Adsorption 7, 27–39, 2001

Oxygen Selectivity on Partially K Exchanged Na-A Type Zeolite at Low Temperature

JUN IZUMI
Mitsubishi Heavy Industry Co. Ltd., Nagasaki R&D Center, 5-717-1 Fukahori, Nagasaki 851-0392 Japan

MOTOYUKI SUZUKI
Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106 Japan

Received August 20, 1999; Revised October 25, 2000; Accepted November 6, 2000

Abstract. In previous work by the authors on Na-A zeolite (Izumi et al., Japan Patent Toku-Kou-Shou 63-058614, 1988), it was shown that the combination of high-temperature calcination and operation of the adsorption step at low temperatures improved the selectivity for oxygen over nitrogen from air (Izumi et al., *CATS J Meeting Abstracts*, **31**(2A), 10, 1989; Izumi and Suzuki, *Adsorption*, **6**, 2000). Berlin discloses in his U.S. Patent 3282028 (1966) that the partial exchange of potassium ions for sodium ions in the Na-A type zeolite also improved selectivity for oxygen by reducing the uptake rate of nitrogen. It was therefore expected that the oxygen selectivity of Na-K-A with high-temperature calcination and low-temperature adsorption might be enhanced. For the confirmation of optimum conditions for the appearance of oxygen selectivity on Na-K-A, samples were prepared with a K exchange ratio varied from 0–20 mol% (0–2.4 K ions/unit cell), and a calcination temperature varied from 923 to 1073 K, and an experiment concerning oxygen and nitrogen adsorption on Na-K-A was undertaken with a small adsorbent column under pressure swing adsorption (PSA) conditions at adsorption temperatures from room temperature to 213 K. It was found that (a) the K exchange ratio of 7 mol% (0.84 K ions/unit cell), and (b) the calcination temperature of 993 K, resulted in a remarkable increase in oxygen selectivity. Under optimum conditions for Na-K-A, the oxygen separation factor was about 8. Na-K-A has the potential to effectively separate oxygen and nitrogen from air by means of PSA.

Keywords: Na-K-A, oxygen selectivity, pressure swing adsorption, low temperature

Introduction

When Na-A subjected to high-temperature recalcination after hydration (calcined Na-A) was used as an adsorbent for oxygen adsorption separation from air with PSA at room temperature, it was confirmed in the previous reports that Na-A showed nitrogen selectivity in a longer cycle, but, in a comparatively short cycle of adsorption time of 30 seconds and adsorption temperature of 213 K, extremely strong oxygen selectivity was indicated by a separation factor of 6.5, with an oxygen adsorption amount eight times greater than that at room temperature, demonstrating excellent oxygen adsorption performance.

This behavior was understood as the molecular sieve effect, such that the 4 Å window diameter of Na-A was shrunken to less than to the 4.2 Å × 3.2 Å molecular diameter of nitrogen (Takaishi, 1985). In addition, Berlin disclosed that partially K exchanged Na-A showed oxygen selectivity (Berlin, 1966) and a similar phenomenon has also been reported by authors (Izumi et al., 1988, 1989; Izumi and Suzuki, 2000; Ruthven et al., 1990; Knaebel et al., 1988). Therefore, if Na-K-A with high-temperature calcination is used as an oxygen adsorbent for PSA oxygen recovery at a low temperature, it was expected to show even greater oxygen selectivity at a low temperature than did calcined Na-A.

Given this expectation, (a) a higher concentration of recovered oxygen, (b) a higher oxygen selectivity at a longer adsorption time, and (c) a reduction in cool heat due to the shift toward a higher adsorption temperature were all expected in comparison with Na-A. Na-K-A pellets were prepared with K exchange ratios of 0 to 25 mol% (3 K ions/unit cell) and at calcination temperatures of 923 to 1073 K for evaluation of oxygen selectivity using a small column apparatus. Adsorption separation was conducted at a low temperature in an oxygen-nitrogen binary system, and Na-K-A oxygen selectivity was studied while comparing the behavior of Na-A.

Experiment

Preparation of the Adsorbent

Figure 1 shows the preparation procedure for extruded pellets of a partially K exchanged Na-A. After Na-A powder (adsorbent grade, manufactured by UOP Ltd.) was saturated with water vapor at 298 K overnight to eliminate adsorbed nitrogen and oxygen, 100 grams of Na-A powder was added to 1 liter of pure water, and the mixture was stirred with a magnet stirrer to produce slurry. KCl liquid was added to the slurry, and, with care taken not to exceed a KCl concentration of 1 w%, the desired ion exchange ratio was attained. Stirring was continued for 30 minutes, and Na was partially exchanged with K according to an ion exchange reaction (1).

$$\begin{aligned}&\mathrm{Na_{12}\cdot(SiO_2)_{12}\cdot(AlO_2)_{12}} + n\mathrm{K^+}\\&\quad\rightarrow \mathrm{Na_{(12-\mathit{n})}\cdot K_\mathit{n}\cdot(SiO_2)_{12}\cdot(AlO_2)_{12}} + n\mathrm{Na^+}\qquad(1)\end{aligned}$$

The slurry was filtered to produce zeolite cake, and, for each 100 grams of zeolite (dry standard), 20 grams of kaolin binder, and 15 grams of cellulose porosity additive agent were thoroughly mixed in, and extruded pellets with a diameter of 1.6 mm were formed using an extruder. The wet pellets were first dried in an electric furnace for 1 h at 373 K to remove surface water, and the temperature was then raised to 923 K at a rate of 100 K/h and maintained for 1 h for calcination and in preparation for the small column experiment.

In order to better understand the main factors influencing oxygen selectivity (i.e., the calcination temperature and the K exchange ratio), samples were prepared

