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Oxygen Selectivity on Na-A Type Zeolite at Low Temperature

JUN IZUMI
Mitsubishi Heavy Industries, Co. Ltd., Nagasaki R&D Center, 5-717-1 Fukahori, Nagasaki 851-0392, Japan
junizumi@ngsrdc.mhi.co.jp

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

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Abstract. Na-A type zeolite (Na-A) shows favorable selectivity for nitrogen in an oxygen-nitrogen bi-component system at room temperature and also it is known that oxygen selectivity is dominated by differences in adsorption rates. In this study, the oxygen adsorption behavior of Na-A pellets at low temperature was evaluated. When temperature decreased, oxygen selectivity was enhanced as a result of the difference in adsorption rates. It was also strongly suggested that the oxygen equilibrium adsorbed amount of Na-A pellets was larger than that of nitrogen below 213 K. Na-A pellets are expected to be a good oxygen adsorbent for oxygen-nitrogen separation from air by pressure swing adsorption (PSA).

Keywords: Na-A type zeolite, Na-A pellets, oxygen selectivity, low temperature, rate selective adsorbent, pressure swing adsorption

Introduction

Na-A shows favorable selectivity for nitrogen in an oxygen-nitrogen bi-component system at room temperature (Berlin, 1966). The nominal window diameter of Na-A crystals is 4 Å, close to the molecular size of nitrogen, 4.2 Å × 3.2 Å. When the adsorption time is shortened, it has been reported that oxygen, which is smaller (3.8 Å × 2.8 Å) than nitrogen, is more selectively adsorbed on Na-A, suggesting that selectivity is dominated by the difference in adsorption rates (de Montgareuil, 1960; Izumi, 1987).

Given these characteristics, there have been several attempts to develop PSA processes, based on the oxygen selectivity of Na-A using rapid cycles.

Breck (1959) reported that the oxygen adsorbed amount on Na-A increased remarkably at low temperatures, while the nitrogen amount adsorbed showed a maximum at around 173 K. At temperatures lower than 163 K, Na-A is expected to show favorable adsorption selectivity for oxygen in terms of both equilibrium and rate characteristics.

These results suggest that Na-A shows not only greater oxygen selectivity but also improvement in the amount adsorbed, which are desirable characteristics for an adsorbent for oxygen recovery by PSA processes. As there have been few reports on oxygen/nitrogen separation from air on Na-A in the temperature range between room temperature and 163 K, this subject has been examined here in order to evaluate the appropriateness of the above speculation. A small column filled with extruded pellets of Na-A was used and oxygen selectivity performance was measured.

Experimental

A gas mixture of oxygen and nitrogen was introduced into a small column of zeolite pellets for a scheduled period and desorbed by evacuation of the column; the adsorbed amount of each gas was determined as a

