Adsorption 6, 23–31 (2000)

Oxygen Selectivity of Calcined Na-A Type Zeolite

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Received November 6, 1998; Revised August 8, 1999; Accepted September 9, 1999

Abstract. Na-A type zeolite (Na-A) pellet showed a greater oxygen selectivity than Na-A powder (Izumi, J. and M. Suzuki, *Adsorption*, submitted; Izumi, J. et al., Japan Patent Toku-Kou-Shou 62-026808 (1987)). It was considered that a water adsorption at calcination stage influenced a window diameter shrinkage to increase the oxygen selectivity. For the confirmation of an optimum preparation condition for the oxygen selectivity enhancement of Na-A pellet, an experiment of oxygen and nitrogen adsorption on calcined Na-A was undertaken with a small adsorbent column under a pressure swing adsorption (PSA) condition at a temperature from 298 K to 213 K. It was found that the secondary calcination (953–1033 K) after the water vapor adsorption provided a remarkable increase of the oxygen selectivity. At the optimum condition for calcined Na-A, the oxygen separation factor is greater than 6. Calcined Na-A has a potential to separate oxygen and nitrogen from air by PSA effectively.

Keywords: calcined Na-A type zeolite, rehydration, recalcination, oxygen selectivity, low temperature, pressure swing adsorption

Introduction

From the low temperature equilibrium adsorption data for oxygen and nitrogen on Na-A powder measured by Breck and Smith (1959), while the adsorption amount of oxygen increases steadily as temperature is reduced, the adsorption amount of nitrogen first increases as temperature is reduced from 298 K to about 163 K, but decreases thereafter. Accordingly, from an equilibrium point of view, it is suggested that Na-A is nitrogen selective adsorbent from 298 K to 173 K, and thereafter Na-A becomes oxygen selective adsorbent.

However, as noted in the previous report (Izumi et al., 1987), while Na-A pellet showed the nitrogen selectivity at 298 K equilibrium adsorption conditions, it showed the oxygen selectivity as the adsorption time is shortened and it was recognized that Na-A pellet performed as a rate selective oxygen adsorbent. And this tendency becomes more pronounced at a low temperature. Since the equilibrium adsorption amount of oxygen on Na-A increases as temperature is reduced, that of nitrogen increases only from 298 K to 213 K and subsequently decreases. Accordingly Na-A pellet shows the oxygen selectivity even under equilibrium condition below 213 K.

Thus, although the temperature from which oxygen selectivity appears for Na-A powder is at less than 163 K, the corresponding temperature for Na-A pellets is shifted to 213 K. It suggests the possibility that some sort of nitrogen adsorption hindrance is introduced during the forming process. From the standpoint of using this material as an oxygen selective adsorbent, the enhancement of oxygen selectivity at a relatively higher temperature is more economical due to the reduction of cool heat.

In addition, while it is well known that Molecular Sieves Carbon-3A (MSC-3A) (Chihara, 1977; Ruthven et al., 1987; Marushige et al., 1991) has been used as an oxygen selective adsorbent for PSA-nitrogen, Ruthven (1987), Knaebel (1990) and Yang (1988) have researched a rate selective adsorbent (RS-10) which is a modified Na-A developed by UOP, and they have shown that PSA-nitrogen can be accomplished with RS-10. The oxygen selectivity enhancement mechanism for RS-10 has not yet been disclosed, but, compared with MSC-3A which uses styrene polymer as the starting material, the use of the inexpensive Na-A starting material is advantageous from a cost performance point view. Also, while MSC-3A is an amorphous substance, the Na-A starting material is formed from homogeneous crystal and it suggests the possibility of more precise control of the oxygen selectivity enhancement mechanism.

In the present research, therefore, in order to grasp the relationship between the Na-A forming process (i.e., mixing with the binder, forming with an extruder, raising the temperature for removing water content, and high-temperature calcination) and the enhancement of oxygen selectivity, sample pellets were rehydrated and recalcined, and the evaluation of the enhancement of oxygen selectivity was conducted in an oxygen-nitrogen binary system under low-temperature adsorption conditions.

Experimental

Preparation of the Adsorbent

Figure 1 shows the preparation procedure for calcined, rehydrated, and recalcined Na-A type zeolite (referred to as Na-A calcined sample basis hereafter). For each 100 grams (dry basis) of Na-A type zeolite powder (adsorbent grade, removing only surface water, manufactured by UOP Ltd.), 20 grams of kaolin binder and 15 grams of cellulose porosity additive agent were thoroughly mixed in, and pellets with a diameter of 1.6 mm were formed using an extruder. The pellets were first dried in an electric furnace for 1 h at 383 K to remove surface water, after which the temperature was raised to 923 K at a rate of 100 K/h and held for 1 h, concluding the calcination. After spontaneous cool-down, the pellets were exposed in wet air to rehydrate at 298 K, and were then calcined for a second time by raising the temperature to predetermined levels (from 923 to 1073 K) at a rate of 100 K/h. Small column samples were prepared after spontaneous cool-down in a desiccator.

