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Mechanism of Oxygen Adsorption on Partially K Exchanged Na-A Type Zeolite

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Abstract. Accordingly, the observation of oxygen selectivity on Na-K-A would indicate that nitrogen has a greater steric hindrance at the window than does oxygen. Using single crystal X-ray diffraction (SCXD), it was confirmed that K at 8-member rings was relocated to 6-member rings and that the location of Na at 8-member rings became uncertain with calcination. It was also observed that Na-K-A was thermally more stable than Na-A. Using magic angle spin nuclear magnetic resonance (MAS-NMR), it was confirmed that Na at 8-member rings irreversibly changed location from a symmetric position to an asymmetric position with calcination.

Using the atomic positions determined by SCXD, the mean square displacements (MSD) of oxygen and nitrogen inside the crystal of Na-A and Na-K-A were estimated by means of molecular dynamic simulation (MD). When temperature was decreased, the MSD of nitrogen was reduced to a greater extent than that of oxygen and the MSD of nitrogen inside Na-K-A was reduced by a greater margin than that inside Na-A.

Keywords: Na-K-A type zeolite, single crystal X-ray diffraction, MAS-NMR, molecular dynamic simulation

Introduction

In a previous report (Izumi and Suzuki, submitted), Izumi and Suzuki found that partially K exchanged Na-A type zeolite (Na-K-A) pellets calcined at a high temperature showed strong oxygen selectivity in Fig. 1.

Compared with the molecular sieves carbon 3A (MSC-3A) used as the oxygen adsorbent and conventionally showing an oxygen separation factor of 3, Na-K-A is characterized by a higher value of 8. When applied to air separation using pressure swing adsorption (PSA), it is expected to greatly reduce the electric power consumption associated with oxygen and nitrogen generation.

The separation performance of Na-K-A was described below.

1) Na-K-A behaved as a rate selective adsorbent, and showed oxygen selectivity even at room temperature.
2) When the adsorption temperature was reduced, the adsorption rates for both oxygen and nitrogen decreased, but the nitrogen adsorption rate decreased to a greater extent as a result, strong oxygen kinetic selectivity was observed at a low temperature.
3) Since Breck's report (1959) showing that Na-A becomes an oxygen adsorbent even under equilibrium conditions at less than 173 K, Na-K-A was found to exhibit oxygen selectivity at comparatively high temperatures up to 243 K.

This result forms an interesting contrast to Breck's report (1959) indicating that Na-A becomes an oxygen

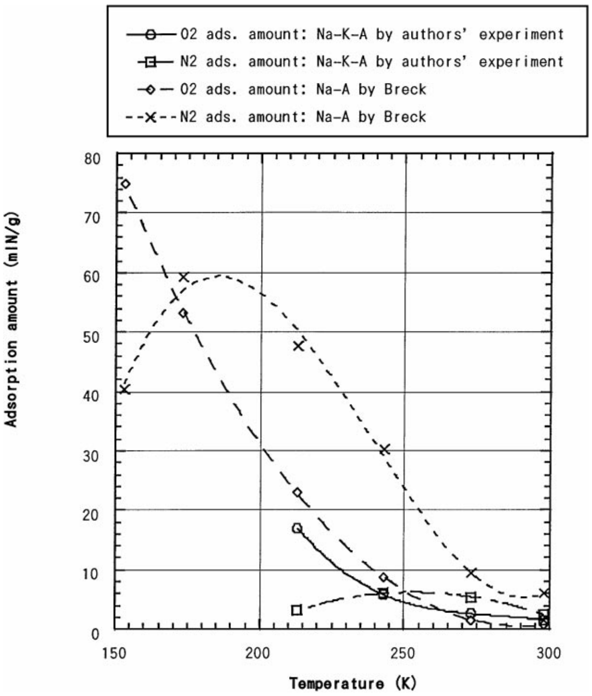

Figure 1. Isobars of oxygen and nitrogen on Na-A and Na-K-A.

adsorbent under equilibrium conditions only at temperatures lower than 173 K.