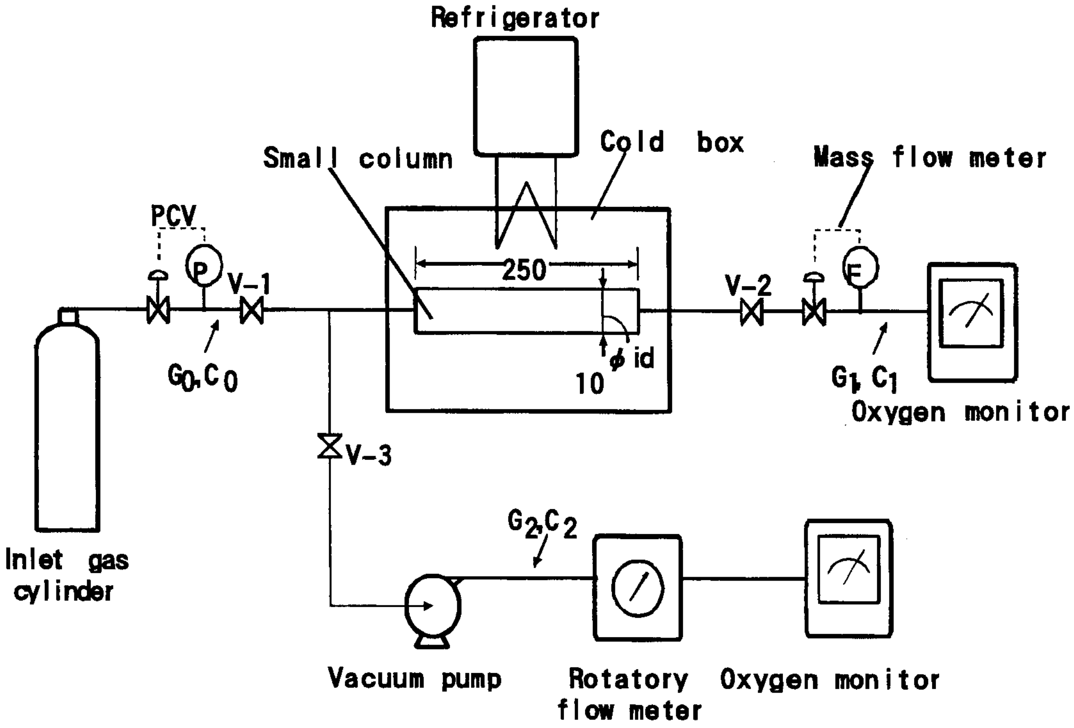


Figure 1. Schematic illustration of the small column apparatus.

function of the adsorption time. This type of experiment was designed so that adsorption properties could be determined under conditions similar to those of actual pressure swing adsorption operations.

Apparatus

A small column adsorption technique was used to obtain adsorption equilibrium and rate characteristics of a bi-component system of oxygen and nitrogen. Figure 1 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. Between 10 and 15 grams of Na-A pellets provided by UOP Co. Ltd., which were in extruded cylindrical form of 1.6 mm in diameter were loaded into the column. The column was first heated to 400 K in an evacuation condition for 2 hrs to remove surface water and then the temperature was raised to 723 K so that the adsorbents were regenerated and became thoroughly free of preadsorbed water vapor. The column was then 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 a mass flowmeter equipped with a pressure gauge PCV. The mass flowmeter at the outlet of the column detected the change of flow rate, and a zirconia electrode sensor was placed at the exit to measure the oxygen concentration of the exit gas. Evacuation of the column was made by a 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 an oxygen electrode sensor was also installed at the outlet of the rotary flowmeter.

Procedure

Adsorption pressure was adjusted by means of a pressure gauge installed on the inlet gas line. The programmed sequence of the adsorption experiment was as follows: (1) Valve V-1 was opened, the inlet gas of oxygen concentration C_0 was introduced into the

Table 1. Sequence of the small column apparatus.

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

column, and the column pressure reached the adsorption pressure P_a (pressurization step). This took about five seconds. (2) Valve V-2 was then opened and adsorption in the column from the inlet gas took place (adsorption step). During this period, the flow rate and concentration of oxygen, G_1 and C_1, were measured. The duration of the adsorption step was programmed according to the experimental schedule, between 10 and 420 seconds. (3) Valves V-1 and V-2 were closed and V-3 was opened and evacuation of the column was performed (desorption step). At the end of the desorption step, the pressure was below 13 Pa after a duration of 600 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 a sequence controller was programmed for each set of conditions so that steps (1), (2), and (3) were repeated for more than one hour. 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_1, were determined from the gas collected at the exit of the rotary flowmeter.

Table 2. Measurement conditions.