In order to better understand the relationship between oxygen selectivity contribution of each of the two main factors influencing it (i.e., the adsorption amount of water vapor before the second calcination, and the highest temperature during the second calcination), samples were prepared using various adsorption amounts of water vapor (0–30 w%) and various final calcination temperatures (923 to 1073 K, for 1 h).

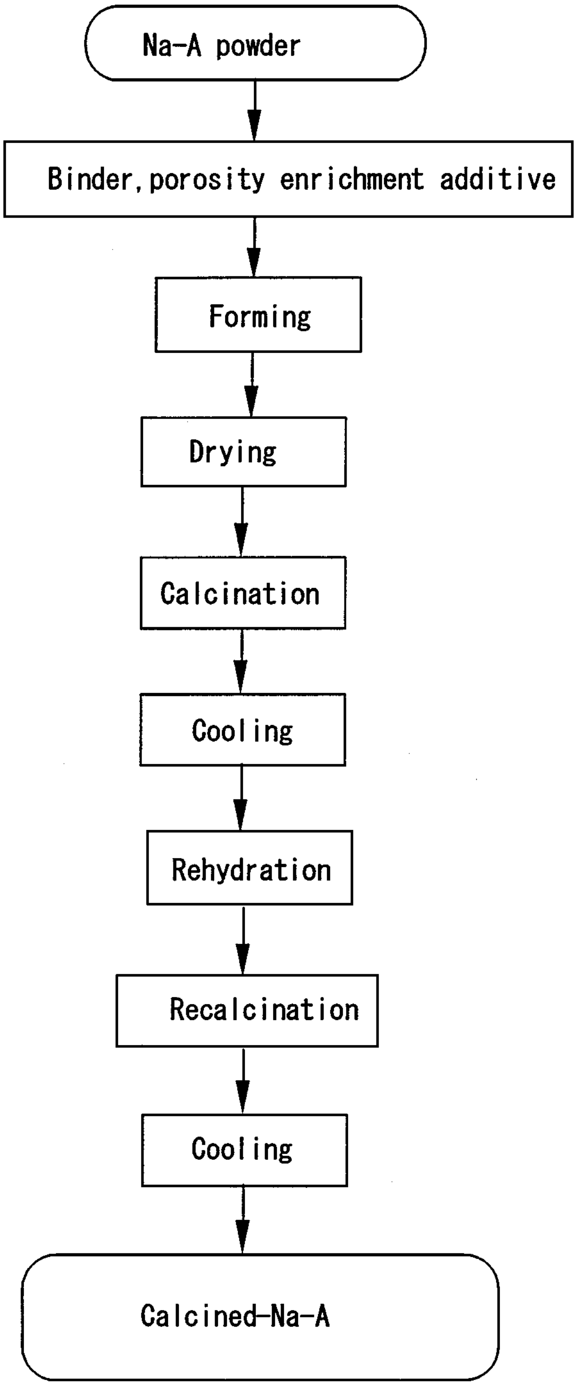


Figure 1. Procedure for calcined-Na-A preparation.

Table 1. Measurement conditions.

Adsorbent	
Crystal	Calcined-Na-A
First calcination temperature	923 K
High temperature retention period	1 hour
Water vapor adsorbed amount (Rehydration)	0–30 w%
Second calcination temperature	923–1,073 K
High temperature retention period	1 hour
Adsorption pressure	120–200 kPa
Desorption pressure	13 Pa
Inlet oxygen concentration	0–100 vol%
Adsorption temperature	213–298 K
Outlet gas rate	500 mlN/min
Sequence mode	
Pressure elevation period	10 seconds
Adsorption period	30–2,000 seconds
Desorption period	900–2,000 seconds

Small Column Evaluation of Oxygen Selectivity on Na-A Calcined Samples

Table 1 indicates the measurement conditions for the small column evaluation. As the measurement procedure was described in the previous report (Izumi et al., 1987) relating to evaluation of the oxygen selectivity on Na-A pellets, it will be omitted here. In the measurement of Na-A pellets, as the adsorption rates for oxygen and nitrogen are relatively high even at the low temperature of 213 K, steady state condition was achieved in PSA operation of 1–2 h, but, because the nitrogen adsorption rate on the Na-A calcined samples is slower, 4 h was required to reach the steady state condition.