With respect to the oxygen selectivity of Na-A at extremely low temperatures, Takaishi (1985) explained that, at room temperature, Na at 8-member rings is in a state of strong thermal vibration and can be pushed out by nitrogen, which is slightly larger than the diameter of the window allowed by Na. Thus, nitrogen is able to pass through the Na-A window. When the temperature decreases, the mobility of Na is reduced and the larger nitrogen molecule is subject to greater steric hindrance than the smaller oxygen molecule. However, Takaishi's model of Na mobility at 8-member rings does not sufficiently explain the effects of high temperature calcination and partial K exchange (i.e., enhanced oxygen selectivity). Given the enhancement of oxygen selectivity resulting from partial K exchange and a high temperature calcination, conventional theory suggests only that the window diameter is reduced from 4 Å to 3 Å by the exchange of Na at the 8-member ring with K. Thus, as the K exchanged window would be anticipated not to adsorb either oxygen or nitrogen any longer, the experimental results were quite surprising. Furthermore, regarding the order of priority of K exchange sites, Na at S_{II} (8-member ring) was found by Takaishi (1985) to exchange with K first, followed by Na at S_I (4-and 6-member rings). If K exchange were to proceed in accordance with conventional theory, all Na-A windows would be reduced to 3 Å when the exchange ratio exceeds 25 mol%. Nevertheless, our previous study (Izumi and Suzuki, submitted) found that the oxygen selectivity increases as the K exchange ratio rises up to 15 mol%, and this phenomenon cannot be explained by the priority of K exchange sites. As this phenomenon has high reproducibility, and as a US patent by Berlin et al. (1966) also disclosed that partially K exchanged Na-A shows a strong oxygen selectivity, it may be inferred that certain unknown factors remain.

In this study, the following procedures were undertaken in order to elucidate the nature of such factors.

(1) The crystal structure of partially K exchanged Na-A that had been calcined at a high temperature was determined using SCXD,
(2) 23Na of Na-K-A pellets was measured by magic angle spin-nuclear magnetic resonance (MAS-NMR), symmetries of Na at the S_I and S_{II} sites were evaluated.
(3) All atomic positions of Na-A and Na-K-A determined by SCXD were used as input data for the following molecular simulations and diffusion rates of oxygen and nitrogen inside the Na-K-A crystal at low temperatures were also evaluated using MD.

SCXD Evaluation of Na-K-A

Sample Preparation

Figure 2 shows the preparation procedure for partially K exchanged Na-A single crystals synthesized with the Charnell method, and Table 1 shows the treatment conditions for each sample. SAMPLE-K1 is Na-K-A having a partial K exchange ratio of 7 mol% and a high temperature calcination at 993 K. SAMPLE-K2 features the same composition as for SAMPLE-K1, but with water adsorption of 15 w% and high temperature recalcination at 993 K. It should be noted that a previously conducted small column experiment (Izumi and Suzuki, submitted) revealed no oxygen selectivity enhancement for Na-K-A subjected to water adsorption and recalcination, although such enhancement was observed for Na-A. SAMPLE-R is Na-A from which surface water was removed at 0.135 kPa and 723 K, and which was prepared as anhydrous standard Na-A.

