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Study of Zeolite Molecular Sieves for Production of Oxygen by Using Pressure Swing Adsorption

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Abstract. Adsorption of nitrogen on Li or Ca exchanged Faujasite at various Si/Al mole ratios (1.00, 1.23, and 1.69) and exchange levels (0 to nearly 100%) has been measured at 298 K. Nitrogen capacities were compared with the positions of Li and Ca. It has been demonstrated that Li at site III and Ca at site II adsorb nitrogen, and nitrogen capacities depend on Li per unit cell in Li-Faujasite and Ca per unit cell in Ca-Faujasite regardless of Si/Al.

Keywords: Faujasite, nitrogen adsorption, positions of cations

Introduction

Production of oxygen by pressure swing adsorption (O_2-PSA) has come into wide use industrially. The zeolite molecular sieve is the most important component of O_2-PSA as an adsorbent. Recently, new types of zeolite molecular sieves have been proposed as high performance adsorbents. For example, Li exchanged X-type zeolite (Baksh et al., 1992; Gaffney, 1996) and Low Silica X (LSX) zeolite (Coe et al., 1988; Coe, 1990) are reported.

In this study, we examined Li or Ca exchanged LSX-, X- and Y-zeolite (Faujasite) molecular sieves. The aim is to clarify the relation between the positions of cations and N_2 capacity on Li or Ca exchanged Faujasite.

Experimental

Parent Na-Faujasite powder samples are listed in Table 1. Li or Ca exchanged Faujasite at various exchange levels were prepared from Na-Faujasite. The Li exchange was performed by using 3.0 M aqueous solution of LiCl (slurry $\mathrm{pH} = 8$, adjusted with LiOH), and the Ca exchange was done by using 1.0 M aqueous solution of $CaCl_2$ (slurry $\mathrm{pH} = 8$, adjusted with $Ca(OH)_2$). After the exchange, the zeolites were washed with pure water and then dried at 313 K. The exchange levels were determined by inductively coupled plasma-atomic emission spectroscope (Perkin Elmer, Optima 3000).

Adsorption capacities of N_2 were obtained through a handmade volumetric apparatus. Isotherms were measured at 298 K after the dehydration at 623 K and 10^{-1} torr for 2 hours.

Positions of cations in some samples were analyzed by the Rietveld method of X-ray powder diffraction. X-ray patterns of dehydrated zeolites were examined in a MAC SCIENCE MXP^3 diffractometer with Cu$K\alpha$ radiation. Crystal structures were refined by using the program RIETAN94 (Izumi, 1993).

Results and Discussion

Li-Faujasite

Figure 1 shows N_2 capacity at 700 torr of Li exchanged Faujasite at various exchange levels. The numbers on the abscissas indicate Li exchange level, Li/Al atomic mole ratio. The numbers on the ordinates indicate milliliter of adsorbed N_2 per gram of zeolite. Adsorbed N_2 of Li-LSX, X, and Y increases abruptly at certain exchange levels. The threshold Li exchange level decreases with a decrease in Si/Al. And adsorbed N_2 of Li-LSX is about 1.5 times larger than Li-X at nearly 100% exchange level. The number of 1.5 is quite larger than the value simply calculated from the number of Li on zeolites.

Table 2 summarizes the data on positions of cations by diffraction method, our result and the data cited

Table 1. Unit cell composition of Na-Faujasite.

Sample	Si/Al mole ratio	Composition
NaLSX*	1.00	$Na_{99}Al_{96}Si_{96}O_{384}$
NaX**	1.23	$Na_{86}Al_{86}Si_{106}O_{384}$
NaY***	1.69	$Na_{71}Al_{71}Si_{121}O_{384}$

*(Na, K)LSX was synthesized by Kuhl's method (Kuhl et al., 1987). NaLSX was then prepared by Na exchange.

**Commercial NaX (F-9 powder, lot No. P960124; Tosoh Corporation).

***NaY was synthesized by Kasahara's method (Kasahara et al., 1986).

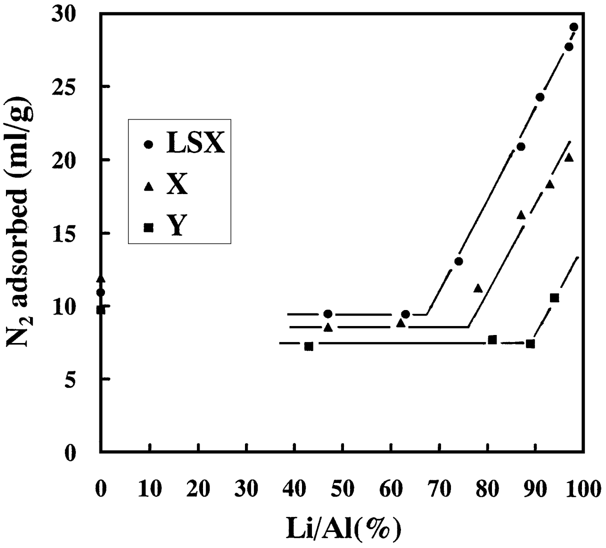

Figure 1. N_2 capacity at 700 torr, 298 K on Li-Faujasite (Li/Al vs. ml/g).