In the operational procedure described above, in order to confirm the enhancement of the oxygen selectivity with respect to recalcination, following an initial calcination at 923 K, calcined Na-A samples were prepared with water adsorption amounts varying from 0–30 w% and a second calcination at 993 K.

These samples were evaluated for oxygen selectivity under the following conditions: a) adsorption temperature of 243 K, b) adsorption time of 60 seconds, c) adsorption pressure of 120 KPa and regeneration pressure of 13 Pa, and d) inlet oxygen concentration of 20.8 vol%. The optimum water adsorption amount for the enhancement of oxygen selectivity was accordingly determined.

Next, in order to determine the optimum recalcination temperature, samples prepared with a water adsorption amount of 15 w% were recalcined for 1 h at temperatures varying from 923 to 1073 K, and the dependence of oxygen selectivity on recalcination temperature was evaluated. Water adsorption amount of 15 w% and calcination temperature conditions of 993 K were selected as the optimum condition for the oxygen adsorbent.

The oxygen adsorption performance of these samples for PSA-oxygen recovery was evaluated at 243 K by a small column adsorption apparatus. Quantitative analysis was then conducted for the following parameters: a) oxygen adsorption amount, b) nitrogen adsorption amount, and c) oxygen separation factors α_{O2} for adsorption temperature, adsorption time, and oxygen partial pressure dependence. The oxygen separation factor α_{O2} is defined by Eq. (1).

$$\alpha_{O2} = \frac{(q_{O2}/P_{O2})}{(q_{N2}/\,P_{N2)}} \tag{1}$$

Results and Discussion

Effects of Water Adsorption Amount and Calcination Temperature on Oxygen Selectivity

For the confirmation of the optimum water adsorption amount before the recalcination, samples, of which water adsorption amount were set at between 0–30 w% and recalcined at 993 K for 1 h, were prepared for the oxygen selectivity evaluation at 243 K. Figure 2 shows summary of the relationships between the water adsorption amount q_w, the oxygen and nitrogen adsorption amounts, q_{O2}, q_{N2} and the respective separation factors for Na-A calcined samples prepared at a recalcination temperature of 993 K.

The oxygen selectivity of these samples were measured at adsorption pressure of 120 KPa, regeneration pressure of 13 Pa, inlet oxygen concentration of 20.8 vol%, and an adsorption temperature of 243 K. Although the adsorption amounts of nitrogen decreased with increases in the water adsorption amount up to 15 w%, the adsorption amount of oxygen remained almost constant in this range. As a result, the separation factor increased as the water adsorption amount increased.

However, the adsorption amount of oxygen also decreased when the water adsorption amount increased beyond 15 w%, and, when this amount reached 25 w%, the amounts of both oxygen and nitrogen fell to 1/4 of their non-hydration values. It was thereby established that the optimum water adsorption amount was approximately 15 w%.

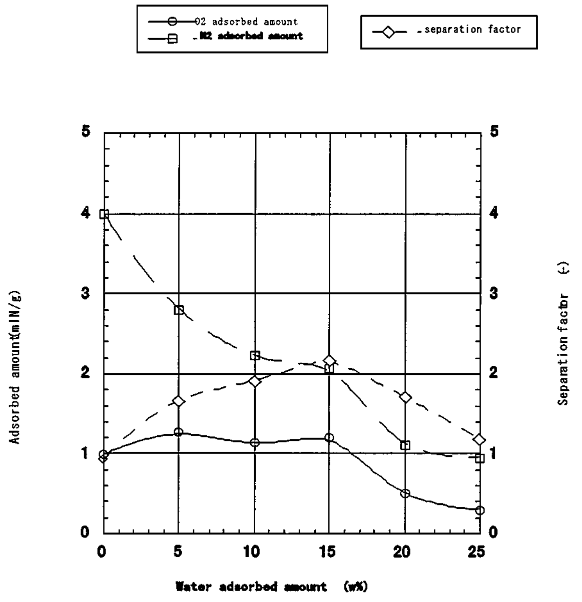


Figure 2. Oxygen and nitrogen adsorption dependency on preadsorbed water. Adsorption period 60 seconds; Adsorption temperature 243 K; Adsorption pressure 120 kPa; Inlet 02 conc. 20.8 vol%; Recalcination temp. 993 K.