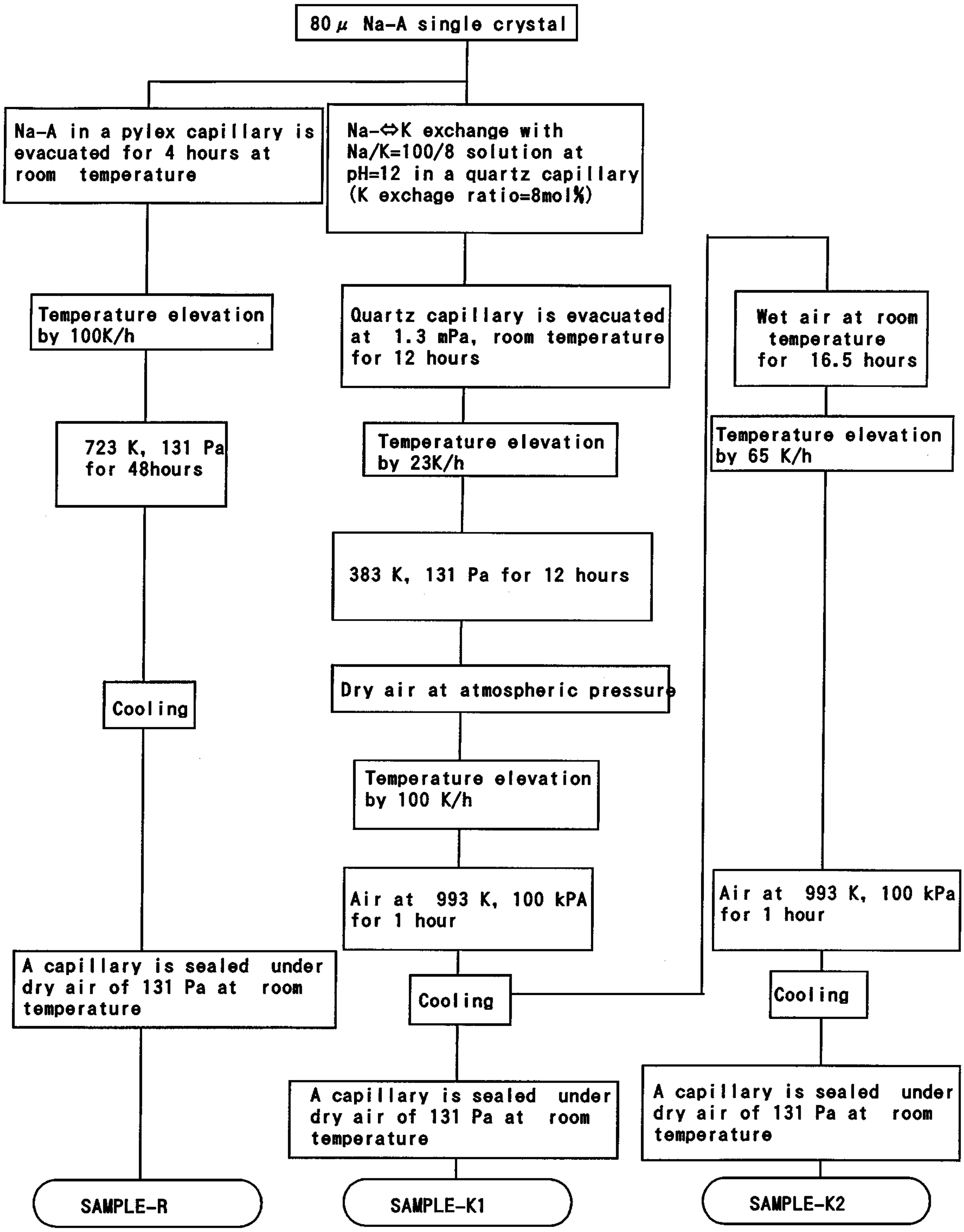

Figure 2. Chemical and thermal modification of single crystal Na-A.

Table 1. Sample preparation conditions for SCXD.

Samples	Calcination temp. (K)	Calcination atmosphere	Recalcination temp. (K)	Recalcination atmosphere	K exchange ratio (mol%)
SAMPLE-R	723	<130 Pa	—	—	—
SAMPLE-K1	993	Air, 100 kPa	—	—	7
SAMPLE-K2	993	Air, 100 kPa	993	Rehydration	7

Measurement

A single crystal of Na-A or Na-K-A was sealed in a quartz or Pyrex capillary and was placed on a three dimensional rotating mount. As this capillary was exposed with monochromatic Mo K_α X-rays filtered by a graphite plate, the diffraction rays emitted from the sample were detected with a scintillation counter and amplified with a pulse height analyzer. Given this diffraction data, the positions of all atoms (Na, K, Si, Al, O) of Na-A or Na-K-A could be determined.

Results and Discussion

a) *Atomic positions of samples*. The lattice constant and diagonal distance of the 8-member rings in each sample as determined by SCXD are shown in Table 2. These data were used as the input data for the molecular viewer software-"Ryuuga" produced by Murakami and the atomic structure of each sample was visualized. Figure 3 shows the atomic structures of SAMPLEs K1, K2 and R.

b) *Crystal structure*. The lattice constant of SAMPLE-K1 was slightly smaller than that of SAMPLE-R, while the lattice constant of SAMPLE-K1 was the same as for SAMPLE-K2. It was initially assumed that the Na-A crystal had shrunk with partial K exchange and high temperature calcination, but additional thermal treatment performed on SAMPLE-K1 had no effect on crystal shrinkage. However, as the shrinkage was only of the order of 0.1% of crystal size, it is doubtful that there was any direct influence on oxygen selectivity. Also, the window diagonal distance of 6.901 to 7.119 Å for SAMPLE-K1 and K2 was about the same or slightly greater than that of 6.717 to 7.2633 Å diagonal for SAMPLE-R. On the other hand, it was highly noticeable that no Na atoms could be found at the 8-member rings. This coincides with the results for calcined Na-A noted in the previous report (Izumi et al., 1996). It was concluded that Na at 8-member rings had relocated irregularly inside the window, and that the SCXD signal became weaker than the lowest limit of detection. In general, when the occupancy probability reaches 1/16 or less at the same position, SCXD cannot detect the locations of atoms.

Table 2. Window size and lattice constant of single crystal samples.