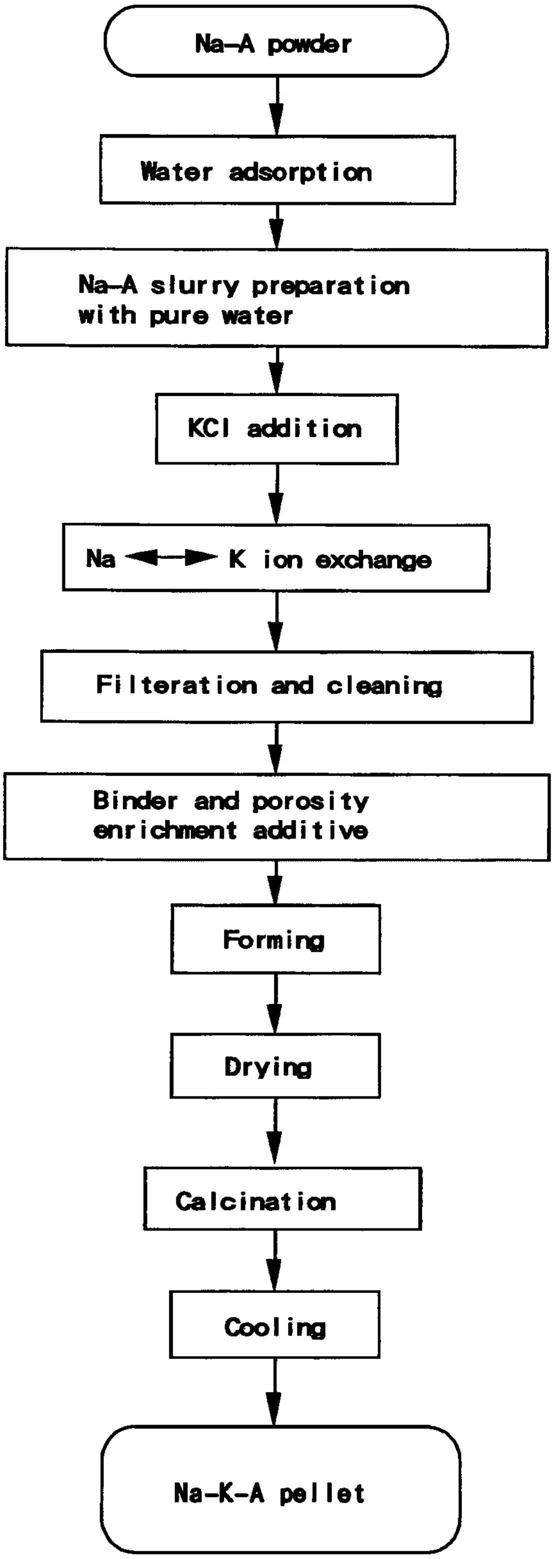


Figure 1. Procedure of Na-K-A preparation.

at temperatures of 923 to 1073 K and with K exchange ratios of 0 to 25 mol% (3 K ions/unit cell). For each Na-K-A of 1 mol, K exchange ratio R was defined as in Eq. (2). (Na was a mol, K was b mol, respectively, and Fluorescence x-ray diffraction was used for quantitative analysis of Na and K.)

$$R = b/(a + b) \tag{2}$$

Na-A was treated with the recalcination after the hydration, the oxygen adsorption selectivity at low temperature was enhanced strongly. Although the recalcination after the hydration was performed on Na-K-A, no enhancement of the oxygen selectivity could be found. Therefore, the recalcination after the hydration was not be applied to samples in this study.

Small Column Evaluation of Na-K-A Oxygen Selectivity

A small column adsorption technique is used to obtain adsorption equilibrium and rate characteristics of a bi-component system of oxygen and nitrogen. Figure 2 shows a schematic illustration of the small column apparatus. The adsorption column was made of a stainless steel cylinder, which was 10 mm in inner diameter and 250 mm in length. 10 to 15 grams of Na-K-A, which were in extruded cylindrical form of 1.6 mm in diameter, were loaded in the column. Then the column was placed in a refrigerator at a constant temperature, which can be set at arbitrary temperatures between 203 K and 298 K.

Mixture gases of oxygen and nitrogen at several concentration levels were prepared in cylinders. A cylinder of a premixed concentration gas was connected to the vacuum line with the adsorption column and oxygen analyzer. Inlet flow rate and pressure were controlled by the mass flowmeter equipped with the pressure gauge PCV. A mass flowmeter at the outlet of the column detects the change of flow rate and the zirconia electrode sensor was placed at the exit to measure the oxygen concentration of the exit gas. Evacuation of the column was made by the vacuum pump with V-3 opened and V-1 and V-2 closed. The amount of gas desorbed by evacuation was measured by a rotary flowmeter connected to the outlet of the vacuum pump and the oxygen electrode sensor was also installed at the outlet of the rotary flowmeter.

Procedure

Adsorption pressure was adjusted by the pressure gauge equipped at the inlet gas line and the programmed sequence of adsorption experiment starts as follows: (1) The valve V-1 is opened and the inlet gas of

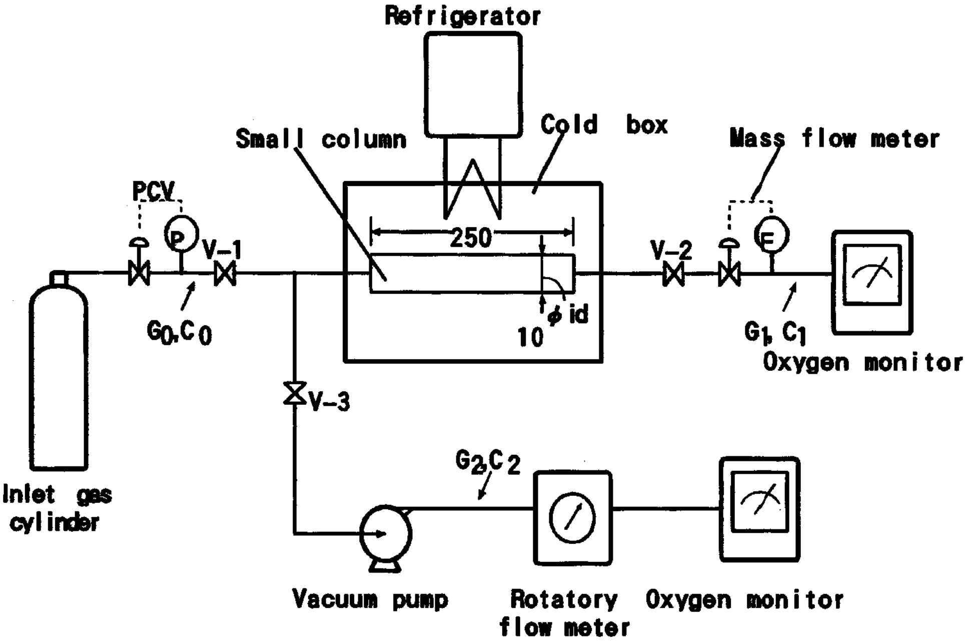


Figure 2. Schematic illustration of the small column apparatus.

oxygen concentration, C_0 was introduced in the column and the column pressure reached the adsorption pressure *Pa* (Pressurization step). This takes about five seconds. (2) Then the valve V-2 is opened and adsorption in the column from the inlet gas takes place (Adsorption step). During this period, flow rate and concentration of oxygen, G_1 and C_1, were measured. The duration of the adsorption step is programmed according to the experimental schedule between 10 and 420 seconds. (3) Valves V-1 and V-2 are closed and V-3 is opened and evacuation of the column is done (Desorption step). At the end of the desorption step, pressure reached below 13 Pa when the duration time was 2,000 seconds. The sequence of the small column apparatus is shown in Table 1 and measurement conditions are summarized in Table 2. Adsorption temperature, adsorption period and adsorption pressure were the parameters examined in this study and for each set of conditions, a sequence controller was programmed so that step (1), (2) and (3) were repeated for more than one hour. Then after the exit concentration profile became constant, the evacuation gas was analyzed: the total amount of desorbed gas, G_2 and the concentration (mole fraction) of oxygen in the desorbed gas, C_2, were determined from the gas collected at the exit of the rotary flowmeter.

Table 1. Sequence of the small column apparatus.

Step	Pressurization	Adsorption	Desorption
Valve			
V-1	○	○	
V-2		○	
V-3			○
Vacuum pump			○
Period (sec)	5	30–2000	600

Table 2. Measurement condition.