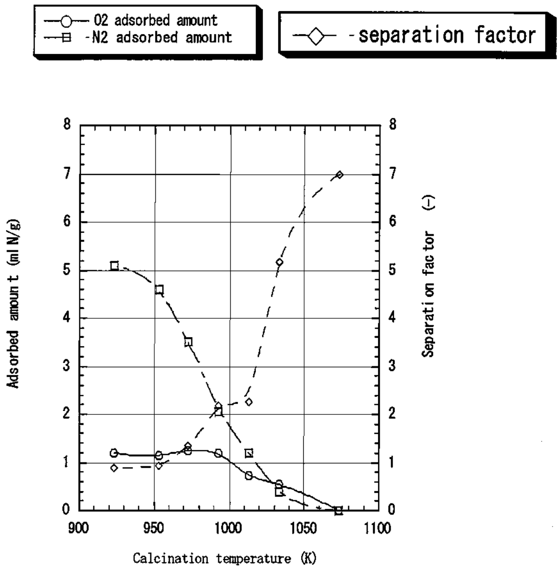


Figure 3. Relation between calcination temperature and oxygen selectivity. Adsorption period 60 seconds; Adsorption temperature 243 K; Adsorption pressure 120 kPa; Inlet 02 conc. 20.3 vol%; Water preadsorbed amount 15 w%.

Na-A is crystallographically considered to be in a meta-stable condition, and it is known to undergo a hydrolysis in a high-temperature water vapor atmosphere. It can therefore be inferred that recalcination causes a slight thermal decomposition in the Na-A crystal. A particular influence occurs at the 8-member ring site which forms the Na-A window and which is specifically related to adsorption. (Na-A is completely decomposed to amorphous alumino-silicate when recalcination is undertaken in a water vapor atmosphere at a temperature of 923 K or higher. And the hypothesis that adsorbed water content causes a crystal decomposition, seems supported by the large reduction in adsorption amount that is observed in the presence of water adsorption of 25 w%.)

Figure 3 shows the relationships between the water adsorption amount, the oxygen and nitrogen adsorption amounts, and the separation factors for Na-A calcined samples prepared at higher calcination temperatures under the same conditions as described above. Again, although the adsorption amounts of both oxygen and nitrogen decreased with increases in the adsorption amount of water, the adsorption amount of nitrogen decreased to a greater extent than that of oxygen, and the separation factor expanded as the water adsorption amount increased.

A sample, of which a calcination temperature is 1033 K and higher, showed an extremely large separation factor, but the adsorption amount of oxygen showed a large decrease. As the oxygen adsorbent for PSA-oxygen recovery, at least the oxygen adsorption amount of 1 mlN/g at an oxygen concentration of 20.8 vol% (that of air at 100 KPa) had to be kept, the optimum calcination temperature seemed to be about 993 K.

The enhancement of oxygen selectivity in the adsorbent evaluated here is assumed to be the result of Na-A crystal strain caused by recalcination after hydration. As Na at the 8-member ring seems shifted from a normal position to a slightly different position by such kinds of thermal treatment, such adsorption of larger nitrogen molecule is hindered. Thus, although the separation factor increases as the recalcination temperature increases, the Na-A crystal decomposition also proceeds and the adsorption amount of oxygen decreases to an unpractical level.

Outlet Oxygen Concentration Profiles Over Adsorption Time

Figure 4 shows oxygen concentration profiles over adsorption time for Na-A calcined samples, which has the highest oxygen selectivity (i.e., with a water adsorption

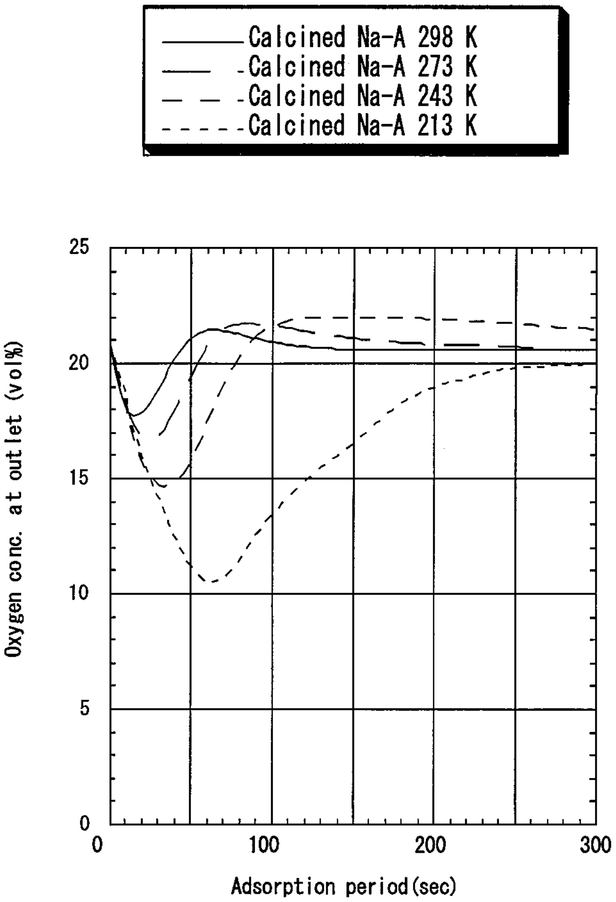


Figure 4. Oxygen profiles at column outlet (993 K, 1 hour calcination).