Sample no.	Lattice constant (Å)	Diagonal distance of 8 member ring (Å)
SAMPLE-R	12.281	6.7177–7.2633
SAMPLE-K1	12.254	6.9284–6.970
SAMPLE-K2	12.254	6.901–7.119

c) *Effect of water adsorption and recalcination*. When Na-A with adsorbed water was recalcined, single crystals decomposed. However, no change was observed when this treatment was applied to Na-K-A. This would indicate that recalcination following water adsorption does not affect Na-K-A, and that K enhances the high temperature resistance of Na-A. As it has been reported that K exchanged Na-A is thermally stable (Blackwell et al., 1985), it was reconfirmed by SCXD in this study. According to our oxygen separation experiment using Na-A (1998), the recalcination of Na-A following water adsorption resulted in increased oxygen selectivity, but not in the case of Na-K-A.

d) *Partial K exchange*. Figure 3 also shows that all exchanged K atoms are located at 6-member rings. According to conventional theory, Na at 8-member rings is first exchanged with K, followed by the Na atoms at 6-and 4-member rings (Takaishi, 1985). If this theory is applied to the K exchange observed, all the windows would be reduced to 3 Å up to a K exchange ratio of 25 mol%.

However, if a working hypothesis is allowed based on our SCXD results, an explanation emerges whereby

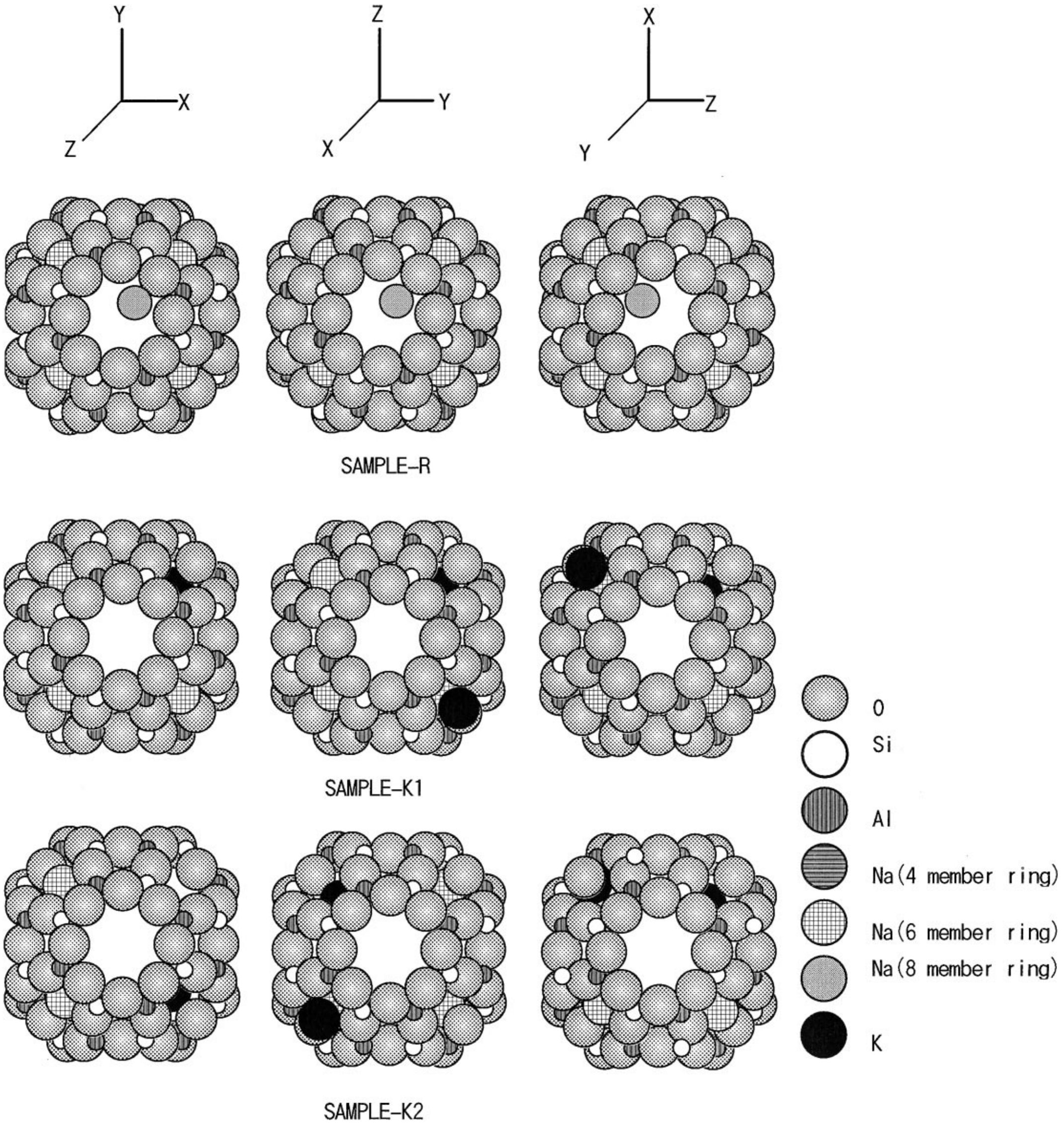

Figure 3. Crystal structure of chemically and thermally modified Na-A.

some exchanged K is relocated from 8-member rings to 6-member rings during high temperature calcination, and some of the Na atoms either shifted to or originally presented at 8-member rings occupy irregular positions inside the windows, thus generating stronger steric hindrance against nitrogen adsorption than against oxygen. With respect to the relationship between oxygen selectivity and Na irregularly occupying at 8-member rings, SCXD data were not sufficient and it was deemed better to investigate the interaction between Na and other atoms (Al, Si, O) using different methods.