Adsorption pressure	120 KPa
Adsorption temperature	213–298 K
Outlet gas rate	500 ml N/batch
Sequence	
Pressurization	5 seconds
Adsorption	30–2000 seconds
Desorption	600 seconds
Desorption pressure	13 Pa
Adsorbent	Partially K exchanged Na-A pellet
Adsorbent weight	10–15 g
Small column size	10 mm ϕ id × 250 mml

Calculation of Amount Adsorbed

The amount of oxygen adsorbed during pressurization and adsorption periods is calculated by the following equation.

$$q_{O_2} = \{G_2 \cdot C_2 - G\text{dead,O}\}/w$$
$$q_{N_2} = \{G_2(1 - C_2) - G\text{dead,N}\}/w$$

where q_{O_2} denotes the adsorbed amount of oxygen on unit mass of zeolite and Gdead,O represents the amount of oxygen in the dead volume of the apparatus. w denoted the amount of adsorbents packed in the column, Gdead,O is estimated from the dead volumes at the inlet part of the apparatus, V_f in the column, V_m and at the exit part of the apparatus, V_r.

The temperatures of these parts are, respectively, T_f, T_m and T_r, Oxygen concentration at the inlet part is C_O, and at the exit is C_{1E} and then in the column is assumed as $C_m = (C_O + C_{1E})/2$. Then the following equations are used for calculation of Gdead,O and Gdead,N.

$$G\text{dead,O} = Pa\left(V_f \cdot \frac{273}{T_f} \cdot C_0 + V_m \cdot \frac{273}{T_m} \cdot C_m + V_r \cdot \frac{273}{T_r} \cdot C_{1E}\right)$$

$$G\text{dead,N} = Pa\left(V_f \cdot \frac{273}{T_f} \cdot (1 - C_0) + V_m \cdot \frac{273}{T_m} \cdot (1 - C_m) + V_r \cdot \frac{273}{T_r} \cdot (1 - C_{1E})\right)$$

Regarding the average concentration in the column, C_m, the approximation assumed here should not introduce appreciable error since the exit concentration at the end of adsorption step, C_{1E}, is close to the concentration at the inlet, C_O. The adsorbed amount of nitrogen is obtained in a similar way by replacing fractional concentration of oxygen C by nitrogen concentration C_N which is equal to $1 - C$.

As a sequence mode in the current experiment is presented in Table 2, the required times for (1) the pressurization stage, (2) the adsorption stage, and (3) the regeneration stage were arbitrarily adjusted, and the process sequence was repeated for several hours.

Following the stabilization of the outlet oxygen concentration profile of the adsorption stage, flow volume, concentration, and pressure were measured. Because the oxygen and nitrogen adsorption rates of calcined

Na-A are relatively rapid even at a low temperature of approximately 213 K, a steady state was achieved in 1 to 2 h. However, the nitrogen adsorption rate of Na-K-A samples with high K exchange ratios is extremely slow and the achievement of a steady state required about 8 h.

Using the above-described operational method, oxygen selectivity was evaluated for a number of different types of Na-K-A under conditions of (1) adsorption temperature of 243 K, (2) adsorption time of 60 seconds, (3) adsorption pressure of 120 KPa, which were considered to be conducive to the stable appearance of oxygen selectivity.

The K exchange ratio was from 0 to 25 mol% (3 K ions/unit cell), and the calcination temperature was from 923 to 1073 K. Subsequently, for the confirmation of the dependence of oxygen selectivity at low temperatures on the K exchange ratio and calcination temperature, Na-K-A samples were evaluated by means of a small column experiment at 243 K. Quantitative analysis was conducted to evaluate (a) the oxygen adsorption amount, (b) the nitrogen adsorption amount, and (c) the dependence of the oxygen separation factors on (1) adsorption temperature, (2) adsorption time, and (3) adsorption pressure.

Results and Discussions

Influence of K Exchange Ratio and Calcination Temperature on the Oxygen Selectivity of Na-K-A.

To determine the optimum K exchange ratio and calcination temperature, Na-K-A samples (K exchange ratio from 0 to 25 mol% (3 K ions/unit cell) and temperatures from 923 to 1073 K) were prepared, and a small column apparatus was used to evaluate the oxygen selectivity of the PSA adsorbent at the target temperature of 243 K, which is rather higher than the optimum adsorption temperature of 213 K for Na-A.

Figure 3 shows the relationships between the K exchange ratio and the oxygen and nitrogen adsorption amounts q_{O_2} and q_{N_2} at adsorption pressure of 120 KPa, regeneration pressure of 0.013 KPa, adsorption time of 60 seconds, inlet oxygen concentration of 20.9 vol%, adsorption temperature of 243 K, and calcination temperature of 993 K (maintained for 1 h). Although the adsorption amounts of both oxygen and nitrogen decreased with increases in the K exchange ratio in the range from 0 to 15 mol% (0–1.8 K ions/unit cell), the adsorption amount of nitrogen decreased to a greater extent than that of oxygen, and, as a result shown in Fig. 3, the separation factor α_{O_2} defined by Eq. (2) expanded as the K exchange ratio increased.

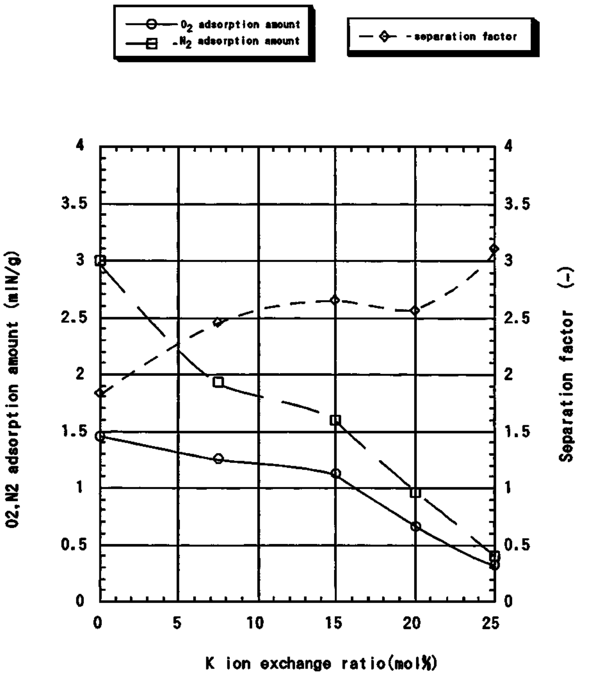


Figure 3. Relation between K ion exchange and oxygen selectivity (adsorption period 60 seconds, adsorption temperature 243 K, adsorption pressure 120 kPa, inlet O_2 conc. 20.8 vol%, recalcination temp. 993 K).

$$\alpha O_2 = (q_{O_2}/P_{O_2})/(q_{N_2}/P_{N_2}) \tag{2}$$

Although the separation factor is generally used at equilibrium conditions, because the adsorbed amounts of oxygen and nitrogen depend upon the adsorption time in this study, this factor was expanded for use with the dynamic adsorption amounts in correspondence with the adsorption time. However, the adsorption amount of oxygen decreased sharply when the K exchange ratio increased beyond 15 mol%(1.8 K ions/unit cell), and, when the ratio reached 25 mol% (3 K ions/unit cell), neither oxygen nor nitrogen could be adsorbed. According to Takaishi (1985), eight of the 12 atoms of Na in Na-A are positioned in a sodalite cage at the S_I site, three are at the window of the S_{II} site, and the remaining one is free Na belonging to the S_{III} site.