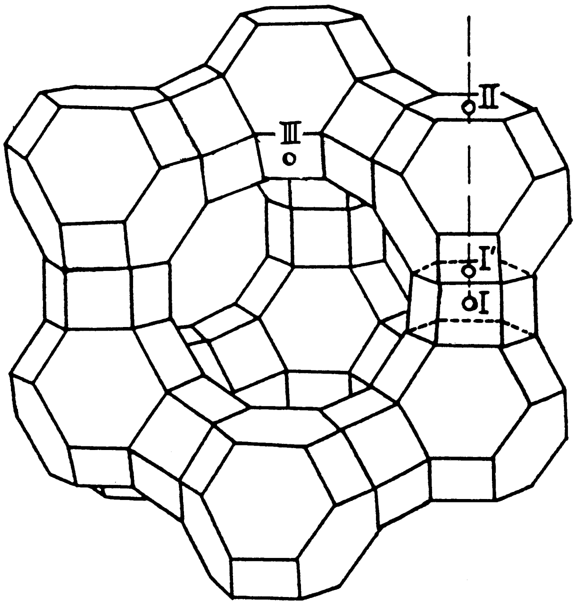

Figure 2. Possible sites of exchanged cations in Faujasite. Nitrogen go through the supercage. And so cations at sites II and III are possible to adsorb nitrogen.

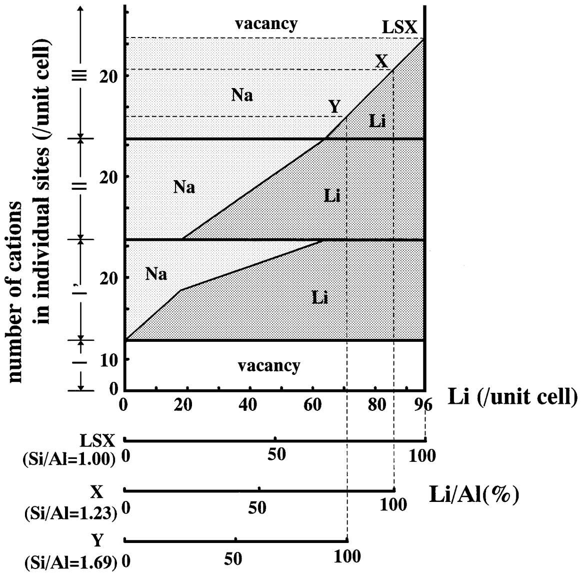

Figure 3. Positions of cations in Li-Faujasite (hypothesis).

from references. Li and Na locate at sites I, I′, II, and III shown in Fig. 2. Herden et al. (1981) also reported that Na at site III must be replaced by Li over 64Li per unit cell by ^{7}Li-NMR study on Faujasite of Si/Al $\geq$ 1.26. Table 2 shows two important tendencies. One is that the number of Li and Na at site III increases with a decrease in Si/Al, in other words, with an increase in the sum of cations. Another is that Li prefers to be located at sites I′ and II rather than Na.

Judging from these results, we hypothesized the positions of cations in Li-Faujasite generally. Figure 3 is the hypothesis. The numbers on the abscissas indicate Li per unit cell and Li exchange level, and the numbers on the ordinates indicate Li and Na per unit cell. For example, Li 50% exchange X has 43Li per unit cell and would have 25Li and 7Na at site I′, 18Li and 14Na at site II, and 22Na at site III. This hypothesis shows Li would locate at site III over 64Li per unit cell regardless of Si/Al, and also indicates at 100% exchange level, 7Li would locate at site III in Y, 22Li in X and 32Li in LSX.

To clarify the relation between the positions of cations and N_2 capacity, the units of the data in Fig. 1

Table 2. Positions of cations in Li-Faujasite.