amount of 15 w%, a calcination temperature of 993 K and a high temperature holding time of 1 h), observed under conditions of 5 minute adsorption time, inlet oxygen concentration of 20.8 vol%, inlet flow rate of 10 cm/second, adsorption pressure of 120 KPa, and adsorption temperatures of 298, 0, 243, and 213 K. It can be seen that, at the adsorption temperature of 298 K and at approximately 20 seconds after the start of adsorption, outlet oxygen concentration falls below inlet concentration, then outlet concentration surpasses inlet concentration and gradually approaches 20.8 vol%.

In comparison with untreated Na-A pellets, the maximum value of outlet oxygen concentration greatly decreased and it suggested that the nitrogen adsorption rate was reduced as a result of recalcination. When the adsorption temperature was further reduced, the minimum value of outlet oxygen concentration declined and it reached its lowest value at 213 K. However, in comparison with untreated Na-A pellets, the minimum outlet oxygen concentration increases, and the oxygen adsorption rate for Na-A pellets is actually higher (Izumi and Suzuki, Submitted).

This has extreme importance in terms of nitrogen generation, but, since the oxygen concentration of desorbed gas is also important in the generation of oxygen, high oxygen selectivity is of the first priority. Thus, functional comparison of adsorbents cannot be conducted on the basis of minimum outlet oxygen concentration alone. (When the oxygen adsorption rate is extremely low, the oxygen adsorption amount per unit time becomes small. Accordingly, as large amount of adsorbent must be used and recovered oxygen is diluted due to dead volume nitrogen, it is concluded that the adsorbent cannot be used.)

In a 5 minute adsorption at 213 K, the outlet oxygen concentration was lower than the inlet concentration from start to finish. It means that the oxygen adsorption amount per partial pressure of Na-A calcined sample is larger than that of nitrogen and oxygen selectivity increases as a result dramatically.

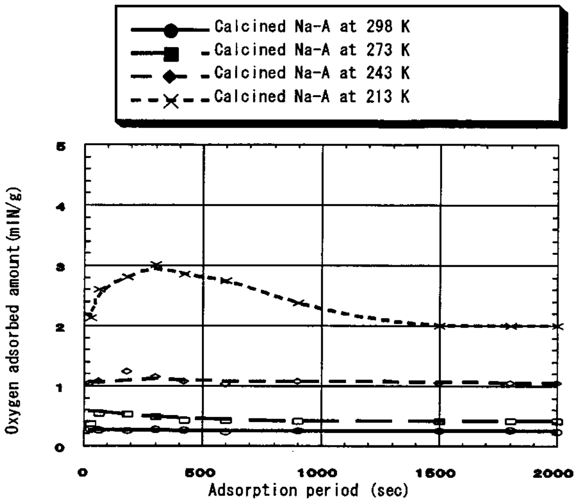
Adsorption Amounts of Oxygen and Nitrogen with Adsorption Time (Kinetic Considerations)

Nitrogen and oxygen adsorption amounts, as well as the separation factors, 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 illustrated in Fig. 5(a)–(c). As the nitrogen adsorption rate of Na-A calcined samples decreased at low temperature, the adsorption time of 420 seconds, which is required for Na-A pellet to reach the equilibrium adsorption amount, seemed insufficient and the time was extended to 2,000 seconds.

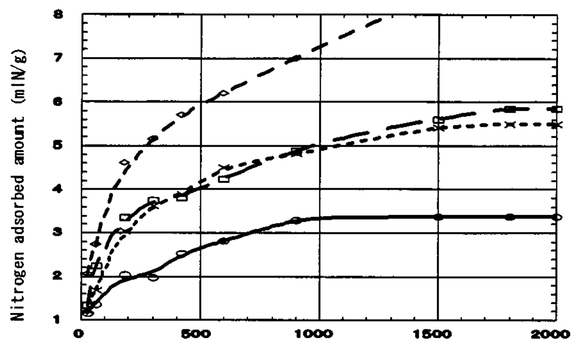
Figure 5(a) shows the oxygen adsorption amount during the adsorption time from 30 to 2,000 seconds at 298 K. As the oxygen adsorption amount was always constant, it means that the oxygen adsorption amount of Na-A calcined samples reached the equilibrium condition within the short period of 30 seconds.