It can be accordingly explained that K would be exchanged mainly with Na at the S_{II} window site when the K exchange ratio is 25% or less. The exchanged K would first make the window smaller to 3 Å, then, when the ratio surpasses 25 mol% (3 K ions/unit cell), the exchange would take place at the S_I sodalite site (At this time all windows would be shrunken to 3 Å.) (Takaishi, 1985).

Based on this mechanism, it was predicted in the current research that, even with a K exchange ratio of less than 25 mol% (3 K ions/unit cell), the 4 Å 8-member ring window of Na-A would quickly shrink to 3 Å, and that neither oxygen (2.8 × 3.8 Å) nor nitrogen (3.2 × 4.2 Å) could not be adsorbed (Takaishi, 1985).

What was in fact observed in response to K exchange, however, was an extreme decline in the adsorption amount of nitrogen and a gentle decline in that of oxygen. This suggests the existence of a continuous window diameter reduction mechanism, not explainable by means of the traditional understanding of the Na-A/K-A molecular sieve effect in terms of an immediate reduction of the Na-A window diameter from 4 Å to 3 Å with the K exchange.

Also, as it was judged that the calcination conducted along with K exchange led to sub-angstrom reduction of the window diameter, the oxygen selectivity was evaluated while holding the K exchange ratio at a constant 7 mol% (0.84 K ions/unit cell) and varying the calcination temperature from 923 to 1073 K, as shown in Fig. 4.

Since Na-K-A at a calcination temperature of 923 K showed the nitrogen selectivity, a temperature increase was accompanied by a highly rapid decline in the adsorption amount of nitrogen and a gentle decline in that of oxygen. As a result, the separation factor surpassed 1 at 973 K and oxygen selectivity was exhibited. When the calcination temperature was raised further,

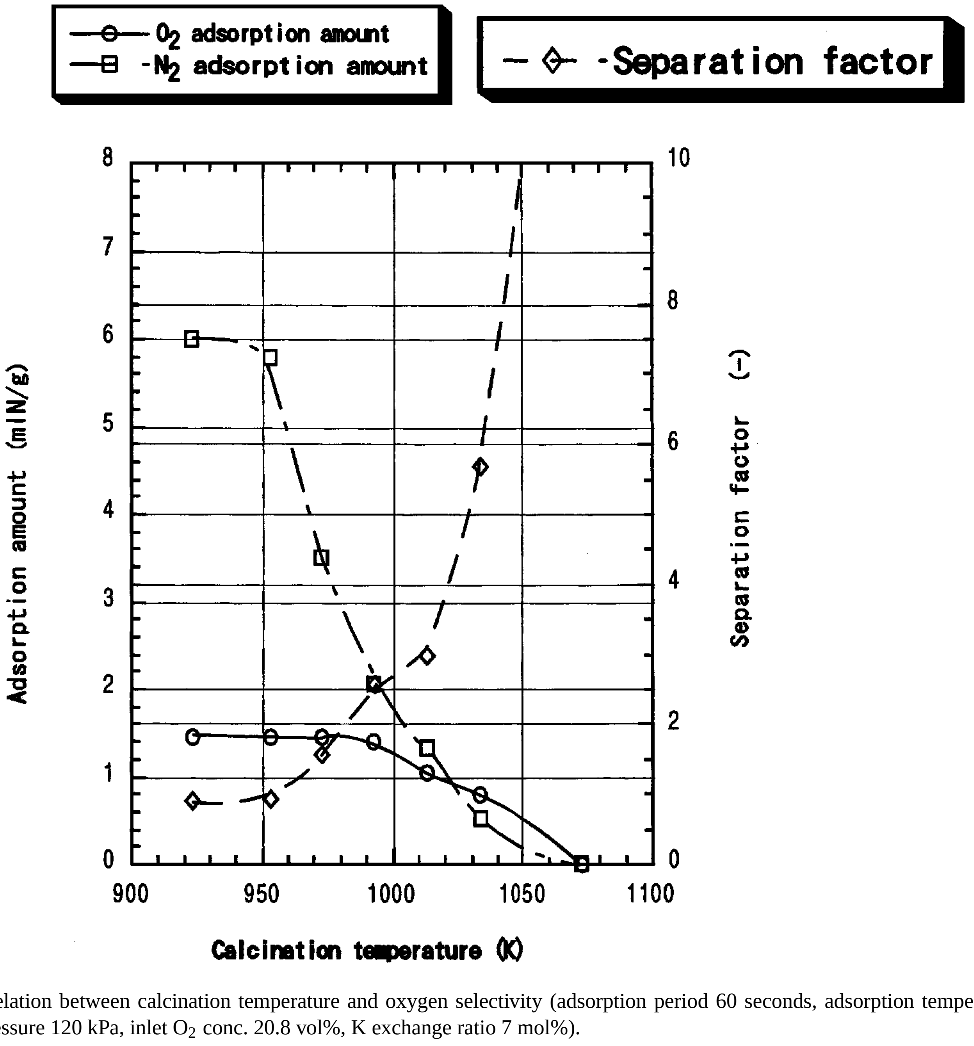


Figure 4. Relation between calcination temperature and oxygen selectivity (adsorption period 60 seconds, adsorption temperature 243 K, adsorption pressure 120 kPa, inlet O_2 conc. 20.8 vol%, K exchange ratio 7 mol%).

however, the adsorption amounts of both oxygen and nitrogen dropped rapidly at 1073 K.

This result supports the speculation that the appearance of a molecular sieve effect is related to the gradual shrinkage of the Na-K-A window diameter and the adsorption rate of nitrogen as a larger molecule falls more than that of oxygen as a smaller molecule. Then, at 1073 K, thermal decomposition of Na-A (which does not have particularly high heat resistance) begins, and the adsorbent stops functioning.

Given the above-stated results, when Na in Na-A was partially exchanged with K and calcination was conducted at temperatures between 973 to 1033 K, it was confirmed that the separation factor surpassed 3 and samples subsequently showed extremely high oxygen selectivity at an adsorption temperature of 243 K. The most applicable oxygen adsorbent for PSA was identified as having a K exchange ratio of 7 mol% (0.84 K ions/unit cell) and a calcination temperature of 993 K (with 1 h holding time).

Compared with the oxygen separation factor of 1.5 shown by Na-A calcined samples under the same conditions (Izumi and Suzuki, accepted), this represents a major improvement. Na-K-A prepared under the above mentioned conditions was found to show strong oxygen selectivity at 243 K and it was determined that Na-K-A has the potential to be used as a suitable oxygen adsorbent for PSA oxygen recovery.