Adsorption pressure	120 kPa
Adsorption temperature	From 213–298 K
Outlet gas rate	500 m/N/batch
Sequence	
Pressurization	5 seconds
Adsorption	30–420 seconds
Desorption	600 seconds
Desorption pressure	13 Pa
Adsorbent	Na-A pellet (1.6 mm ϕ) prepared at our laboratory
Adsorbent weight	10–15 g
Small column size	10 mm ϕ id × 250 mm^1

Calculation of Amount Adsorbed

The amount of oxygen adsorbed during the pressurization and adsorption periods was calculated using the following equation.

$$q_{O2} = \frac{\{G_2 \cdot C_2 - G_{\text{dead,O}}\}}{W}$$

$$q_{N2} = \frac{\{G_2(1 - C_2) - G_{\text{dead,N}}\}}{W}$$

where q_{O2} denotes the adsorbed amount of oxygen on unit mass of zeolite and $G_{\text{dead,O}}$ represents the amount of oxygen in the dead volume of the apparatus. W denotes the amount of adsorbents packed in the column, $G_{\text{dead,O}}$ 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 is C_O at the inlet, C_{1E} at the exit and is thus assumed as $C_m = (C_O + C_{1E})/2$ in the column. The following equations were then used for calculation of $G_{\text{dead,O}}$ and $G_{\text{dead,N}}$.

$$G_{\text{dead,O}} = P_a\Bigg(V_f \cdot \frac{273}{T_f} \cdot C_O + V_m \cdot \frac{273}{T_m} \cdot C_m + V_r \cdot \frac{273}{T_r} \cdot C_{1E}\Bigg)$$

$$G_{\text{dead,N}} = P_a\Bigg(V_f \cdot \frac{273}{T_f} \cdot (1 - C_O) + V_m \cdot \frac{273}{T_m} \cdot (1 - C_m) + V_r \cdot \frac{273}{T_r} \cdot (1 - C_{1E})\Bigg)$$

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_0. The adsorbed amount of nitrogen was obtained in a similar way by replacing the fractional concentration of oxygen C by nitrogen concentration $C_N(1 - C)$.

Results and Discussion

Oxygen Profiles at the Outlet

Figure 2 shows the concentrations of oxygen measured at the outlet of the column during runs at different

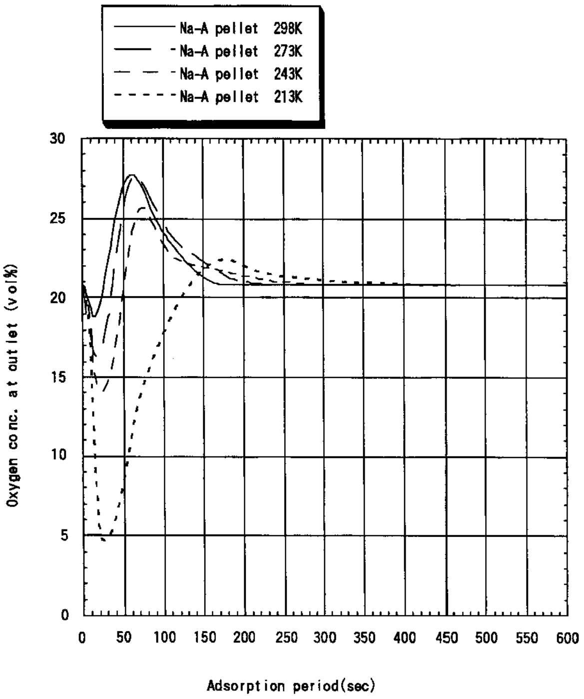


Figure 2. Oxygen profiles at column outlet.

temperatures. The adsorption pressure, the inlet oxygen concentrations, and the flow rates for all the runs were about the same; $P_a = 120$ KPa, $C_0 = 0.208$ and $G_1 = 500$ ml/min. The adsorption temperatures were (a) 298 K, (b) 273 K, (c) 243 K and (d) 213 K. The adsorption period was 600 seconds.

From Fig. 2, the oxygen concentration became lower than the inlet concentration level for about 10 seconds after the initiation of the adsorption step, then became higher than the inlet concentration, and finally reached the inlet concentration level, 0.208. This behavior suggests that Na-A shows favorable selectivity to oxygen at the initial stage of adsorption, which is then replaced by nitrogen selectivity as adsorption proceeds. At the final stage, adsorption of both oxygen and nitrogen is considered to have reached bi-component equilibrium.

