

STRUCTURAL SYNTHESIS AND MODIFICATION OF ZEOLITE AS METHANE ADSORBENT*

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ABSTRACT

Improvements in the technologies for the synthesis of zeolites and development of zeolite with different pore sizes hold a great promise in the chemical and petrochemical industries. Adsorption of methane in porous materials such as zeolite offers a possibility of storing methane at low pressure with high capacity. In this research, zeolite X (Y) have been hydrothermally synthesized in the laboratory with different composition ($6.4\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : x\text{SiO}_2 : 180\text{H}_2\text{O}$, $2 < x < 20$) followed by characterization procedure using XRD method and BET surface analyser. Post synthesis or modification using cation exchange technique has been carried out to observe the effect different cation (Li, K, Ca, Mg) on zeolite's properties. Zeolites with faujasite type of framework were produced with different relative crystallinity and surface area. The surface area of exchanged zeolite varied depending on cation types and groups. Molecular simulation was also carried out to determine surface area of zeolites and followed by methane adsorption at 273K and 100kPa. Result shows that cation exchange modification can increase the surface area, hence increase methane adsorption.

Keywords: zeolites; synthesis; modification; adsorption; characterization.

1. INTRODUCTION

Zeolites are commercially attractive because of their unusual crystalline structures that give them unique chemical properties. They consist of a tetrahedral network of oxygen and silicon atoms where aluminium replaces some of the silicon to form aluminosilicates. The result is an extended honeycomb of channels and cavities. Aluminium atoms have fewer electrons than silicon available for bonding with the oxygen atoms (three instead of four), thus causing an imbalance of electrical charge. Positively charged metal ions and cations, such as sodium, potassium, magnesium, and calcium can neutralize the charge (Barrer, 1982). Si atoms in tetrahedral units can be replaced by aluminium (Al) that results in a deficit of positive valence, requiring the addition of suitable cations such as alkaline or alkaline earth ions corresponding to the number of Al atoms. These actions are easily exchangeable and the size and properties of these ions modify adsorption characteristics of zeolites since they affect the size of the window between the cells (Suzuki, 1990). In most zeolite structures, the primary structural unit of AlO_4 or SiO_4 tetrahedra are assembled into secondary building units which may be simple polyhedra such as cubes, hexagonal prisms, or octahedral. The final structure framework consists of assemblages of the secondary units (van Bekkum *et al.*, 1991).

In principle, all microporous materials can be used as adsorbents. However those with well-controlled and high microporosity and are produced in large quantities are more preferable than the others (Yang, 1997). To be useful as an adsorbent, a solid must present a large surface area per unit mass (up to 1500 m^2 per gram). This can only be achieved with porous solid such as activated carbon, silica gels, aluminas, and zeolites which contains many cavities or pores with diameters as small as a fraction of a nanometer. The

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relatively weak electrostatic, induction and dispersion forces favor mobility and results in physical adsorption (Smith *et al.*, 1996).

The adsorptive property of zeolite was considered to be due to the crystalline nature of the materials. The porous crystal were thought to be permeated by channel networks, the free dimensions of which were determined by the positions of the framework oxygen just as exactly as the rest of the crystal lattice was defined by the position of its constituent atoms. In practice, the separating ability of zeolites can be achieved or altered by molecular sieving caused by size and/or shape differences between the zeolite aperture and the gas molecule. The adsorptive selectivity can be affected by the difference in the interaction energy between adsorbate molecules in a specific zeolite. Both molecular sieving and adsorption selectivity may be altered by cation exchange, preadsorption of polar molecules or a chemical modification of zeolitic structure using reactants containing silicon or boron hydride functions (Impens *et al.*, 1999).

Zeolites are seen as a potential adsorbent for natural gas/methane due to the ability of the microporous structure to adsorb molecules selectively, depending upon the size of the pore window. Zeolite frameworks are also flexible and the degree of flexibility is a function of a structure of the framework as the presence of extra-framework cations and molecules (Coker *et al.*, 1998). Methane is a major component in natural gas with more than 90% composition. Therefore, the properties of natural gas are assumed similar to methane.