Evaluation of Na-K-A by MAS-NMR

Sample Preparation for MAS-NMR

For the observation of Na's state of Na-K-A after a calcination, measurement of Na-K-A was undertaken by MAS-NMR.

To prepare water free adsorbent, Na-K-A was ground in a dry atmosphere in a glove box, and 300 mg of Na-K-A powder was placed in an NMR sample tube.

A sample of Na-K-A pellet with a K exchange ratio of 7 mol% and a calcination temperature of 993 K was

Table 3. Sample preparation conditions for MAS-NMR measurement.

Sample	Na-K-A pellet
Calcination temperature (K)	993
Calcination period (hrs)	1
K exchange ratio (mol%)	7
Binder species	kaolin
Binder content (w%)	18

Table 4. MAS-NMR measurement conditions.

Element	Si	Al	Na
Nuclear species	29Si	27Al	23Na
Observation frequency (MHz)	79.495	104.264	105.847
Pulse program	Single pulse	Single pulse	Single pulse
Observation width (Hz)	41666	41666	41666
Pulse width (second)	4 μ	2 μ	1 μ
Sampling point	4096	8192	8192
Repetition time (second)	1	0.2	0.5
MAS spin number (KHz)	4	4	0
Accumulation time	100	100	1000
Receiver gain	2860	2860	2860

prepared for MAS-NMR in the same way. Tables 3 and 4 show treatment and measurement conditions respectively.

Results and Discussion

MAS-NMR spectra of 23Na for Na-K-A with a K exchange ratio of 7 mol% are shown in Fig. 4. The spectrum of Na-K-A calcined at 723 K is the same as that of Na-A (Izumi et al., 1996).

According to Veeman's study (1973) of 23Na in Na-A and Na-K-A at a low temperature, 23Na has two lines. One line is assigned to Na located at a symmetric position, corresponding to Na at an 8-member ring. Another line is assigned to Na located at an asymmetric position, corresponding to Na at either a 4- or 6-member ring. As the temperature was raised, the symmetric line decreased and the asymmetric line increased dramatically at 823 K, although little change was observed at temperatures above 823 K. As Veeman measured 15 mol% K exchanged Na-A at high temperatures up to 823 K by MAS-NMR, it was found that the measured spectrum was highly similar to Na-K-A in this study, which we calcined at a higher temperature, and then allowed to cool to room temperature and subsequently measured (See Fig. 4). Veeman demonstrated that as temperature increased, asymmetric line intensity increased and symmetric line intensity decreased, and he found that this phenomenon was thermally reversible. However, the Na-K-A spectrum, for which samples were calcined at high temperature and measured at room temperature in this study, showed thermal irreversibility, and crystal structures at high temperatures were observed to be frozen even at room temperature. Therefore, Na at the 8-member rings of Na-K-A is assumed to be located in an asymmetric position, and deviates slightly from the symmetric position even at room temperature.

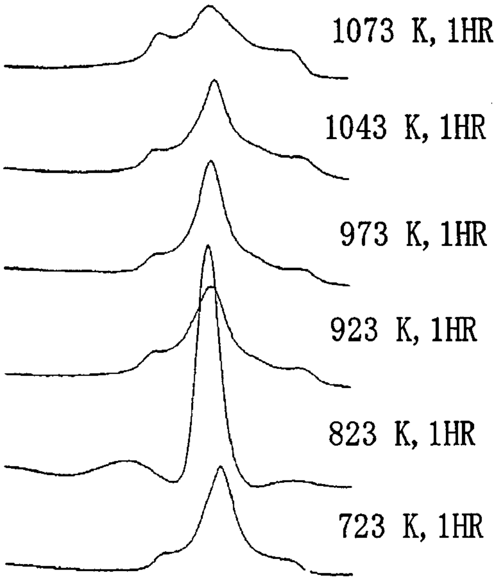

Figure 4. MAS-NMR spectrum of 23Na of Na-K-A (K exchange ratio of 7 mol%).