As de Montgareuil (1960) showed, Na-A clearly shows rate-type selectivity to oxygen. The result obtained at 298 K suggests that the period when oxygen selectivity appears is too short for practical application. For conventional PSA design, an adsorption period of more than 30 seconds is desirable.

At lower adsorption temperatures, oxygen selectivity further increases. For instance, at 213 K, the selectivity for oxygen adsorption is much improved and adsorption extended to a period of 200 seconds.

The remarkable oxygen selectivity increase observed at lower temperatures might suggest that the hindrance at the zeolite crystal window first appears on the diffusion of the larger molecule (nitrogen) and then at lower temperatures on the smaller molecule (oxygen). When a similar experiment was tried with a carbon molecular sieve, MSC-3A (Chihara, 1977), which is known as an adsorbent for rate-type separation of oxygen and nitrogen, no appreciable improvement in selectivity was observed by lowering the temperature to 213 K.

Dependence of Adsorbed Amounts on Adsorption Period

Figure 3(a) and 3(b) respectively show the amounts of adsorbed oxygen and nitrogen measured from the desorbed gas amount and composition. Figure 3(c) shows the change of separation factor with adsorption period, where the separation factor α_{O2} is defined for the index of oxygen selectivity as

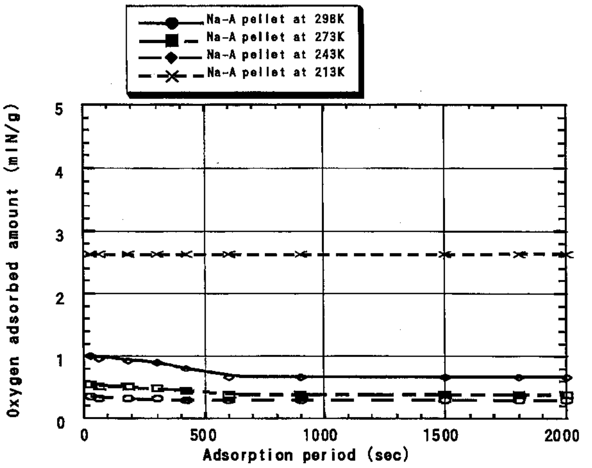
$$\alpha_{O2} = \frac{q_{O2}/C_m}{q_{N2}/(1 - C_m)}$$

Generally, the separation factor α_{O2} is used at equilibrium conditions, but it can also be used even in the case of the dynamic adsorption conditions in this study. The data shown here are for an adsorption period of 30 to 420 seconds. The other conditions were the same as shown in Fig. 2.

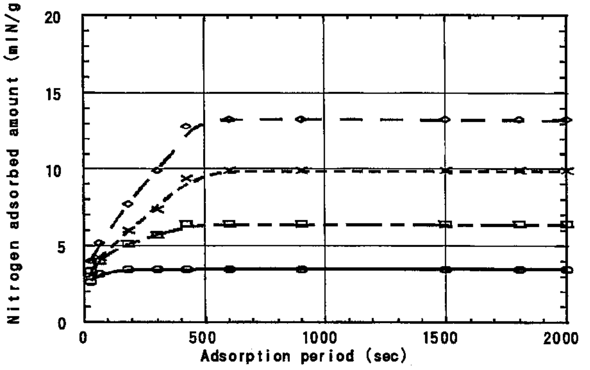
In Fig. 3(a), the oxygen amount adsorbed at 298 K is constant regardless of adsorption period, 30 to 300 seconds, which means that oxygen adsorption reaches the equilibrium within 30 seconds at this temperature. Nitrogen adsorption at the same temperature, on the other hand, as shown in Fig. 3(b), increases with the increase of adsorption period. The adsorbed amount at 30 seconds is about 70% of that at 420 seconds. For nitrogen, obviously, it takes roughly 300 seconds to reach the adsorption equilibrium, and the separation factor α_{O2} at 30 seconds is about 25% higher than that at 420 seconds. It should be noted, however, that the magnitude of α_{O2} is far smaller than unity, and that oxygen selectivity does not appear at this condition.