Methane is extremely stable molecule with low bond polarity and London dispersion forces are most likely to be involved in adsorption. Solids with extensive microporous structures are considered to have potentials energy wells, which would be more favorable to adsorption of methane than a plane surface (Barton *et al.*, 1984). Adsorption behavior of molecules on porous adsorbent strongly depends on the characteristics of pores, which are their shape, size and chemical aspects (Chen *et al.* 1999). In particular in the adsorption on a micropore of less than twice the diameter of the adsorbate molecule, the enhancement of adsorption by the overlapping of the interactive potential of the pore wall, called micropore filling, takes place. Therefore, in the adsorption on microporous materials such as zeolite A, X and Y (entry aperture between 0.42 nm – 7.4 nm), methane with kinetic diameter of 0.38 nm is expected to adsorbed strongly even at low pressure. This paper reports preliminary results of zeolite synthesis and modification for methane adsorbent. It is aimed to investigate the effect of physical structure and properties of zeolite on the methane adsorption.

2. EXPERIMENTAL PROCEDURE

2.1 Zeolite Synthesis.

The synthesis was carried out by using reactant mixture with the 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 90 – 100°C. Sodium aluminate anhydrous (Riedel-de Haën) was added into sodium hydroxide (MERCK) solution and heated under rigorous stirring until dissolved. Ludox was added into sodium hydroxide solution and heated under rigorous stirring until clear solution appeared. Both solutions were mixed and stirred for 2 hours to obtain a homogeneous mixture. Then, the mixture was transferred into polyethylene bottle and heated in an oven at 100°C for 24 hours. After crystallization, 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 Zeolite Modification – Ion Exchange.

The cation exchange modification was carried out by adding 5g zeolite into polyethylene bottle containing 250mL of 0.5M nitrate solution (Li, K, Ca, and Mg). 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.

2.3 Characterization.

The structure of synthesized zeolite was characterized using X-Ray Diffraction (XRD) method (Bruker) to determine unit cell parameter and Si/Al framework ratio. XRD patterns were recorded with $\text{CuK}\alpha_1$ radiation with $\lambda = 1.5418\text{\AA}$ at 40 kV and 20mA in the range of $2\theta = 5^\circ - 50^\circ$ at scanning speed of 0.05° per second. From the unit cell parameter, the framework Si/Al ratio was calculated using Breck's equation,

$$R = \frac{1.66656}{a_o - 24.191} - 1$$

The surface area of each sample was determined by measuring nitrogen adsorption at 77K with surface area analyser Qsurf Series (ThermoFinnigen) based on Brunauer, Emmet and Teller (B.E.T.) equation,

$$S_t = K (1 - P/P_o) \times V_a$$

where

- S_t - total surface area;
- K - 4.03, a constant for nitrogen, assuming STP condition;
- P/P_o - 0.294 for gas mixture of 30% N_2 / 70% He;
- V_a - volume of gas (N_2) adsorbed.

3. RESULTS AND DISCUSSION

3.1 Synthesis

Synthesis was carried out for the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between 2 and 12. Results show that the crystalline powder (SZ-16, SZ-18, and SZ-21) produced have a faujasite type of framework except for low the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio which amorphous structure exists in the sample. The crystallinity increases as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increases (Figure 1).

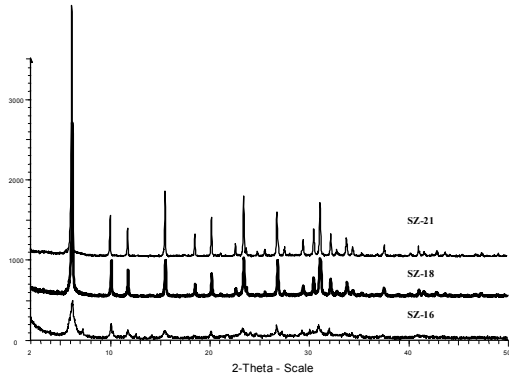


Fig. 1: Diffraction patterns of SZ-16, SZ-18, and SZ-21 different that have a faujasite type of framework.

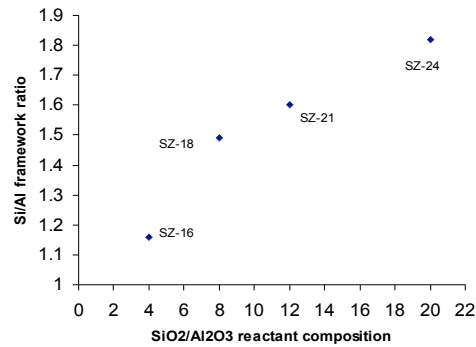


Fig. 2: Si/Al framework ratio formed with $\text{SiO}_2/\text{Al}_2\text{O}_3$ reactant composition.