A sample with a K exchange ratio of 7 mol% (0.84 K ions/unit cell) and a calcination temperature of 993 K (kept for 1 h), was evaluated using a small column apparatus. Relationships were studied between an operating conditions such as (1) adsorption temperatures between 298 and 213 K, (2) adsorption time between 30 and 2,000 seconds, and (3) equilibrium adsorption amounts in an oxygen-nitrogen binary system on the one hand and oxygen adsorption properties such as a) oxygen adsorption amount, b) nitrogen adsorption amount, and c) separation factor on the other.

Oxygen Concentration Profiles at Outlet

Figure 5 shows oxygen concentration profiles at the column outlet, as observed under conditions of adsorption time between 0 and 300 seconds, inlet oxygen concentration of 20.8 vol%, outlet flow rate of 500 ml N/batch, adsorption pressure of 120 KPa, and adsorption temperatures of 298, 273, 243, and 213 K.

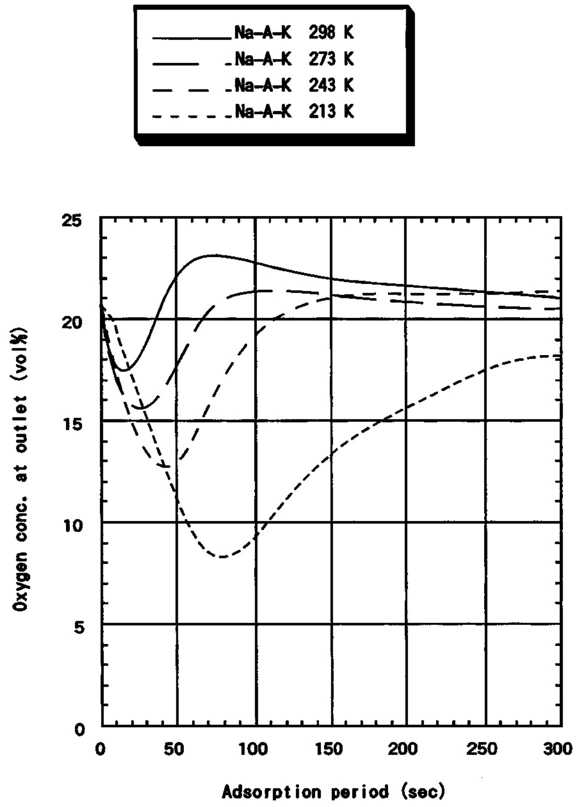


Figure 5. Oxygen profiles at column outlet (K exchange ratio 7 mol%, 993 K, 1 hour calcination).

For previously noted calcined Na-A, oxygen concentration fell below inlet concentration at about 40 seconds following the start of adsorption, and, after showing a minimum concentration of 18 vol%, oxygen concentration again surpassed inlet concentration to reach 22 vol%. It then gradually subsided back to inlet concentration. For 7 mol% (0.84 K ions/unit cell) K exchanged Na-K-A at 298 K, however, the time until oxygen concentration fell below inlet concentration was extended to about 40 seconds, the minimum concentration decreased to 17.5 vol%, and the subsequent maximum was limited to 23.5 vol%, showing considerable improvement in oxygen selectivity.

When the adsorption temperature was reduced to 273 K, the outlet oxygen concentration declined to 16.5 vol% and then rose again, but the maximum concentration stopped at 21.5 vol%, and the high concentration peak disappeared in the same manner as calcined Na-A, from which it can be seen that the nitrogen adsorption rate decreases greatly at low temperature in the same way as calcined Na-A. At an adsorption temperature of 243 K, outlet oxygen concentration fell to 12.8 vol%, with the subsequent rise stopping at a maximum value of 21 vol% and the decrease in the nitrogen adsorption rate became even more pronounced.

At 213 K, the concentration dropped to 8 vol%, and the rise thereafter did not surpass the inlet oxygen concentration. As the value at the end of the adsorption stage was still 18 vol%, it was confirmed that the adsorption amount of oxygen was greater than that of nitrogen over the entire period of the adsorption stage. As calcined Na-A at 213 K showed the minimum value of 12 vol% and the value at the end of the adsorption stage of 20 vol%, the oxygen selectivity of Na-K-A was more pronounced than that of calcined Na-A at low temperature.

Dependence of Adsorption Time on the Adsorption Amounts of Oxygen and Nitrogen

Nitrogen and oxygen adsorption amounts q_{O_2} and q_{N_2}, as well as the separation factor α_{O_2} were evaluated under the same basic conditions as for oxygen selectivity, again at the temperatures of 298, 273, 243, and 213 K, and with a gas volume of 500 ml in each batch. The results are shown in Fig. 6. As the nitrogen adsorption rate decreased in the low-temperature range for Na-K-A, the time required to reach the equilibrium adsorption amount for Na-A (420 seconds) was seen to be insufficient, and the time was extended to 2,000 seconds.

Figure 6 shows that the oxygen adsorption amount at 298 K was constant during the adsorption time from 30 to 2,000 seconds meaning that equilibrium was reached within the short period of less than 30 seconds. When the oxygen adsorption amount of Na-K-A is compared with calcined Na-A, the adsorption amount of the former is two times larger than that of the latter. As the calcination process for Na-K-A is much simpler than that for calcined Na-A, the oxygen adsorption amount appears to be effectively maintained.

For nitrogen adsorption, however, Fig. 6 shows that only about 40% of the equilibrium adsorption amount was realized at the 30 second mark, and that it was eventually reached during the extended adsorption time period, at about 300 seconds. As calcined Na-A took about 1,000 seconds to reach an equilibrium adsorption amount, the nitrogen adsorption rate of calcined Na-A was smaller than that of Na-K-A. However, the nitrogen adsorption amount of Na-K-A is smaller than that of calcined Na-A by 25%.

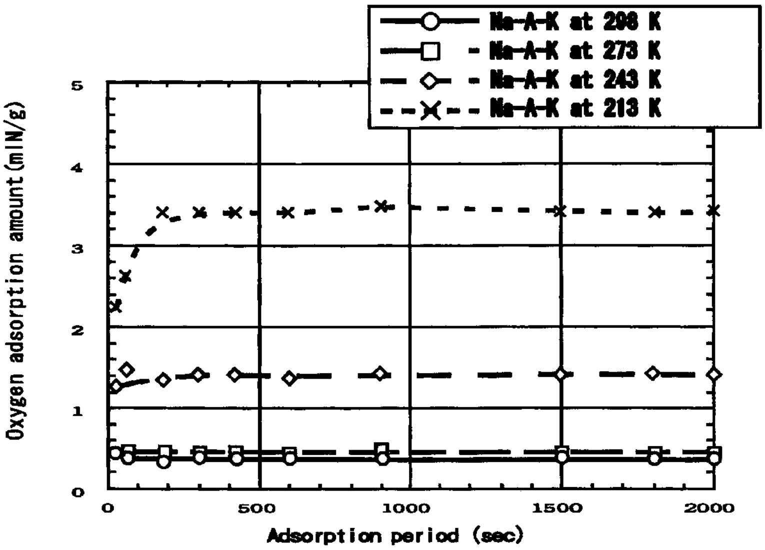
Even in a comparatively short adsorption time of 30 seconds, the separation factor for calcined Na-A did not surpass 1, and only nitrogen selectivity or azeotropic property was shown. For Na-K-A at an adsorption time of 30 seconds, however, the separation factor exceeded 1, and it was confirmed that oxygen selectivity was exhibited even at room temperature.