When temperature is reduced below 273 K, the adsorbed amount of oxygen increases dramatically. The adsorbed amounts at 273 K and 243 K, respectively, become 1.75 times and 3.4 times the amount at 298 K.

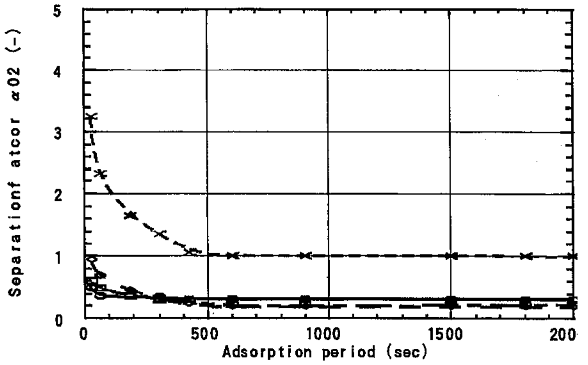
It is apparent from Fig. 3(a) that the adsorbed amounts of oxygen at 273 and 243 K decrease with the



a)Oxygen adsorption



b)Nitrogen adsorption



c)Separation Factor

Figure 3. Dependence of adsorbed amounts on adsorption period (Na-A pellet).

adsorption time. This is one of the typical behaviors of bi-component systems. The coadsorption of nitrogen and oxygen is expected on most of the adsorption sites and the rate of adsorption of nitrogen is much slower. At the beginning of the adsorption step the adsorbed amount of oxygen approaches the value expected from a single component adsorption system. Then, with the increase of the adsorbed amount of nitrogen, part of the adsorbed oxygen is replaced by adsorbed nitrogen. Finally the adsorbed amount of oxygen reaches the equilibrium value for the bi-component system, which is naturally lower than that of a single component system. Oxygen-nitrogen mixture equilibrium relations are discussed in the following section. From Fig. 3(b) it is clear that for nitrogen to reach a steady state requires about 300 seconds at 273 K, and more than 420 seconds at 243 K.

With respect to the separation factor shown in Fig. 3(c), the lower the adsorption temperature and the shorter the adsorption period, the more favorable the oxygen selectivity becomes. For a practical pressure swing operation, an adsorption time longer than 30 seconds is desirable. The results obtained for the temperatures 273 and 243 K are not satisfactory from this standpoint since selectivities are smaller than 1 for adsorption periods longer than 30 seconds.

When adsorption runs were carried out at 213 K, the adsorbed amount of oxygen again increased in a dramatic fashion. The amount adsorbed at this temperature was about eight times that at 298 K.

The amount of oxygen adsorbed at 213 K seems to reach an equilibrium value in a short time and stays constant as shown in Fig. 3(a). This behavior is different from the cases at 243 and 273 K, and might be because the rate of nitrogen adsorption is too slow at 213 K and single component adsorption equilibrium of oxygen was first reached. If this is the case, the amount of oxygen adsorbed might decrease when adsorption time is extended because of replacement by nitrogen molecules adsorbed later. The amount of nitrogen adsorbed is still increasing at 420 seconds after the start of adsorption, which suggests that nitrogen adsorption is suppressed at lower temperatures.

