STRUCTURAL AND GAS ADSORPTION PROPERTIES OF CATION EXCHANGED ZEOLITES

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ABSTRACT

Zeolite containing silica-alumina and positively charges metal ions has the ability to adsorb molecules selectively, depending upon the size of the pore window. This is due to the arrangement of structural unit in zeolite framework that results in the generation of pores and cavities of various dimensions. However, structural properties of zeolites can be altered in a controlled manner by several modification methods. Pore modification by cation exchange method is selected to replace sodium in zeolite structural framework with other metal ions. Cationic variants of zeolite Y (LiY, MgY, BaY, AgY, and NiY) were prepared via aqueous cation exchange. Their structural properties were characterized using X-ray powder diffraction and nitrogen adsorption measurement. It was found that the presence of cation affects the structural properties of zeolite and gas adsorption characteristics. Magnesium- exchanged zeolite Y showed the strongest affinity towards methane. Sample NiY has the highest adsorption capacity for carbon dioxide.

Keywords: Zeolite, Cation Exchange, Adsorption, Methane, Carbon Dioxide.

1 INTRODUCTION

Zeolites are composed of TO_4 tetrahedra (T=Si or Al) strongly bonded together via oxygen bridges to form well-defined channels and cavities. There are also extra framework species such as cations and water molecules inside the void space of the frameworks. Cations that balance the negative charge of the framework are mobile and exchangeable but water molecules are removable by heating without affecting the topology of zeolite (Yang and Navrotsky, 2000). Zeolite Y (NaY) possesses a comparatively large number of exchangeable cations and remarkably stable and open framework. Exchangeable cations in NaY are located in two independent but interconnected three dimensional networks of the cavities. One network consists of the supercages (α-cages) with inside diameter of about 12 Å that linked to four others via twelve-membered rings of 7.5 Å diameter. The other network is formed by linking smaller sodalite cages (7.0 Å free diameter) to supercages by double 6-rings of 2.2 Å free diameter (Yang and Navrotsky, 2000; Joshi et al., 2001). When these characteristics are coupled with its unique structure, NaY has a tremendous potential either in adsorptive, ion-exchange, or catalytic application.

Modification by cation exchange is one approach of tuning the adsorptive properties of zeolite. Different cationic form of zeolites may lead to significant differences in the selective adsorption of a given gas, due to both the location and size of the interchangeable cations that affect the local electrostatics and the polarization of the adsorbent. Studies on zeolites containing polyvalent cations showed that adsorption characteristics varies when different cation exist as extra framework species in the zeolite structura. (Harlfinger et al., 1983; Keane, 1995; Joshi et al., 2001; Öhman et al., 2002). Even though zeolites have been recognized as potential gas adsorbent, studies on the effect of structural modification and gas adsorption capacity need to be further clarified. Therefore, this paper presents the effect of structural modification of NaY by cation

exchange on the effects of pore size, surface area, micropore volume and gas adsorption characteristics.

2 EXPERIMENTAL

2.1 CATION EXCHANGE

Sodium in zeolite Y (NaY, Zeolyst International) was exchanged with metal cation by adding 5 g of NaY powder into 250 ml of 0.5 M nitrate solution. The solutions were prepared separately using different group of cations; alkali metal (Li^+), alkaline earth metals (Mg^{2+} and Ba^{2+} and transition metals (Ag^+ and Ni^{2+}). The slurries were stirred for 5 hours at 80 ° C in a temperature controlled water bath. The cation exchanged zeolites were recovered by vacuum filtration and rinsed with deionized water and dried overnight in an oven at 100 °C.

2.2 CHARACTERIZATION

Metal exchanged zeolites were characterized using X-ray diffractometer (Bruker) to determine relative crystallinity and unit cell parameter, a. X-ray diffractogram patterns were recorded with $CuK\alpha_1$ radiation (λ = 1.5418 Å) at 40 kV and 20 mA in the scanning range of $2\theta = 2°$ - $50°$ at scanning speed of $0.05°$ per second. The porosity of the samples was determined using nitrogen adsorption analyser (Quantachrome, Nova 1000) at 77 K. Surface area, pore volume and average pore diameter were calculated from nitrogen adsorption isotherm data obtained.

2.3 GAS ADSORPTION MEASUREMENT

Gas adsorption study of methane (CH_4) and carbon dioxide (CO_2) were carried out using themogravimetric analyzer (Perkin Elmer, TGA7) at 50 °C and 1.3 bar. Initially, a sample was loaded on the sample pan and outgassed carried out at 400°C for at least 1 hour. The samples were then cooled and held at 50°C for adsorption to occur until it reached equilibrium. The amount of gas adsorbed was calculated as mole of gas adsorbed per mass of adsorbent.