For nitrogen adsorption, however, Fig. 5(b) indicates that only about 20% of the equilibrium adsorption amount was achieved within 30 seconds, and about 1,000 seconds are necessary to reach the equilibrium condition.

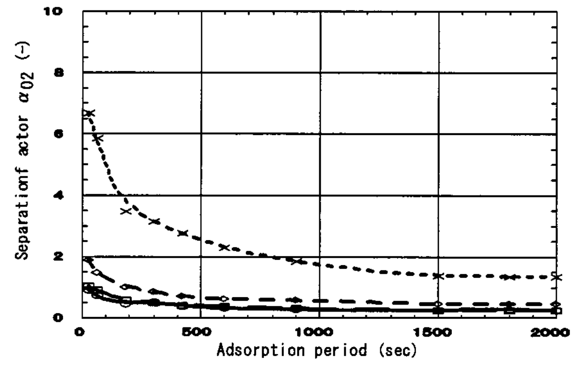
Both the oxygen and nitrogen adsorption amounts increased at 273 K, but, while a steady state value was



a)Oxygen adsorption



b)Nitorgen adsorption



c)Separation Factor

Figure 5. Dependence of adsorbed amounts on adsorption period (Calcined Na-A).

shown for oxygen in the short period of less than 10 seconds, the nitrogen adsorption amount required about 2,000 seconds for attainment. It means that the nitrogen adsorption rate was dramatically reduced.

However, the oxygen separation factor in Fig. 5(c) is still less than 1, and, if the adsorption time is not adjusted to a short period, oxygen selectivity will not appear.

At 243 K, the adsorption amounts of oxygen and nitrogen showed further increase. Also, while the oxygen adsorption amount reached its steady state value in about 200 seconds, the nitrogen adsorption amount reached its steady state in about 3,000 seconds. The oxygen separation factor surpassed 1 within approximately 200 seconds. As the nitrogen adsorption amount increased gradually, Na-A-calcined showed the nitrogen selectivity after 200 seconds.

At 213 K, the oxygen adsorption amount increased, however, the nitrogen adsorption amount became less than that at 243 K and a sample at 213 K showed the maximum value of the separation factor 6.5. And also it showed the strong oxygen selectivity over all adsorption times.

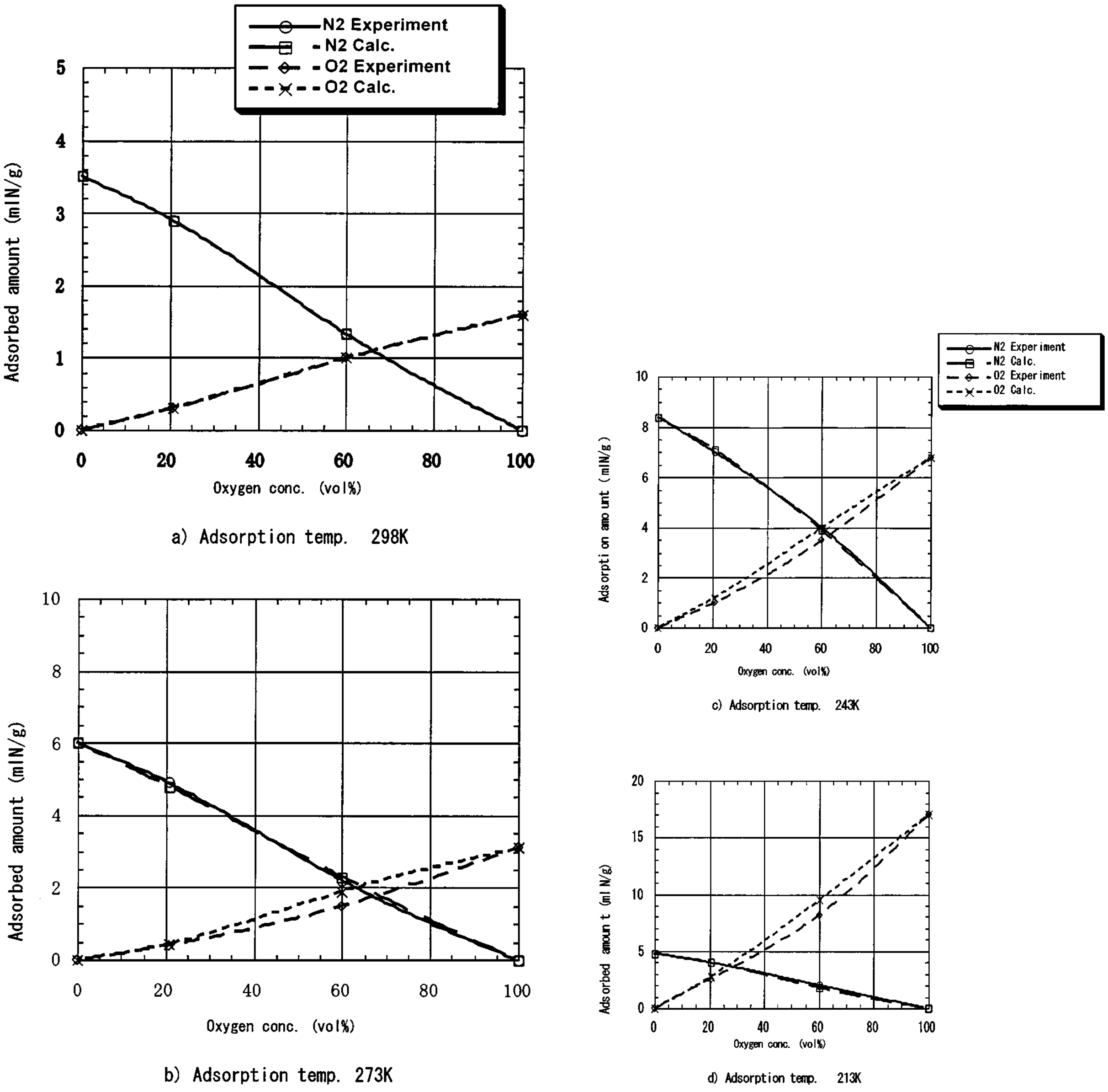
Also, while the oxygen adsorption amount reached its steady state value in about 1,500 seconds, a close examination of the time progression reveals that the amount at an earlier time was extremely large and then gradually decreased thereafter to approach the steady state value. This suggests that, during the period when nitrogen was not adsorbed, oxygen surpassed the equilibrium adsorption amount at the adsorption active point, and, with subsequent adsorption of nitrogen, previously adsorbed oxygen was displaced from adsorbent.