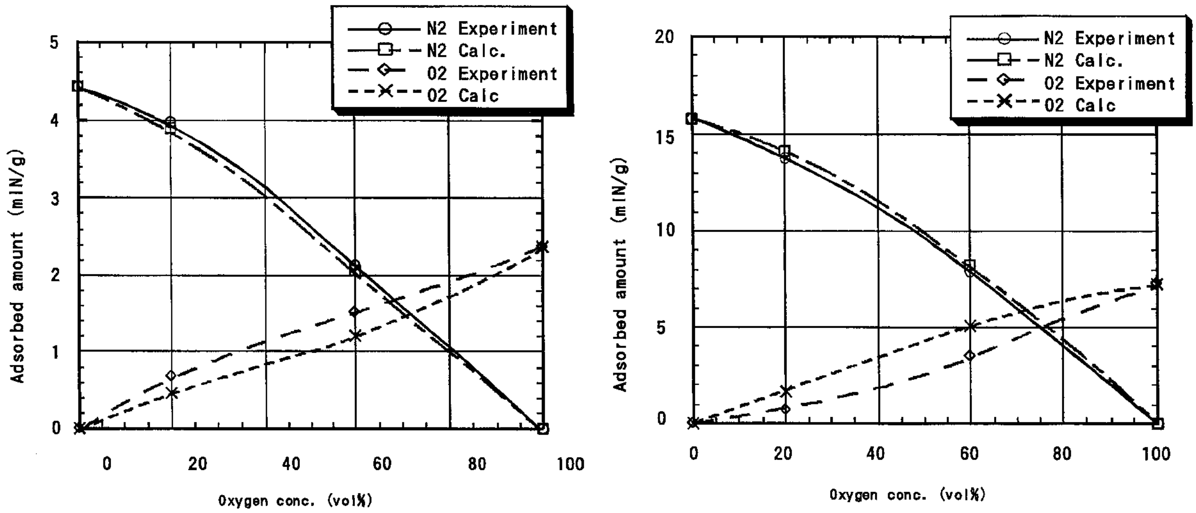
The oxygen selectivity at this temperature subsequently increases, resulting in an oxygen separation factor $\alpha_{O2} = 3.4$ at 30 seconds. Although α_{O2} decreases because of the increase of coadsorbed nitrogen with the extension of adsorption time, oxygen selectivity was higher than unity within the adsorption time of 420 seconds examined in this experiment.

In ordinary PSA separation units with zeolitic adsorbents, the nitrogen separation factor α_{N2} is of the order of 2.8, which is similar to the oxygen separation factor obtained in this study. When α_{N2} or α_{O2} and the separation operation conditions are given for the PSA system, the mass balance of the PSA unit (the inlet and outlet gas rates at the adsorption stage, and the desorption gas rate), and the electric power consumption of the blower and the vacuum pump, etc. can be determined. Since similar performance (particularly with regard to electric power consumption per unit oxygen product) is expected for PSA processes with similar separation factors, oxygen recovery by means of the oxygen adsorption type operations is considered feasible in comparison with conventional nitrogen adsorption type PSA. As the lowest electric power consumption per unit oxygen product by means of the nitrogen adsorption type (α_{N2} of 2.8) is 0.35 kwh/m3N, the oxygen selective adsorption type PSA (α_{O2} of 3.4) can be expected to provide a smaller value.