3 RESULTS AND DISCUSSION

3.1 STRUCTURAL PROPERTIES

Figure 1 shows the XRD patterns of NaY and cation-exchanged zeolites. The number of diffraction peaks for Li-, Mg- and Ni-exchanged zeolites is the same as NaY sample, which indicates that no crystalline transformation occurred during the exchanged procedures. However, the diffraction peak at $2\theta \approx 12$ ° disappeared in sample BaY and AgY. Replacing Na^+ with larger cations caused distortion at plane (3 1 1) of BaY and AgY samples as the ionic radius of cation Ag^+ (0.113 nm) and Ba^{2+} (0.143 nm) are larger than cation Na^+ (0.098 nm). These two cations distorted the framework to achieve the best environment for possible coordination because of high charge density.

Figure 1 also shows the intensities of diffraction peaks of modified samples that are lower than NaY. According to ASTM D3906, the total intensities of the six peaks assigned to (331), (511), (440), (533), (642), and (555) reflections were used to calculate relative crystallinity by using NaY as a reference. The intensities for modified samples decreased after cation exchange process, especially for samples AgY and BaY. The sequence of relative crystallinity is NaY>LiY>NiY>MgY>AgY>BaY. When two Na^+ cations were replaced by one divalent cation, the divalent cation caused changes in local distribution and electrostatic fields. The changes might cause an alteration of the framework, leading to the reduction of diffraction peaks intensities. Such changes in cation exchange between cations with different valence were usually more obvious than those in cation exchange between ions with the same valence. Although cation Ag^+ has the same valence as Na^+, it relative crystallinity is low (40.33 %) which also suggest that larger cation size also cause structural distortion. For divalent cations, the relative crystallinity of MgY and NiY were 86.05 % and 90.62 % respectively. Again the Ba-

exchanged sample shows the lowest relative crystallinity (33.07 %) due to its larger cationic size.

The unit cell dimensions of zeolite Y is characterized by a single lattice constant a from X-ray diffraction analysis since it has a cubic symmetry structure ($a = b = c$). The lattice constant or unit cell parameter was calculated from selected reflection peak positions. The calculated unit cell parameters of the zeolite NaY and cation-exchanged samples are listed in Table 1. The unit cell parameter of NaY is 24.65 Å but as a consequence of cation exchange, values for modified samples are slightly reduced.
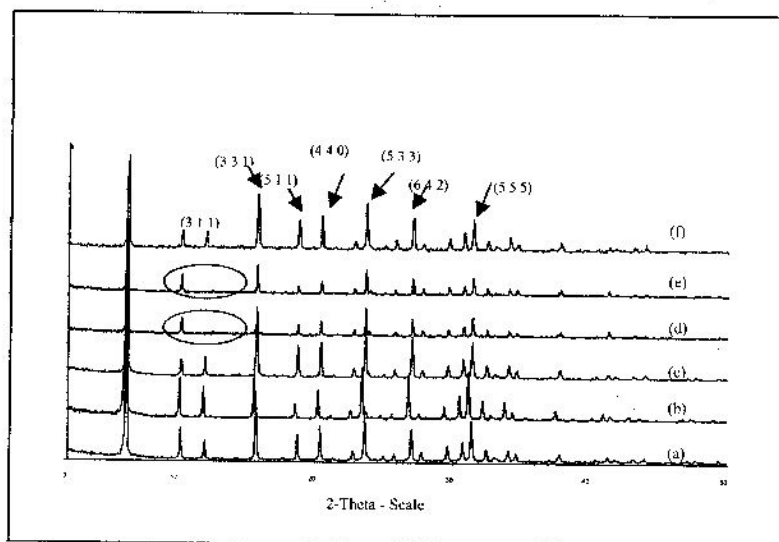

FIGURE 1. XRD patterns of the zeolite samples: (a) NaY; (b) LiY; (c) MgY; (d) BaY (e) AgY; and (f) NiY 0.5M.

TABLE 1. The relative crystallinity of zeolite NaY and modified samples.

Sample	Ionic radius (nm)	Relative crystallinity (%)	Unit cell parameter (Å)
LiY	0.078	98	24.63
NaY	0.098	100	24.65
MgY	0.078	86	24.63
BaY	0.143	33	24.62
NiY	0.078	90	24.63
AgY	0.113	40	24.62

Table 2 shows the porosity data of NaY and cation exchanged samples, obtained from nitrogen adsorption data. Specific surface area significantly decreased as a result of cation exchange in zeolite structure. during cation exchange process. The sequence of specific surface area is NaY>LiY>MgY>BaY>NiY>AgY. The deterioration of the zeolitic framework structure is indicated by low micropore area and micropore volume of sample AgY, it was also revealed by the relative crystallinity values (Table 1).