It is thus expected that, in cases where a large amount of oxygen adsorption from air is not required (e.g., nitrogen generation), Na-K-A could be employed similarly to molecular sieves carbon (MSC3A) in practical use (Chihara, 1977).

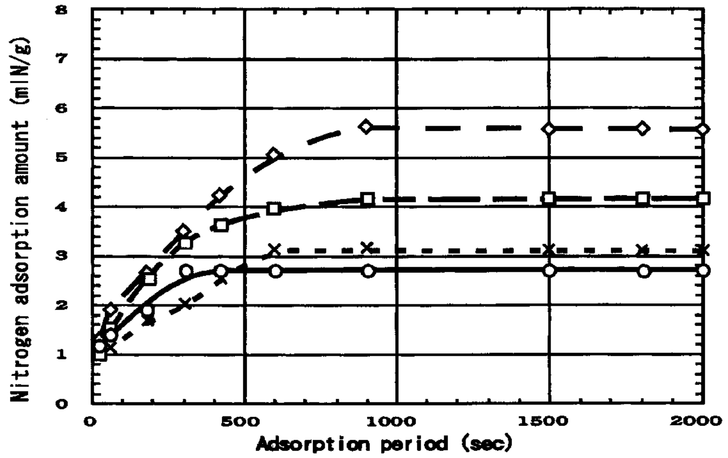
The oxygen adsorption amount at 273 K was not particularly different from that at 298 K. For the nitrogen adsorption amount, an extended period of 900 seconds was required to reach the equilibrium nitrogen adsorption, it was recognized that the nitrogen adsorption rate had decreased. Nevertheless, as the equilibrium adsorption amount increased by approximately 1.7 times, it was seen that the separation factor at an adsorption temperature of 273 K, like that at 298 K, exceeded 1 and indicated oxygen selectivity for an adsorption time of 30 seconds only.

At 243 K, however, the oxygen adsorption amount increased by about 2.5 times of that at 298 K and 273 K, and 90% of the equilibrium adsorption amount was reached in an adsorption time of 30 seconds. The time required to reach the equilibrium nitrogen adsorption amount was 2,000 seconds and Na-K-A demonstrated a further fall in the nitrogen adsorption rate. Although the separation factor gradually declined with increased adsorption time, it was thus 3.8 at an adsorption time of 30 seconds. As it was in excess of 1 until 450 seconds, Na-K-A showed highly pronounced oxygen selectivity.

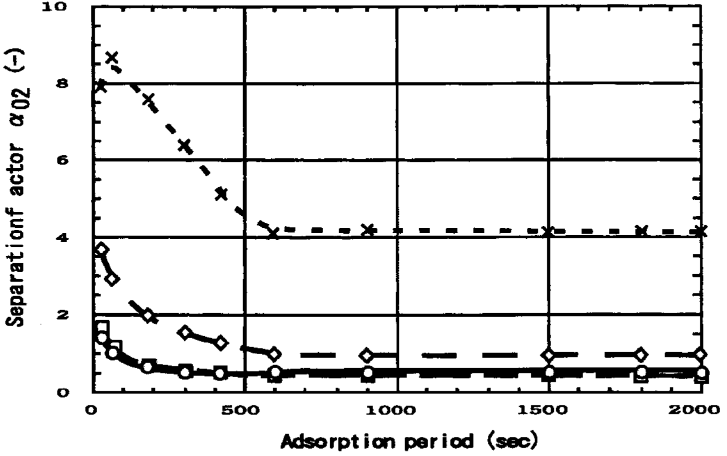
At an adsorption temperature of 213 K, the equilibrium oxygen adsorption amount was seven times that at room temperature. However, the adsorption amount at an adsorption time of 30 seconds was only 60% of the equilibrium amount, showing that not only the adsorption rate for nitrogen but also that for oxygen had decreased substantially. While calcined Na-A showed the overshoot phenomenon whereby the oxygen adsorption amount increases beyond the equilibrium adsorption amount at an earlier point in the adsorption stage, Na-K-A did not exhibit overshoot. The nitrogen adsorption rate was extremely slow, as was the case at 243 K, but it should be pointed out that the nitrogen equilibrium adsorption amount at 213 K was less than that at 243 K. This phenomenon was observed with Na-A as well, but was even more noticeable with Na-K-A.



a)Oxygen adsorption



b)Nitorgen adsorption

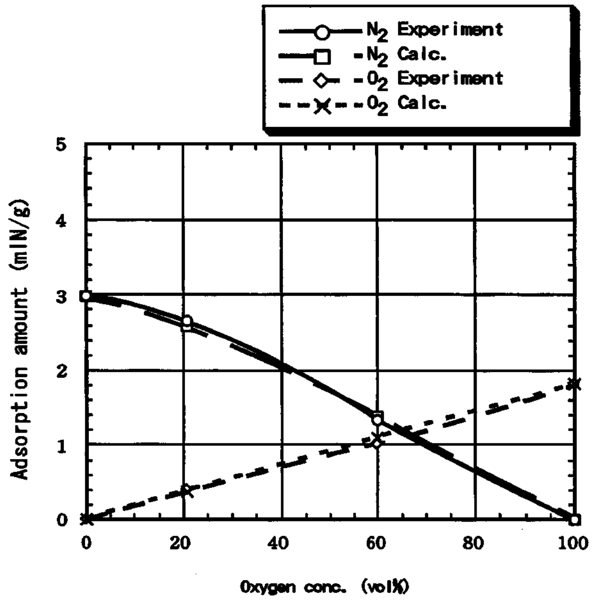


c)Separation Factor

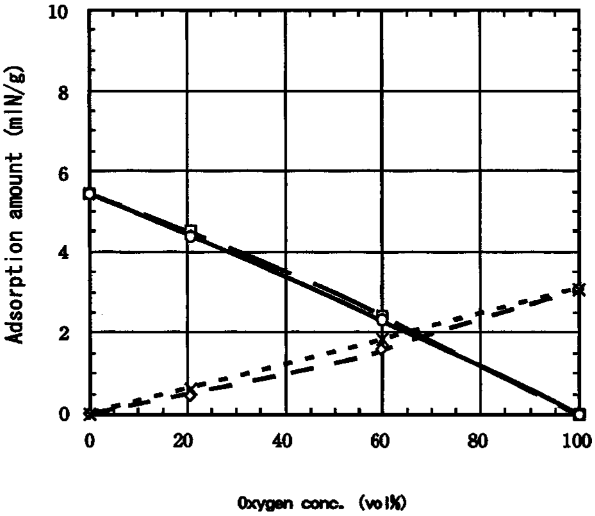
Figure 6. Dependence of adsorbed amounts on adsorption period (Na-K-A).

Takaishi (1985) has suggested a mechanism regarding nitrogen adsorption hindrance and he speculated that, because the bond between Na and Al at the S_{II} site is quite weak, even for molecules larger than the window diameter, Na would be slightly shifted by the adsorption molecule and adsorption would take place at a high temperature. At low temperatures, however, the increased strength of the Na-Al bond would make adsorption more difficult. The details of this mechanism have not yet been clarified, but it is supposed that partial exchange of K influences the degree of shifting of Na or K at the window.