Study of Na-K-A Oxygen Selectivity by MD

Objective

Since the effectiveness of K exchange was confirmed in the preceding oxygen adsorption experiment, conventional theory does not explain the presence of oxygen selectivity. However, as the positions of all atoms were confirmed by SCXD, and the states of chemical bonds such as Na—Al, K—Al, Si—O—Al were evaluated by MAS-NMR, the experimental results can be summarized that Na at 8-member rings appeared to be located irregularly, and generated greater steric hindrance against larger nitrogen molecules than against smaller oxygen molecules.

In order to confirm this result, the following points require clarification.

1) The interaction between Na at 8-member rings and adsorbed oxygen and nitrogen at low temperatures.
2) The influence of K on oxygen and nitrogen mobility within crystals at low temperatures. Accordingly, MD was performed so as to supplement and expand upon experimental data and chemical state analyses.

MD Investigation of the Behavior of Oxygen, Nitrogen and Structural Atoms at Low Temperatures

Calculation was undertaken as follows:

1) For Na-A, Seff's data (1973) was used for all atomic positions of a unit cell, which was surrounded by eight replicas. For Na-K-A, atomic positions of SAMPLE-K1 were adopted.
2) A three point charge BMH (Born-Mayer-Huggins)+ Morse potential, which is most commonly used for light elements, was adopted, and the corresponding equations are shown in (1) and (1′) respectively.

$$u_{ij}(\text{inter}) = \sum_{\substack{\alpha\in 1\\ \gamma\in j}} \left\{ f_0(b_\alpha + b_\gamma)\exp\frac{a_\alpha + a_\gamma - r_{\alpha\gamma}}{b_\alpha + b_\gamma} - \frac{c_\alpha c_\gamma}{r^6_{\alpha\gamma}} \right\} + \sum_{\substack{p\in i\\ f\in j}} \frac{Z_p Z_f e^2}{r_{pf}} \tag{1}$$

$$u_{\alpha\gamma}(\text{intra}) = \sum_{\substack{\Omega\in i\\ \gamma\in j}} D_{\alpha\gamma}[\exp\{-2\beta_{\alpha\gamma}(r_{\alpha\gamma} - r^*_{\alpha\gamma})\} - 2\exp\{-\beta_{\alpha\gamma}(r_{\alpha\gamma} - r^*_{\alpha\gamma})\}] \tag{1′}$$

Parameters for the BMH potential function are shown in Table 5, and those for Morse potential function are shown in Table 6; calculation details are shown in Table 7.

Table 5. Parameters of BMH potential.

Atom	z (e)	a (Å)	b (Å)	c (kJ/mol)$^{1/2}$ Å^3)	1 (Å)
N(N_2)	0.662	1.697	0.135	41.613	1.095
O(O_2)	0.366	1.619	0.161	42.449	1.191

Table 6. Parameters of Morse potential.

Atom	D (kJ/mol)	β (Å^{-1})	R^* (Å)
N(N_2)	1475.87	2.3001	1.095
O(O_2)	559.911	2.6374	1.191

Table 7. MD calculation conditions.

MD software	MXDORTO
Initial atoms position	K. Seff and author's diffraction data
Numerical integration	Verlet method
Static electric interaction	Ewald method
Potential	Three points charge Born-Mayer-Huggins+Morse potential
Integration period Δt (fs)	2
Total integration steps	20,000
Ensemble	NPT constant
Temperature range (K)	523–1273 K, 213–298 K
Atoms number in a unit cell (% Standard Na-A)[a]	
0	384
Si	96
Al	96
Na	96

[a] Atoms number can be kept constant with three dimensional periodical boundary conditions.

MXDORTO PC software by Kawamura (1989) was used for MD. Calculation results were obtained using the molecular crystal viewer software known as "Ryuuga".

One unit cell and eight replicas were set for Na-A; one oxygen and one nitrogen were placed in the central cell, and MD calculation was started. Diffusion behavior of oxygen and nitrogen within crystals were assumed based upon molecular trajectories. For quantitative evaluation, the mean square displacement (MSD) of each molecule was calculated. For Na-K-A, the atomic positions of SAMPLE-K1 determined by SCXD were adopted. Using MD simulation for Na-A and Na-K-A, the following were evaluated:

(1) The influence of K at 6-member rings on Na at 8-member rings.
(2) The influence of Na at 8-member rings on oxygen and nitrogen transferring from one cell to another.
(3) Visualization of the results, and the calculation of MSD.

