CHEMISTRY LETTERS, pp. 5-8, 1994.

Improvement in Adsorption Capacity of Nitrogen over X-type Zeolites by n-Hexane Plasma Processing and Heat Treatment

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The X- and Y-type Faujasite zeolites were modified with n-hexane plasma processing followed by thermal treatment at 600 °C to produce the carbon coated zeolites. Amount of carbon coated was up to 2.8 wt% for Ca-X zeolite, depending on the time of plasma processing. Although the pore volume of the zeolites was reduced by the carbon modification, the adsorption uptake of N_2 at 30 °C increased preferentially to that of O_2 and/or Ar only for the modified X-type zeolites. The increase of the N_2 uptake was up to 150% for the Na-X zeolite at carbon coating around 1 wt%. Both H_2O-DSC and NH_3-TPD measurements supported that carbon cluster from plasma processing was present in the Faujasite cage.

Nitrogen(N_2) is generally adsorbed on zeolites preferentially to oxygen (O_2) and argon(Ar). This is the fundamentals of the separation of air into N_2 and O_2 when the zeolite is applied for pressure swing adsorption (PSA) process as an adsorbent. The molecular size1) of N_2, 0.375 nm is larger than that of O_2, 0.354 nm or Ar, 0.346 nm. Therefore the molecular sieving property of N_2 over zeolite is not based on the molecular size effect, but on the chemical interaction between an N_2 molecule and zeolite surface, mainly due to the quadrupole moment of an N_2 molecule2).

Many studies have been reported on improving the molecular sieving properties of zeolites for air separation. CVD method reported by Niwa et al.3) controls the window size of the Na-A zeolite by depositing silicon methoxide on the external surface of the zeolite. Ion-exchanged method by Iwamoto et al.4) also controls the window size of K-A zeolite by exchange with Zn^{2+} ions. These attempts inevitably suppress the adsorption rates and uptakes of all components such as N_2, O_2 and Ar. But the suppression effect for N_2 was much more significant than that for O_2 because of the molecular size effect. At the final stage of closure of the window, no N_2 can be adsorbed into cage, and only O_2 is adsorbed so small amount. In contrast, our finding in this paper is that the adsorption uptake of N_2 increased over X-type zeolites without any significant changes in uptake of O_2 and Ar, when the zeolites were coated with carbon by the method described below. A typical example of the improvement in adsorption uptake of N_2 is shown in Fig. 1.

Faujasite zeolites used in this study were Ca-X (atomic ratio: Si/Al= 1.15, Ca/Al=0.41, Na/Al=0.21), Na-X (Si/Al=1.16, Na/Al=0.95, Ca/Al=0.03) and Na-Y(Si/Al=1.87, Na/Al=0.60, Ca/Al =0.00). They were crashed and sieved to an average diameter of 0.5 mm. The two X-type zeolites were supplied from Bayer Japan Co. Ltd., and the Y-type zeolite from Mizusawa Chemical Industry Ltd.. The zeolites were processed in cold plasma flame (13.56 MHz, 30 W) of n-hexane vapor at about 133 Pa for a preset period of 30 min to 19 h, and the plasma treated zeolite was subjected to the non-isothermal heat treatment in a N_2 stream at a heating rate of 1.6 °C/min up to 600 °C and held at 600 °C for 1 h. The zeolite processed with plasma and thermal decomposition is designated as PC samples. Thermogravimetry was applied for determining the amount of carbon coated in wt% unit based on dry mass of the parent zeolite.

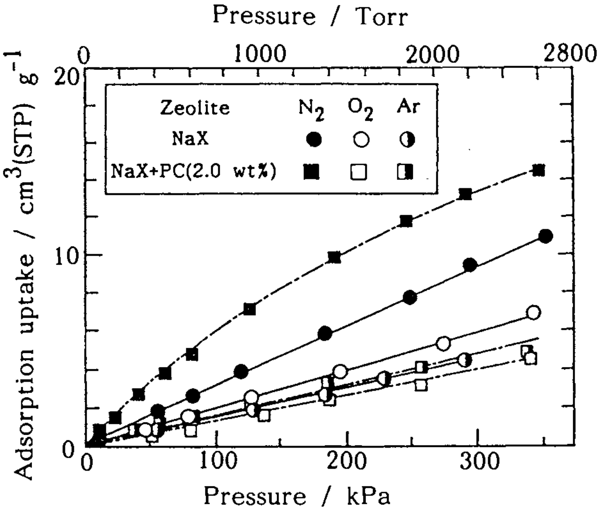

Fig.1. Adsorption isotherms at 30 °C.

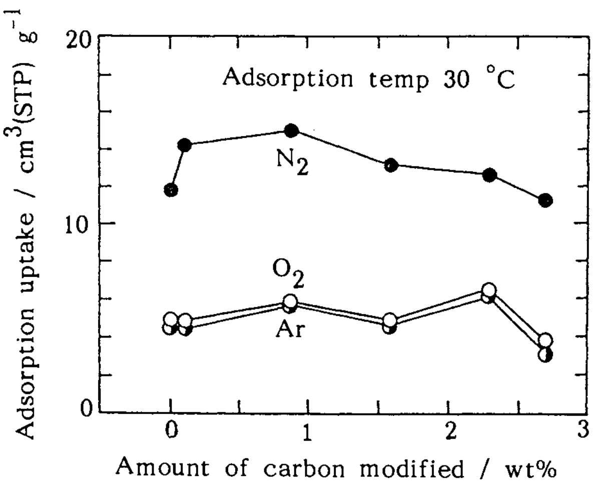

Fig.2. Effect of the amount of carbon coated over Ca-X zeolite on adsorption uptake of N_2, O_2 and Ar at 253 kPa.