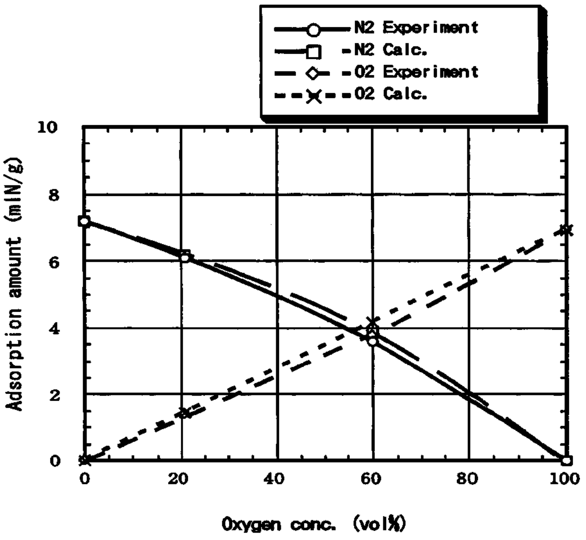
As a result, a separation factor of nearly 8 was achieved at an adsorption time of 30 seconds and an extremely strong oxygen selectivity was shown. As the maximum value of the separation factor for calcined



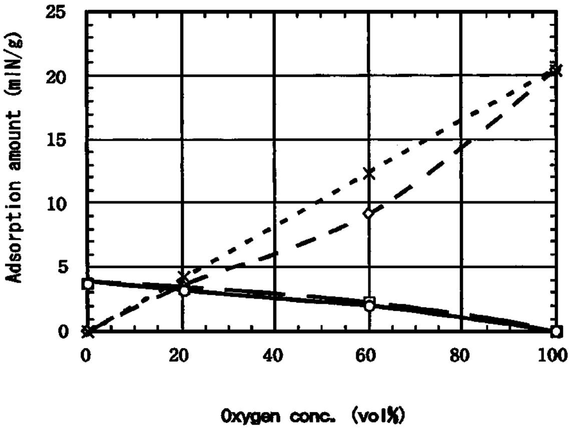
a) Adsorption temp. 298K



b) Adsorption temp. 273 K



c) Adsorption temp. 243 K



d) Adsorption temp. 213 K

Figure 7. Equilibrium adsorption amount of oxygen and nitrogen under bi-component system (Na-K-A).

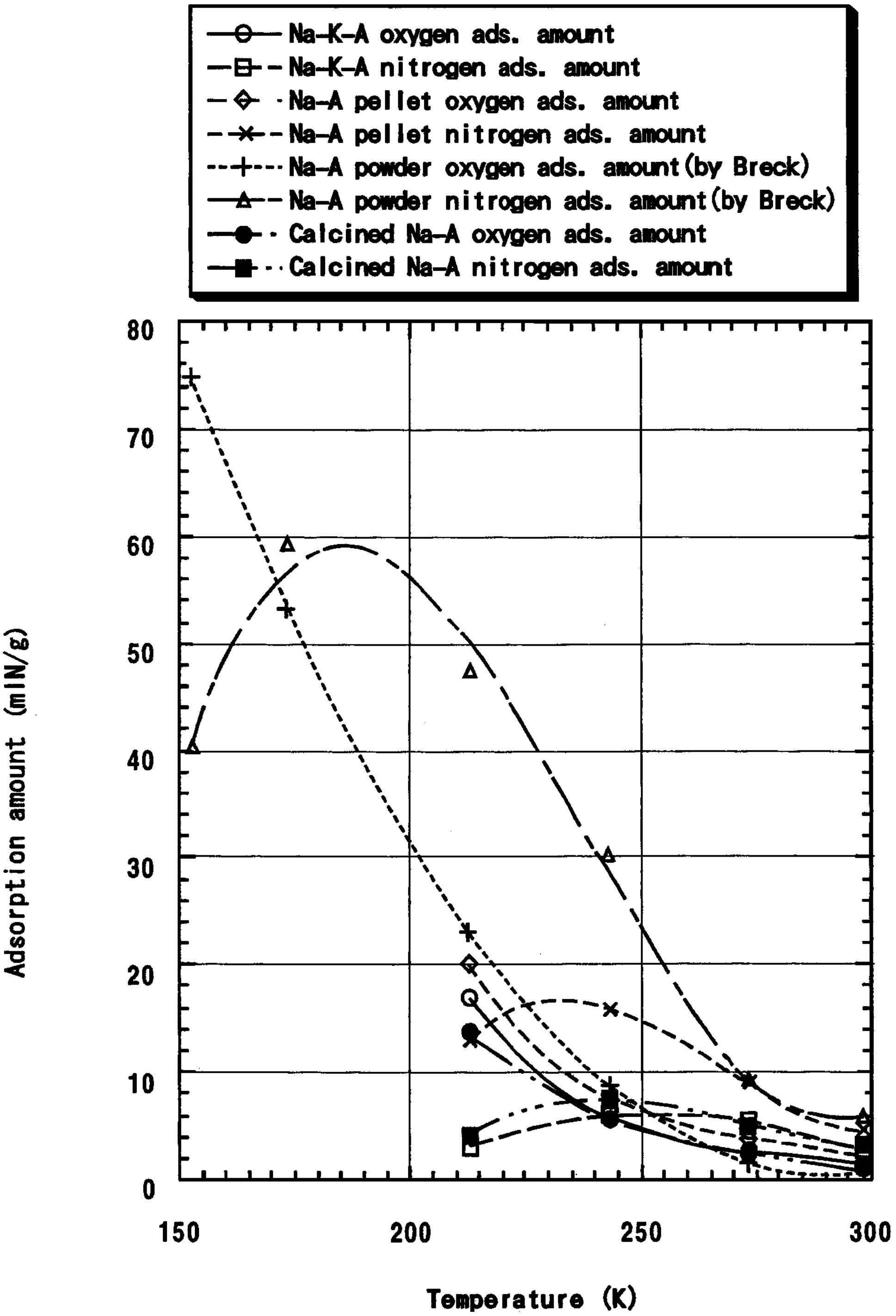


Figure 8. Isobar of oxygen and nitrogen on Na-K-A (adsorption pressure 100 kPa).

Na-A at 213 K and an adsorption time of 30 seconds was 6.5, the separation factor of 8 for Na-K-A was the largest value thus far identified.

The additional electric power consumption required for cool heat by PSA oxygen recovery at a low temperature of 213 K is much smaller than that needed for cryogenic separation which is operated at about 83 K. As no adsorbent shows such a high oxygen selectivity and oxygen adsorption amount at room temperature, PSA oxygen recovery with Na-K-A at 213 K would probably allow the lowest electric power consumption per unit oxygen volume as well as the lowest use of adsorbent.