Sample	Si/Al	Li/Al	I	I′	II	$III^{(\prime)}$	Missing (excess)	Reference
$Li_{93}Na_3$[96]*	1.00	97%	4Li	30Li	27Li	63Li	31Li (excess) 3Na	This study
$Li_{81}H_5$[86]	1.23	94%		26Li	32Li	22Li	5H	Forano et al., 1989
$Li_{65}H_{10}Na_{11}$[86]	1.23	75%		32Li	32Li		1Li 10H, 11Na	Herden et al., 1989
$Li_{62}Na_{30}$[92]	1.09	67%		25Li 5Na	16Li 11Na	9Na	21Li 5Na	Shepelev et al., 1990
$Li_{46}H_6Na_5$[57]	2.37	81%		24Li	21Li		6H, 5Na	Forano et al., 1989
$Li_{39}H_4Na_{13}$[56]	2.43	70%		32Li	7Li 13Na		4H	Herden et al., 1989
Na_{96}[96]	1.00	0		27Na	28Na	42Na	1Na (excess)	Kamioka et al., 1997
Na_{85}[85]	1.25	0	1Na	26Na	31Na	27Na		Kamioka et al., 1997

*[X]: $Al_XSi_{192-X}O_{384}$ ex.[86]: $Al_{86}Si_{106}O_{384}$.

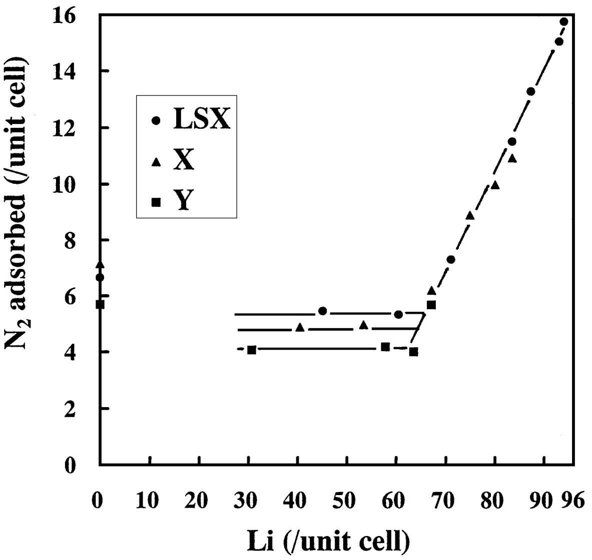

Figure 4. N_2 capacity at 700 torr, 298 K on Li-Faujasite (Li/u.c. vs. N_2/u.c.).

were converted to number of N_2 per unit cell (Fig. 4). The abscissa indicates the number of Li per unit cell, and the ordinate indicates the number of N_2 adsorbed per unit cell. The numbers of N_2 adsorbed agree well with LSX, X, and Y, and adsorbed N_2 increases abruptly at 64Li per unit cell. This fact indicates Li at site III is an adsorption site, and suggests that the hypothesis is approximately correct. And also, it is considered that the electrostatic strength around Li at site III is less influenced by Si/Al.

The threshold Li exchange level at which N_2 capacity increases abruptly can be described by the equation:

$$\text{threshold Li exchange level} = \frac{100(1 + \text{Si/Al})}{3} \quad (\%) \tag{1}$$

LSX (Si/Al = 1.00)	67%
X (Si/Al = 1.23)	74%
Y (Si/Al = 1.69)	90%

Ca-Faujasite

The results of Ca-Faujasite were similar to those of Li-Faujasite. Figure 5 shows N_2 capacity at 700 torr of Ca exchanged Faujasite. The data on positions of cations is summarized in Table 3, and our hypothesis is shown in Fig. 6. The converted data of Fig. 5 is shown in Fig. 7.

An adsorption site is Ca at site II and adsorbed N_2 increases abruptly at 16Ca per unit cell when Ca begins to locate at site II. These findings suggest that the electrostatic strength around Ca at site II is less influenced by Si/Al.

Incidentally, Li at site II does not adsorb N_2. There are two reasons for this. First, the charge density of Li is not as large as that of Ca. Secondly, the ionic radii of Li is small, and so Li at site II does not jut toward the supercage like Ca.

Table 3. Positions of cations in Ca-Faujasite.

Sample	Si/Al	2Ca/Al	I	I′	II	III$^{(\prime)}$	Missing (excess)	Reference
$Ca_{47}Na_3$[96]*	1.00	97%	14Ca	9Ca	29Ca		5Ca (excess) 3Na	This study
$Ca_{41}Na_3$[86]	1.23	96%	13Ca	4Ca	26Ca		2Ca (excess) 3Na	Costenoble et al., 1978
Ca_{40}[80]	1.40	100%	13Ca	5Ca	25Ca		3Ca (excess)	Pluth et al., 1972
$Ca_{31}Na_{34}$[96]	1.00	64%	16Ca	4Ca	23Ca	11Na	12Ca (excess) 23Na	This study
$Ca_{27}Na_3$[57]	2.37	94%	14Ca	4Ca	10Ca		1Ca (excess) 3Na	Costenoble et al., 1978
$Ca_{26}K_2Na_4$[57]	2.37	91%	11Ca	7Ca	11Ca		3Ca (excess) 2K, 3Na	Van Dun et al., 1985

*[X]: $Al_XSi_{192-X}O_{384}$ ex.[86]: $Al_{86}Si_{106}O_{384}$.