Results and Discussion

Behavior of Oxygen and Nitrogen Inside Crystals at Low Temperatures. As shown in Fig. 5, as temperature was reduced from 298 to 213 K, the MSDs of both nitrogen and oxygen inside Na-A were reduced, with the MSD of nitrogen becoming smaller than that of oxygen at lower temperatures in this range. It is known that both nitrogen and oxygen can transfer from one cell to another at room temperature, but, as temperature decreases a frequency of nitrogen transfer decreases gradually. The simulation in our study was limited to transfer between crystals, but this phenomenon might occur at the interface between gas phase and crystal surface, and it was assumed that the reduction of nitrogen transfer frequency at lower temperatures was induced as a result. When nitrogen is transferred through windows, the interaction between Na atoms at 8-member rings and nitrogen is strongly suggested. This phenomenon was simulated and visualized by Ryuuga. Snap shots of oxygen transferring through a window are shown in Fig. 6. When oxygen passed through the window, Na at 8-member ring was pushed out toward another cell and oxygen was able to pass through this space. As oxygen continued its travel to another cell, Na returned to its normal position. With respect to nitrogen, a similar phenomenon occurred at room temperature. When temperature was reduced, oxygen was able to pass through the window and push out Na, although nitrogen could not do so.

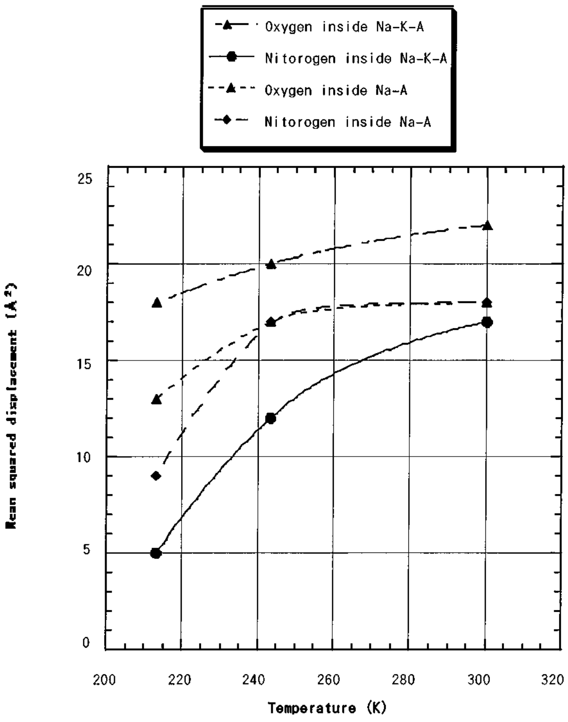

Figure 5. Mean squared displacement of oxygen and nitrogen inside Na-A and Na-K-A.

The MSD of Na-K-A is also shown in Fig. 5. As with Na-A, when the temperature was lowered, the MSDs of both nitrogen and oxygen were reduced and the MSD of nitrogen became smaller than that of oxygen at lower temperatures. Comparing the difference of MSDs between Na-A and Na-K-A, the MSD of nitrogen inside Na-K-A was smaller than that calculated in Na-A. It is speculated that the binding energy between Na at 8-member rings and other atoms (mainly Al) in Na-K-A became stronger than that in Na-A, meaning that the steric hindrance against nitrogen at lower temperatures inside Na-K-A might be more pronounced.

Conclusion

The mechanism of oxygen selectivity of Na-A and Na-K-A at low temperatures as suggested by the results of SCXD, MAS-NMR, and MD is as follows:

1) The cause of the non detection of Na at 8-member rings for calcined Na-A and Na-K-A was inferred to be the irregular location of Na inside 8-member rings, and the relocation of Na from 8-member rings to other rings was substantiated.
2) According to the commonly accepted priority of K ion exchange with Na in Na-A, Na atoms at 8-member rings were exchanged first, followed by exchange of Na at 4- and 6-member rings. However, our SCXD results indicated that K was relocated to 6-member rings. Thus, the conventional explanation, that the windows shrink to 3 Å and neither oxygen nor nitrogen can be adsorbed, is avoided.
3) According to MAS-NMR of 27Na at high temperatures by Veeman, the Na position at 8-member rings was found to be symmetric at low temperatures, becoming asymmetric at high temperatures and this symmetry/asymmetry was reversible by varying the temperature. In this study, Na-A and Na-K-A which were calcined at a higher temperature and measured at room temperature showed similar spectra to those reported by Veeman. This indicates that our calcination of Na-A and Na-K-A resulted in a significant and irreversible positional change of Na inside the window.
4) The atomic positions of Na-A determined by Seff and those of Na-K-A determined by the authors were used as the input data for MD calculation and