TABLE 2. The porosity data of the parent NaY and cation exchanged samples.

Sample	Micropore surface area (m²/g)	Micropore volume (cm³/g)	Average pore diameter (Å)
LiY	604.4	0.214	17.3
NaY	847.4	0.299	15.6
MgY	376.3	0.133	23.7
BaY	333.7	0.118	17.8
NiY	273.7	0.097	15.2
AgY	196.9	0.070	14.8

3.2 GAS ADSORPTION PROPERTIES

NaY consists of supercages with a free diameter of about 12 Å and smaller sodalite cages of free diameter 7.5 Å. Both adsorbates have kinetic diameter smaller than the channel diameter of NaY (δ_{CO2} = 3.3 Å and δ_{CH4} = 3.8 Å). It was obvious that diffusion of CO_2 and CH_4 are not limited by the steric factor. CO_2 and CH_4 molecules can freely penetrate the entrance windows into the micropore for NaY.

The study result shows that the adsorption capacity of methane is in the order of AgY<NaY<BaY<NiY<LiY<MgY (Figure 2). Although the specific surface area of modified samples decreased, the adsorption capacity increased after exchanged with cation Mg^{2+}, Li^+, Ni^{2+} and Ba^{2+}. This result indicates that the adsorption capacity of zeolite does not only depend on specific surface area, but also on size and density of cations. Since charge density of Mg^{2+}, Ni^{2+} and Ba^{2+} are higher than Na^+, the presence of the cations increase the electrostatic field within the modified zeolite. Adsorption capacity of MgY for gas methane is the highest among all the samples. Exchanging Na^+ in NaY with Ba^{2+} only causes slight increase in the methane adsorption. Even though it is known that charge density of Ba^{2+} was higher than Na^+, deterioration of structure inevitably reduced the adsorptive capability of the zeolite. However, CO_2 adsorption followed different sequence, AgY<BaY<NaY<MgY<LiY<NiY (Figure 2). Sample NiY has the highest adsorption capacity for carbon dioxide. Different cation leads to the significant differences in the gas carbon dioxide adsorption capacity because both the location and size of the interchangeable cations affect the local electrostatic field and the polarization of the adsorbates. But, similar to CH_4 adsorption, AgY adsorbed least CO_2.

Further investigation revealed that charge density also influenced the initial rate of CO_2 and CH_4 adsorptions (Table 3). It was found that initial rate of CO_2 adsorption following order: NiY<MgY<BaY<AgY<NaY<LiY. However, the rate of CH_4 adsorption follows different sequence, AgY<LiY<NaY<NiY<BaY<MgY. By comparing the cation of same group, the initial rate of CH4 adsorption of decrease as the saiz of cation increase. However the rates of CO_2 adsorption increase as the cation size increase. This phenomenon does not apply to cation alkali metal.
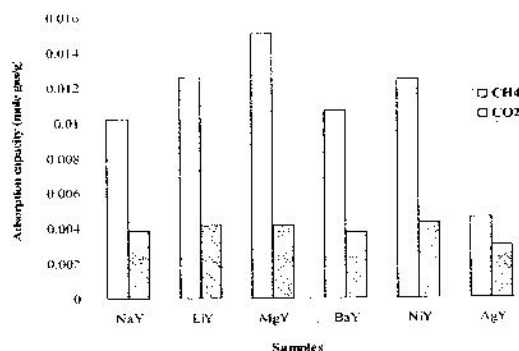

FIGURE 2. Adsorption capacity of methane and carbon dioxide.

TABLE 3. Initial rate of adsorption for cation-exchanged zeolites.

Sample	Initial rate of adsorption ($\times 10^3$ mmol/min)	
	CH_4	CO_2
LiY	0.818	1.225
NaY	0.868	1.007
MgY	3.533	0.814
BaY	1.174	0.825
NiY	0.841	0.587
AgY	0.508	0.924

4 CONCLUSION

Methane adsorption capacity for the cation-exchanged samples was remarkably greater than carbon dioxide. This study revealed that types of cations influence the structural and adsorptive properties of zeolite adsorbent. In term of structure, cation of the same valence imposes less damage than cations of different valence. The large cation such as Ag^+ and Ba^{2+} caused the distortion of structure and significantly reduced the micropore area of the adsorbent. Combination properties of micropore surface area, electrostatic field, cation charge density, and adsorbent/adsorbate interaction affect gas adsorption characteristics of zeolites.

ACKNOWLEGMENTS

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