecules adsorbed either in linear configuration on cations (ν_2 band), or in non-linear (bent) manner in the form of carbonate or bicarbonate ions. These peaks are in accordance with previous observation by Rege and Yand (2001). Quadrapole moment caused strong interaction between CO_2 molecules and zeolite surfaces especially in the ν_3 band region. A weak band is visible in the region of 1500 – 1700 cm^{-1} for ZSM-5. This is due to the fact that the amount of cation exists in the ZSM-5 is less than NaX and NaSZ-18.

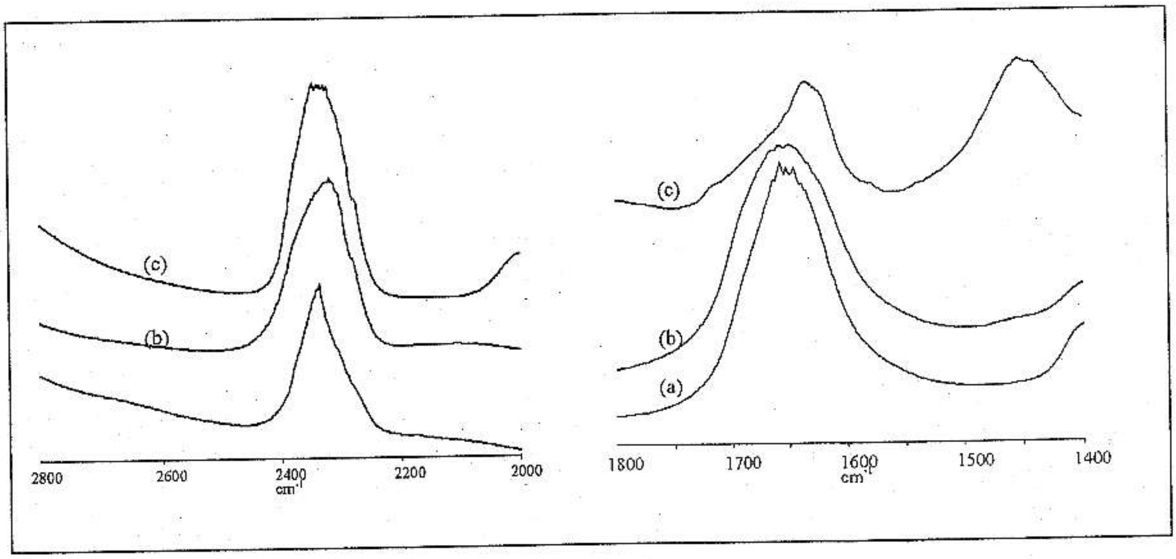

Figure 6: FTIR spectra of CO_2 adsorbed on different zeolites at 323 K and 137.8 kPa: (a) NaX, (b) NaSZ-18, and (c) ZSM-5.

Again, the role of cation could be observed from the FTIR spectra of metal cation-exchanged zeolites. Peaks can be observed in both region, but at different intensity. Strong affinity of Mg^{2+} could be observed through FTIR spectra especially in the region of 1500 – 1700 cm^{-1} that indicates the interaction of carbon dioxide molecules with the cation. Strong adsorptive centre and interaction of the cations with double bond that exists in carbon dioxide is likely to be the reason for strong adsorption.