Equilibrium Adsorbed Amount in Oxygen-Nitrogen Bi-Component System

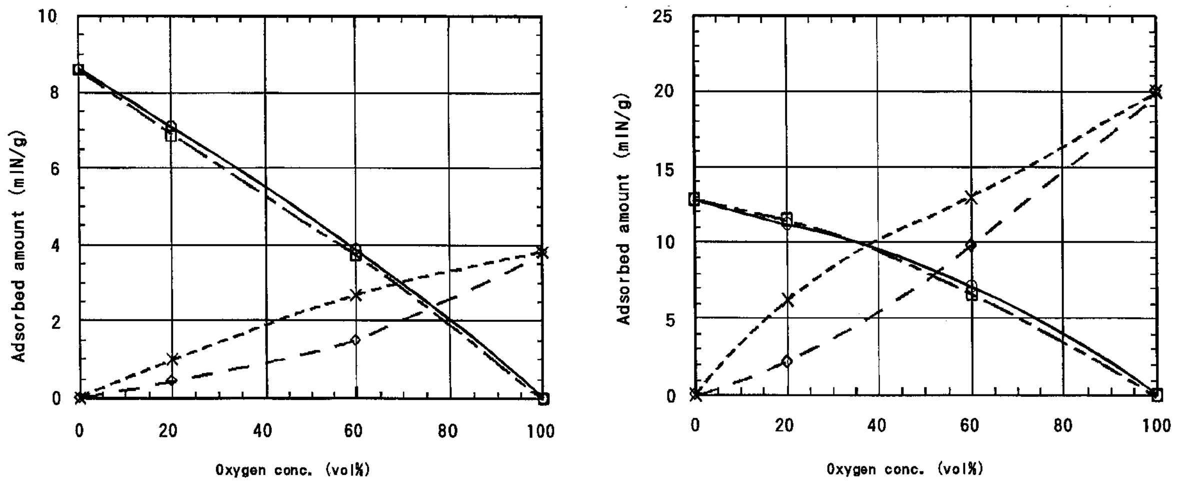
When the adsorption time dependence on the oxygen and nitrogen adsorbed amounts was evaluated, it was strongly suggested that oxygen adsorption was affected by coadsorbed nitrogen at low temperatures. The oxygen and nitrogen adsorption behaviors in the equilibrium conditions of the bi-component system were studied.

The relationships between the oxygen concentration and the oxygen and nitrogen adsorbed amounts at a total pressure of 120 KPa and several adsorption temperatures from 213 to 298 K are shown in Fig. 4. Straight



a) Adsorption temp. 298K

c) Adsorption temp. 243K



b) Adsorption temp. 273K

d) Adsorption temp. 213K

Figure 4. Equilibrium Adsorbed amount of oxygen and nitrogen in a bi-component system (Na-A pellet).

lines indicate experimental data and dashed lines show calculated data assumed with the oxygen and nitrogen equilibrium adsorbed amounts in a mono-component system. As is recognized in Fig. 4, the measured adsorbed amounts of oxygen and nitrogen at 298 K in a bi-component system agree with the assumed amounts in a mono-component system. When the temperature decreases, there is no difference in the nitrogen adsorbed amount between the bi-component system and the mono-component system, but the oxygen adsorbed amount in the bi-component system is lower than in the bi-component system because of the effect of the coadsorbed nitrogen. When Knaebel et al. (1987) studied the oxygen and nitrogen adsorption on Ca-A under an oxygen-nitrogen bi-component system, they reported a similar phenomenon on Ca-A at low temperatures.

In Fig. 5, straight lines represent the isotherm data of oxygen and nitrogen for Na-A pellet (1.6 mm ϕ) in the mono-component system at temperatures between 213 K and 298 K and at a pressure of 100 KPa. As the pellet contains 20 w% binder, the adsorbed amounts of Na-A pellets were corrected as net weight of Na-A. Dashed lines are the isotherm data of oxygen and nitrogen for Na-A powder measured by Breck et al. (1959). The oxygen adsorbed amount of the 1.6 mm ϕ pellets in this study increased smoothly, while the increase of the nitrogen adsorbed amount reached a plateau at less than 243 K.