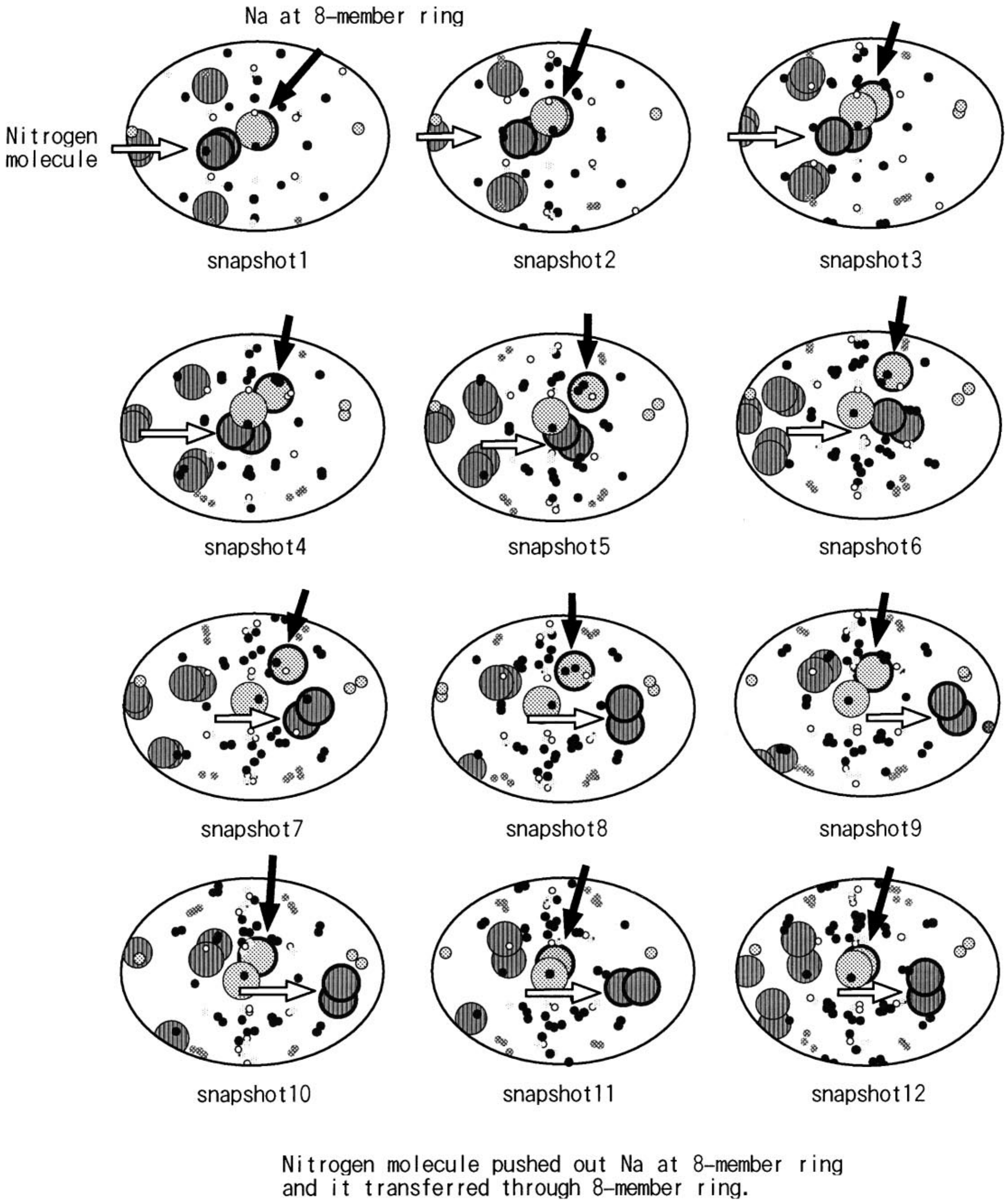

Figure 6. Snapshot of nitrogen molecule transferring through 8-member ring.

oxygen and nitrogen behavior inside crystals were simulated by MD as follows:

(1) At room temperature both oxygen and nitrogen could be transferred from one crystal to neighboring crystals. However, when the adsorption temperature decreased, less nitrogen was transferred than oxygen could.

(2) According to a visualization of nitrogen transfer through 8-member ring, nitrogen pushed away Na, and passed through after which Na returned to its normal position.

(3) The MSDs of nitrogen and oxygen inside Na-A and Na-K-A crystals were evaluated; the MSD of oxygen was smaller than that of nitrogen in lower temperature regions in the cases of Na-A

and Na-K-A and the MSD of oxygen in Na-K-A was smaller than that in Na-A.

Nomenclature

Z	Electric charge (e)
A	Particle length (Å)
b	Particle length (Å)
c	Van der Waals force (kJ/mol$^{1/2}$ Å^3)
Greek Letters	
γ	Inter-atoms distance between atom-α and atom-γ
γ^*	Equilibrium inter-atoms distance between atom-α and atom-γ
Suffix	
α, β, γ	Atoms of three points charge for BMH potential
i, j	Atoms for Morse potential, and Watanabe-Austin potential

Acknowledgment

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