Table 1 summarizes values of unit cell parameter (a_o), Si/Al ratio and surface area of zeolites. Unit cell diameter and Si/Al ratio of each sample was determined from XRD results. As expected, the unit cell dimensions decrease upon increase of the Si/Al ratio because Si-O bond is shorter than Al-O bond, which leads to smaller dimensions of the cages. However, the surface area of synthesized zeolites increases as the unit cell parameter decrease. This is due to the crystallinity of sample, which increases as the Si/Al ratio increases. It is also expected that higher methane adsorption with higher Si/Al ratio due to higher surface area.

Table 1: Unit cell diameter and surface area of zeolite samples with different Si/Al ratio.

Sample	Si/Al Ratio	a_o (\AA)	Surface Area (m^2/g)
Na-16	1.16	24.96	424.60
Na-18	1.49	24.86	598.88
Na-21	1.60	24.83	629.57
Na-24	1.82	24.80	407.83

3.2 Ion Exchange

Na-SZ18 was exchanged with alkali metal (Li, K, Mg, and Ca). The patterns are nearly the same as those of the as-synthesized crystal, with regard to position and sharpness of the peaks. The crystallinity increases after exchanged with lithium ion, but it decreases with calcium and magnesium ions.

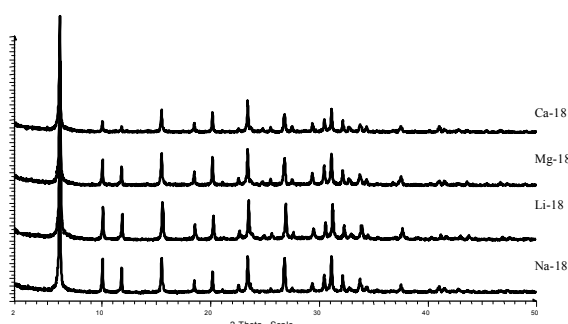


Fig. 3: SZ-18 exchanged with cations (Li, Mg, Ca).

Table 2 shows changes in zeolite surface area when exchanged with different cations. As one would be expected, the surface area of exchanged zeolite depends on the size of cation and the quantity that being exchanged. The surface area of zeolite exchanged with lithium is higher than the synthesized zeolite in its sodium form.

Table 2: Surface area of zeolites exchanged with different cations.

Sample	Surface Area, m ² /g
Na-18 (sodium form)	598.88
exchanged with lithium	660.38
potassium	544.85
magnesium	620.22
calcium	586.42

The surface area decreases as the ionic radius of cation increases for alkali metal group I. Even though the ionic radius of magnesium and calcium is larger, the surface area is relatively higher than as-synthesize zeolite. This is due to the number of cation exchanged is half of the number of sodium. Result from molecular simulation (Cerius2, Ver 4.2 MatSci, Accelrys Inc.) also shows a similar trend if replacing sodium with several cations (Table 3). Molecular simulation of methane adsorption was also carried out at 273K and 100 kPa. The amount of methane adsorbed onto zeolite framework depends on the surface area of zeolite as well as cation types and groups.

Table 3: Surface area, pore volume and amount of methane adsorbed into FAU framework.

Zeolite	Surface Area (m ² /g)	g (Methane)/g (Zeolite)
Li-FAU	781.22	0.012
Na-FAU	476.67	0.010
K-FAU	256.23	0.009
Cs-FAU	123.92	0.003
Mg-FAU	645.79	0.012
Ca-FAU	643.52	0.014

4. CONCLUSION

Adsorption of low bond polarity molecules on zeolite such as methane is a challenge in the adsorption applications. However, by understanding physical properties of zeolite that may affect the adsorptive performance of methane, zeolite can be re-engineered towards an effective adsorbent. By using molecular simulation, the adsorptive behaviour of different zeolites can be predicted. As-synthesize zeolite with high crystallinity produces high surface area, which plays an important role in the adsorption of methane. Furthermore, by introducing other cations into zeolite framework, the available surface area and volume changes. The size and number of cations replacing sodium in zeolites determine the surface area and pore volume of zeolite. Hence, the presence of cations other than sodium will affect the adsorption of methane.

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