Equilibrium Adsorption Amounts in an Oxygen-Nitrogen Binary System

As the phenomenon was confirmed that the oxygen adsorption under calcined Na-A low-temperature adsorption conditions was affected by co-adsorbed nitrogen and the oxygen adsorption amount was reduced, the behavior of Na-K-A was evaluated under equilibrium adsorption conditions in an oxygen-nitrogen binary system. Figure 7 shows the relationships between oxygen concentration and the equilibrium adsorption amounts of oxygen and nitrogen at a pressure of 120 KPa and at adsorption temperatures of 298 to 213 K.

At 298 K, as shown in Fig. 7, derived adsorption amounts for a single component system (N_2 calc. and O_2 calc.) a are very close to the amounts actually measured in a binary system. However, while the derived nitrogen adsorption amount and the measured adsorption amount exhibit a close correlation as temperature decreases, the measured value for oxygen becomes lower than the value derived for the single component, and it showed the effect of co-adsorbed nitrogen.

Figure 8 represents the adsorption isobar for oxygen and nitrogen on (1) Na-K-A, (2) calcined Na-A and (3) Na-A-powder as measured by Breck (1959) in a single component system, with respective partial pressures of oxygen and nitrogen of 1 atm, and at adsorption temperatures of 298 to 213 K. Although the Na-K-A used here showed an increase in oxygen adsorption amount with decreasing temperature, the adsorption amount of nitrogen reached a maximum in the vicinity of 243 K and decreased thereafter.

It can be seen that the temperature at which the maximum nitrogen adsorption amount is given for Na-K-A is shifted in the direction of higher temperature in comparison to that for Na-A powder. Thus, the cross-point of the adsorption amounts of oxygen and nitrogen is at about 173 K for Na-A powder and at about 238 K for Calcined Na-A samples, but this point shifts substantially in the higher temperature direction to about 243 K for Na-K-A.

This fact suggests that the appearance of oxygen selectivity is due to partial exchange of K in Na-A and high temperature calcination, which results in the reduction of the window diameter and a corresponding hindrance of the adsorption of nitrogen. Although calcined Na-A showed oxygen selectivity at less than 228 K even under equilibrium conditions in an oxygen-nitrogen binary system, Na-K-A showed the oxygen selectivity under the same conditions at a higher temperature of 243 K.

Conclusion

As Na-A with (1) a partial exchange of K and (2) a high temperature calcination showed high oxygen selectivity under low-temperature PSA conditions, samples in this study (Na-K-A) were evaluated in the temperature range from room temperature to 213 K, and the following results were obtained.

1. Na-K-A with a 993 K calcination temperature and a partial K exchange ratio adjusted in the range from 0–15 mol% (0–1.8 K ions/unit cells) was evaluated under conditions of 243 K adsorption temperature, 60 seconds adsorption time, 20.8 vol% inlet oxygen concentration, and the oxygen adsorption amount decreased with an increase in the K exchange ratio; the decrease in the nitrogen adsorption amount was particularly large, with the result that extremely strong oxygen selectivity was shown. However, an increase in the K exchange ratio to 15 mol% (1.8 K ions/unit cell) or more resulted in major decreases in the adsorption amounts of both oxygen and nitrogen, and no adsorption amount could be measured at a ratio of 25 mol% (3 K ions/unit cell).
2. Na-K-A was prepared with a K exchange ratio of 7 mol% (0.84 K ions/unit cell) and calcined in the temperature range of 923–1073 K. When the calcination temperature was increased, the adsorption amount of oxygen decreased and the adsorption amount of nitrogen decreased even further, showing an extremely strong oxygen selectivity. However, due to the thermal decomposition of Na-A at temperatures of 1073 K and above, no adsorption

amounts of either oxygen or nitrogen could be measured.

(3) Na-K-A showed a stronger oxygen selectivity than calcined Na-A at low temperatures. For example, when the oxygen adsorption behavior of Na-K-A was evaluated at 213 K and an adsorption time of 30 seconds, Na-K-A showed a separation factor of 8, the most remarkable oxygen selectivity of any oxygen adsorbent examined. The oxygen selectivity of Na-K-A is 20% larger than that of calcined Na-A and the oxygen adsorption amount of Na-K-A is twice than that of calcined Na-A. Na-K-A can be therefore expected to be a good adsorbent for oxygen enrichment from air under low-temperature conditions.

(4) The transition temperature of 243 K from nitrogen selectivity to oxygen selectivity, identified under equilibrium conditions for Na-K-A at a K exchange ratio of 7 mol% (0.84 K ions/unit cell), represents a substantial shift in temperature from the 173 K for Na-A powder reported by Breck as well as from the 228 K for calcined Na-A, suggesting that the window diameter may have been reduced by K exchange and calcination.

(5) In an oxygen-nitrogen binary system, as with calcined Na-A, the measured adsorption amount of Na-K-A was smaller than that derived from a single component system, as the co-adsorption of nitrogen tended to limit oxygen adsorption.

Nomenclature

C	Concentration (mol/mol)
G	Gas flow rate (ml N/batch)
P	Pressure (Pa, atm)
R	K exchange ratio (mole/mole)
T	Temperature (K)
V	Dead volume (ml)
W	Adsorbent weight (g)
a	Mole number of Na in zeolite (mole)
b	Mole number of K in zeolite (mole)
q	Adsorption amount (ml N/g, g/g)
t	Time (sec)

Greek Letter

α	Oxygen separation factor (-)

Suffixes

a	Adsorption
d	Desorption
dead	Dead volume
f	Front part of the column
m	Middle part of the column
m	Mean value
r	Rear part of the column
0	Inlet in the adsorption stage
1	Outlet in the adsorption stage
2	Desorption line

References

Berlin, N.H. , US Patent 3282028, 1966.

Breck, D.W. and J.V. Smith, "Molecular Sieves," *Sci. Am.*, **280**, 85 (1959).

Chihara, K., Doctor thesis, University of Tokyo, 1977.

Izumi, J., H. Tsutaya, M. Kubo, T. Amitani, and K. Maehara, Japan Patent Toku-Kou-Shou 63-058614, 1988.

Izumi, J., A. Yasutake, K. Ohshima, N. Iwama, N. Funayama, and Y. Itakura, *CATSJ, Meeting Abstracts,* **31**(2A), 10 (1989).

Izumi, J., A. Yasutake, K. Ohshima, N. Iwama, N. Funayama, Y. Itakura, "Oxygen Selectivity of Na-A Type Zeolite Modified with Iron Additional and Partial Potassium Exchange," *Shokubai*, **31**(6), 397–400 (1989).

Izumi, J. and M. Suzuki,"Oxygen Selectivity on Na-A Type Zeolite at Low Temperature," *Adsorption*, **6**, 205–212 (2000).

Izumi, J. and M. Suzuki, "Oxygen Selectivity of Calcined Na-A Type Zeolite," *Adsorption*, **6**(1), 23–31 (2000).

Knaebel, K.S. and H.S. Shin, "Pressure Swing Adsorption: An Experimental Study of Diffusion-Induced Separation," *AIChE Journal*, **34**, 9 (1988).

Ruthven, D.M. and S.Farooq, "Air Separation by Pressure Swing Adsorption," *Gas Separation & Purification,* 4, 141–148 (1990).

Takaishi, T., "Physical Chemistry of Zeolite," *Koubutu Gakukaishi,* **17**(3) (1985).