It can be seen from the foregoing that, compared with untreated Na-A pellets, oxygen selectivity is greatly improved, and that recalcination after hydration made a major contribution to this improvement.

Equilibrium Adsorption Amounts in an Oxygen-Nitrogen Binary System

As it has been suggested that the oxygen adsorption amount of untreated Na-A at low temperature might be affected by co-adsorbed nitrogen, the behavior of Na-A calcined samples was considered under equilibrium adsorption in an oxygen-nitrogen binary system.

Figure 6 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. The solid line in the figure is the line of actual measurement, while the dotted line shows the equilibrium adsorption amounts for oxygen and nitrogen as derived from the respective single component systems.



a) Adsorption temp. 298K

b) Adsorption temp. 273K

c) Adsorption temp. 243K

d) Adsorption temp. 213K

Figure 6. Equilibrium adsorbed amount of oxygen and nitrogen in binary system. (a, b) Calcined-Na-A, 993 K; (c, d) Calcined-Na-A.

At 298 K, derived adsorption amounts are very close to the amounts actually measured in a binary system. However, while both of the nitrogen adsorption amounts remain in close correlation as temperature decreases, the actually measured value for oxygen becomes lower than the derived value from the single component figure. And it is well recognized that the co-adsorbed nitrogen reduces the oxygen adsorption amount in a binary system.

When oxygen and nitrogen adsorption on Ca-A and Na-X were measured in an oxygen-nitrogen system from 298 K to low temperatures and the equilibrium adsorption equation was expressed by Knaebel (1988), this phenomenon was reported. And also this phenomenon on Na-A was found by authors (Izumi and Suzuki, submitted).

Figure 7 shows the adsorption isobar for oxygen and nitrogen on 1) Na-A calcined sample, 2) untreated Na-A pellet and 3) Na-A powder measured by Breck et al. (1959). Respectively in a single component system, with partial pressures of oxygen and nitrogen of 100 KPa, and at adsorption temperatures of 298 to 213 K.