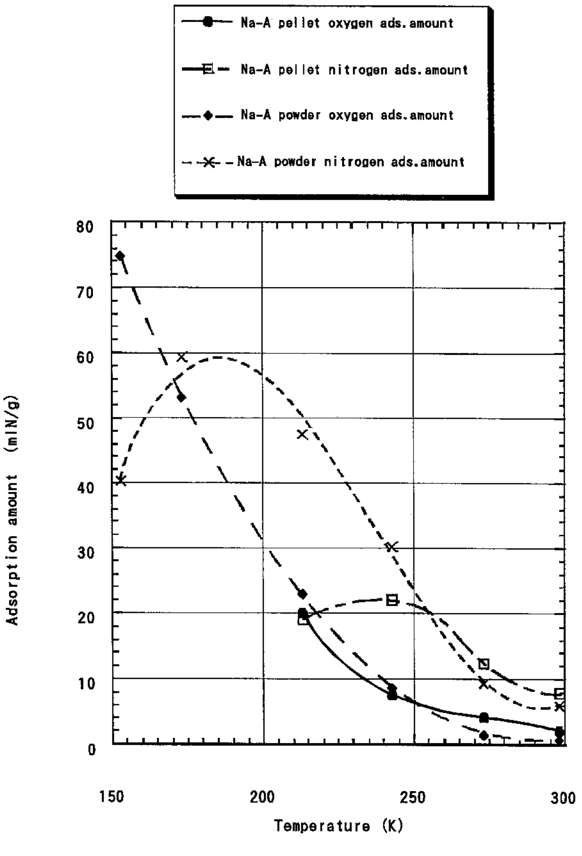


Figure 5. Isobar of oxygen and nitrogen on Na-A (Adsorption pressure 100 KPa, as pellets contains 20 w% binder, the adsorption amounts of Na-A pellets were corrected as net weight of Na-A).

Ruthven (1988) remarked that the adsorption capacity and the adsorption rate of pellets and beads indicated some deviation. Although no explanation of the cause was given at that time, it might be considered that the physical and chemical properties of zeolite crystal would be influenced by the forming process, and it is assumed that the calcination, the solid-solid diffusion between zeolite crystal and inorganic binder, and the water vapor from surface water and crystal water are likely causes of crystal deformation. When Na-A crystals deform, there is some probability that the window of Na-A shrinks and that the larger nitrogen molecule would be more greatly affected by steric hindrance than the smaller oxygen molecule, with oxygen selectivity enhancement occurring as a result.

Since the adsorbed amount of oxygen on Na-A powder becomes larger than that of nitrogen at 173 K, this phenomenon is shifted to a higher temperature of 213 K. Thus, Na-A pellets show the oxygen selectivity as a rate type adsorbent in a higher temperature region, but at 238 K the adsorbed amount of oxygen became the same as that of nitrogen and it is assumed that the adsorbed amount of oxygen exceeds that of nitrogen even at equilibrium conditions under 213 K.

Conclusion

As Na-A pellets are expected to show oxygen selectivity both as a rate type adsorbent at room temperature and also as an equilibrium type adsorbent at less than 213 K, the relationship between the adsorption time and the oxygen selectivity at a temperature between room temperature and 213 K was studied. The following new facts were found:

1) When the adsorption temperature decreases, the oxygen adsorbed amount increases dramatically, but its adsorption rate does not decrease by a large margin. Since the nitrogen adsorbed amount reaches a maximum at 243 K, its adsorption rate

decreases remarkably and, as a result, high oxygen selectivity appears at low temperatures.

2) As an example, the separation factor of Na-A at 243 K and at an adsorption period of 30 seconds in an air composition shows remarkably high oxygen selectivity of 3.8, with an oxygen adsorbed amount 8 times higher than that at room temperature. Na-A is expected to serve as an oxygen selective adsorbent for oxygen and nitrogen separation from air with PSA.
3) As the oxygen adsorbed amount measured in a bi-component system is lower than the calculated value at the same partial pressure in a mono-component system, it is assumed that the oxygen adsorbed amount is suppressed by the coadsorbed nitrogen in the oxygen-nitrogen bi-component system. This tendency becomes more remarkable at lower temperatures.

Nomenclature

C	Concentration (mol/mol)
G	Gas flow rate (mlN/batch)
P	Pressure (Pa)
q	Adsorption amount (mlN/g, g/g)
T	Temperature (K)
t	Time (sec)
V	Dead volume (ml)
W	Adsorbent weight (g)

Greek Letters

α	Separation factor

Suffix

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

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