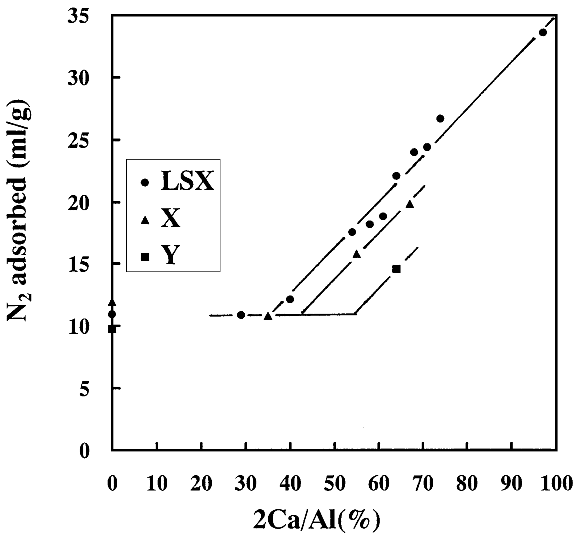

Figure 5. N_2 capacity at 700 torr, 298 K on Ca-Faujasite (2Ca/Al vs. ml/g).

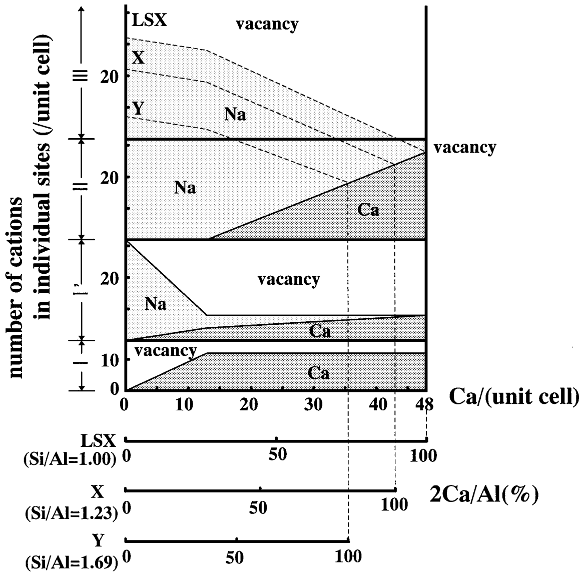

Figure 6. Positions of cations in Ca-Faujasite (hypothesis).

The threshold Ca exchange level at which N_2 capacity increases abruptly can be described by the equation:

$$\text{threshold Ca exchange level} = \frac{100(1 + \text{Si/Al})}{6} \quad (\%) \tag{2}$$

LSX (Si/Al = 1.00)	33%
X (Si/Al = 1.23)	37%
Y (Si/Al = 1.69)	45%

Conclusions

The conclusions of this study can be summarized as follows:

1. Li at site III approximately depends on Li/u.c. regardless of Si/Al.
   Ca at site II approximately depends on Ca/u.c. regardless of Si/Al.
2. Li at site III adsorbs N_2.
   Ca at site II adsorbs N_2.

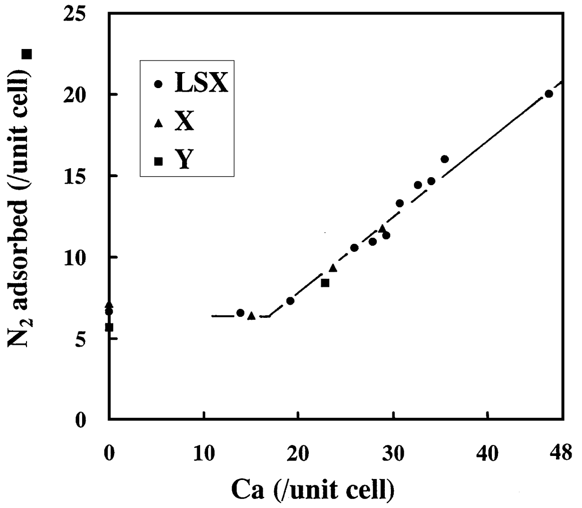

Figure 7. N_2 capacity at 700 torr, 298 K on Ca-Faujasite (Ca/u.c. vs. N_2/u.c.).

3. N_2 capacity depends on Li at site III, Li/u.c. in Li-Faujasite.
   N_2 capacity depends on Ca at site II, Ca/u.c. in Ca-Faujasite.

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