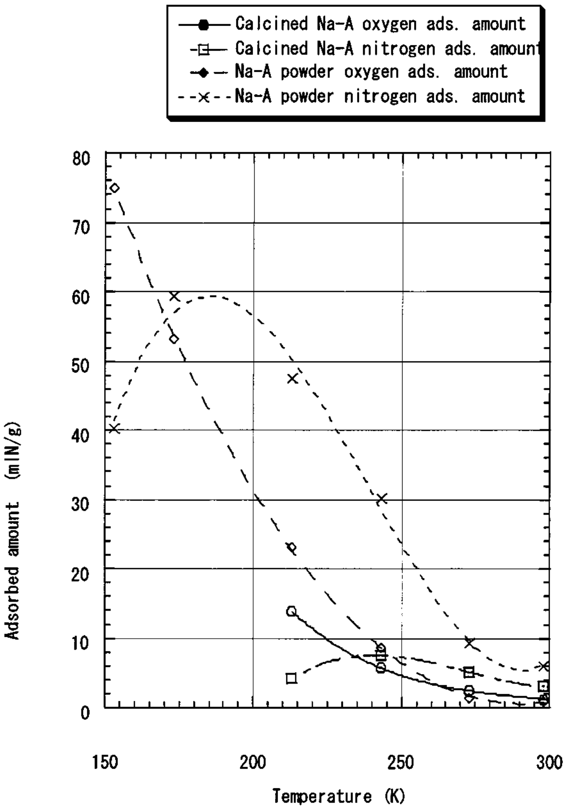


Figure 7. Isobar of oxygen and nitrogen on calcined Na-A (adsorption pressure 100 kPa).

Although the Na-A calcined sample used here showed an increased oxygen adsorption amount with temperature decrease, the adsorption amount of nitrogen reached a maximum at 243 K for calcined sample and actually decreased thereafter. Since this tendency was found not only at Na-A calcined pellet sample but also at untreated Na-A pellet and Na-A powder, the cross-point of the adsorption amounts of oxygen and nitrogen at about 173 K for Na-A powder and at about 213 K for untreated Na-A pellets.

For Na-A calcined samples, however, this point rises substantially to about 228 K, and this fact suggests that the enhancement of oxygen selectivity is due to hydration and recalcination of Na-A pellets, and that the adsorption of nitrogen is hindered, as its molecules are larger than the window diameter after recalcination. Even for untreated Na-A pellets in an oxygen-nitrogen binary system, the equilibrium oxygen selectivity appeared at 218 K and lower, but this cross point was shown at an even higher temperature of 228 K for Na-A calcined samples.

Conclusion

For Na-A pellets showing oxygen selectivity under low-temperature pressure swing conditions, since hydration and recalcination were expected to further improve oxygen selectivity, Na-A calcined adsorbent was evaluated in the temperature range from 298 K to 213 K, and the following results were obtained.

1) At 243 K adsorption temperature, 60 seconds adsorption time, 20.8 vol% inlet oxygen concentration, 993 K calcination holding temperature, and a water adsorption amount adjusted in the range from 0–30 w%, both the oxygen and nitrogen adsorption amounts of the Na-A calcined material were found to decline with an increase of water vapor adsorption amount for hydration. However, the decrease of nitrogen adsorption was greater than that of oxygen, the oxygen selectivity appeared as a result. As the minimum amount of oxygen adsorption required for PSA is about 1 mlN/g, the optimum water adsorption amount seemed to be 15 w%.
2) Under the same adsorption conditions as above, when Na-A pellets, which were hydrated to 15 w% and recalcined in the temperature range of 923–1073 K, it was found a reduced amount of oxygen adsorption and an even further reduced amount of nitrogen adsorption by the calcination temperature increase and they showed an extremely strong oxygen selectivity as a result. However, due to the thermal decomposition of A-type zeolite at temperatures of 1073 K and above, the adsorption amounts of both oxygen and nitrogen show very rapid decline. In conjunction with the knowledge presented above in item 1), the optimum recalcination temperature was judged to be 993 K.
3) The Na-A calcined samples hydrated to 15 w% and recalcined at 993 K showed stronger oxygen selectivity with reduced temperature than did untreated Na-A pellets. For example, when air was supplied from the small column inlet at 213 K, a separation factor of 6 at an adsorption time of 30 seconds demonstrated remarkable oxygen selectivity. This represents a major improvement over the oxygen selectivity of 3.8 obtained with untreated Na-A

pellets under the same conditions, and application as a good adsorbent for oxygen recovery with PSA from air can be expected.

4) The oxygen selectivity transition temperature of 228 K, identified for Na-A calcined samples featuring a water adsorption amount of 15 w% and recalcination temperature of 993 K as in this study, is considerably higher than 173 K for Na-A powder reported by Breck or 218 K for untreated Na-A pellets. It suggests that nitrogen adsorption is hindered at the window due to hydration and recalcination.
5) At low temperatures, the amount of oxygen adsorption at the earlier time showed a peak and then gradually declined to reach a steady state value.
6) In an oxygen-nitrogen binary system, as with untreated Na-A pellets, Na-A calcined samples were found to adsorb a lower oxygen adsorption amount than the derived value from a single component system. It was assumed that co-adsorbed nitrogen tended to limit oxygen adsorption.

Nomenclature

q	Adsorbed amount (mlN/g), (g/g)
α	Separation factor (–)

Suffix

O2	Oxygen
N2	Nitrogen

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