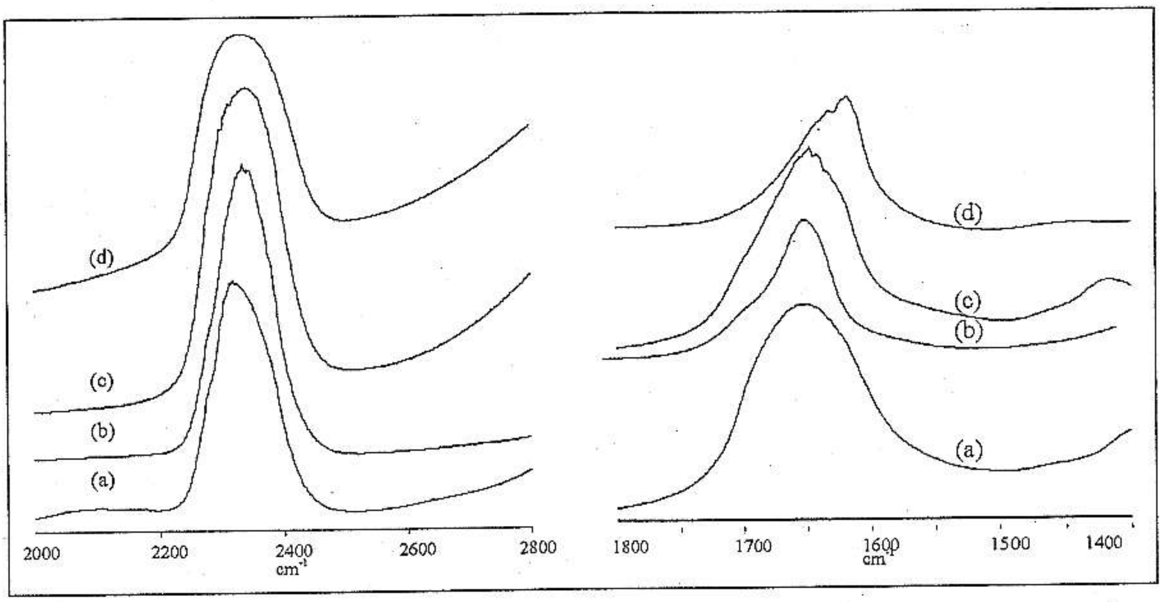

Figure 7: FTIR spectra of CO_2 adsorbed on metal exchanged zeolites adsorbed at 323 K and 137.8 kPa: (a) NaSZ-18, (b) LiNaSZ-18, (c) MgNaSZ-18, and (d) MnNaSZ-18.

In general, adsorption of CO_2 was affected by the interaction between the quadrapole moment of gas molecules and the electric field created by the structural cations in zeolites. Strong interactions between CO_2 and zeolites are clearly shown in the FTIR spectra especially in the region of 1500 – 1700 cm^{-1}. However, CH_4 is a non-polar molecule and has no specific interaction with zeolite surfaces. The adsorption mechanism of CH_4 might follow micropore filling theory in which the adsorption increases gradually until it reaches saturation.

4. Conclusions

This study shows that adsorptive capability of cage-type zeolite is better than channel type zeolite, and the presence of other metal cations could enhance the adsorption capacity of zeolite. In addition, the FTIR spectra indicate not only the amount of gas adsorbed but also the strength of interaction between adsorbed molecules and zeolites surface especially in the presence of different cations. This finding shows the fundamental importance of zeolite structure and gas properties on gas adsorption mechanisms in microporous materials.

Acknowlegment

The authors would like to acknowledge the financial support from Ministry of Science, Technology and Innovation (IRPA grant No. 74512), and the Universiti Teknologi Malaysia for the scholarship awarded to Khairul Sozana Nor binti Kamarudin.

References

Dabrowski A., (2001) "Adsorption – From Theory To Practice" *Adv. Colloid Interface Sci.* 93, 135 – 224.

Kamarudin K. S. N, H. Hamdan, and H. Mat, (2003) "Methane Adsorption Characteristic Dependency on Zeolite Structures and Properties" In The Proceedings of 17th Symposium of Malaysian Chemical Engineers,

Kaushik V.K, R.P. Vijayalakshmi, N. V. Choudhary, and S.G. T. Bhat, (2002) "XPS Studies On Cation Exchanged Zeolite A" *Micropor. Mesopor Mater.*, 51, 139-144.

Murata K., J. Miyawaki, and K. Kaneko, (2002) "A Simple Determination Method of The Absolute Adsorbed Amount for High Pressure Gas Adsorption" *Carbon,* 40, 425 – 428.

Rigby S. P., R. S. Fletcher, and S. N. Riley, (2004) "Characterization of Porous Solid using Intergrated Nitrogen Sorption and Mercury Porosimetry" *Chem. Eng. Sci.*, 59, 41 – 51.

Sing K. S. W., (1984) "Reporting Physisorption Data For Gas /Liquid Systems" Fundamental of Adsorption: In Proceedings of the Engineering Foundation Conference, 567 – 583.

Smith J.M., H.C. Van Ness, and M.M. Abbot, (1996) Introduction to Chemical Engineering Thermodynamics 5th Edition, McGraw Hill Intl.: New York.

Tielens F. and P. Geerlings, (2001) "An ab Initio Study of Adsorption Related Properties of Diatomic Molecules in Zeolites" *J. Mol Catal. A.*, 166, 175 – 187.

Yang L., K. Trafford, O. Kresnawahjuesa, J. Šepa , and R. J. Gorte, (2001) "An examination of Confinement Effects in High-Silica Zeolites" *J. Phys. Chem. B.* 105, 1935 – 1942

Yang X., (2004) "Thermodynamic Modeling of Solute Adsorption Equilibrium from Near Critical Carbon Dioxide" *J. Colloid Interface Sci.*, 273, 362 – 368.

Zhou L., Y. Zhou , S. Bai , and B. Yang, (2002) " Studies on the Transition Behavior of Physical Adsorption from the Sub- to Supercritical Region: Experiments on Silica Gel" *J. Colloid Interface Sci.*, 253, 9 – 15.