Fig. 1 is the representative finding of this study, comparing the isotherms of the parent Na-X zeolite with the zeolite modified with 2 wt% carbon for adsorption of N_2, O_2 and Ar. In this case, the carbon modification not only increases N_2 uptake, but also decreases O_2 uptake, being improvement in the zeolite property for air separation by PSA process. The increase of N_2 uptake depended on the amount of carbon coated on the zeolite, showing the maximum improvement in N_2 uptake at around 1 wt% carbon for Ca-X zeolite; but too much coating suppressed the improving effect, as shown in Fig. 2. The PC-treatment seems to be more effective for Na-X zeolite than for Ca-X zeolite. It was interesting that Na-Y zeolite was hard to be coated with carbon even by a longer plasma processing, and no improvement in N_2 uptake was found by the carbon modification. Ca-A

Table 1. Pore dimension analyzed[a)] from N_2 adsorption at 77 K

Zeolite	Na-X		Ca-X		
Carbon coated / wt%	0	2.0	0	0.9	2.3
Pore volume / ml g^{-1}	0.17	0.14	0.28	0.26	0.24
Total surface / m^2 g^{-1}	561	548	1000	921	864
External surface	35	32	29	28	29
Pore surface	526	516	971	893	835

a) Sample zeolite was measured with Nippon Bell Co. Ltd. BELSORP 28, after treating at 300 °C in vacuum for 5 h. The t-plot analysis was applied for analyses by using γ-Al_2O_3 as reference material.

type zeolite also showed the negative result. As a conclusion, the PC effect was strongly dependent on the type or structure of zeolite and the amount of carbon coated.

The physical dimension of pore structure measured by the adsorption of nitrogen at 77 K were shown in Table 1. The pore volume and pore surface area analyzed by t-plot method[5)] decreased as the amount of carbon coated increased, suggesting that the adsorption room/cage of zeolite were partially filled with the carbon which was produced from thermal decomposition of n-hexane plasma residue.

Differential scanning calorimetry (DSC) was applied for parent zeolite and PC-treated zeolites. Samples were moistened with air of 98% relative humidity for 24 hours before the measurement. Heating rate in DSC was 10 °C/min from 70 °C to 420 °C. A typical result is shown in Fig. 3 which revealed that the PC-treatment improves hydrophobic property of the parent zeolite. As shown in Fig. 4 of temperature

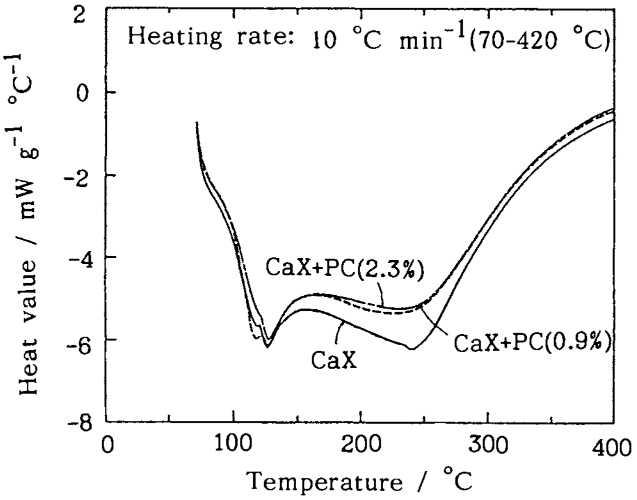

Fig.3. H_2O-DSC analysis of Ca-X zeolites.

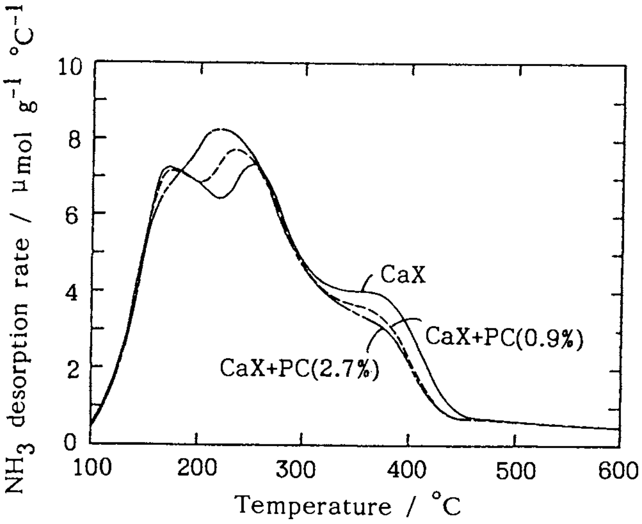

Fig.4. NH_3-TPD analysis of Ca-X zeolites. Adsorption and evacuation at 100 °C, Heating rate: 4 °C min^{-1}.

programmed desorption (TPD) of NH_3, the carbon modification suppressed the intensity of a peak above 300 °C ascribable to strong acid sites and increased the intensity of a peak below 300 °C ascribable to the weak acid sites. This suggests that carbon introduced by the PC-treatment was present not only on the outer surface of zeolite but inside faujasite cage.

There are some possible reasons for specific improvement in N_2 uptake by the PC-treatment; for examples, generation of a) new adsorption site, b) multi layer adsorption, c) dense configuration6,7) of nitrogen molecule on the surface. The most plausible explanation is that carbon in the cage is supposed to intensify the chemical interaction of adsorption field, such as quadrupole moment, leading to increased N_2 uptake. Further work on the PC effect is now in progress.

This work was partially supported by the Ministry of Education, Science and Culture of Japan through a Grant-in Aid for Scientific Research(No.04650870) in 1992. We are also grateful to Research Center of Shinagawa Refractory Co. Ltd., Bizen city, Okayama, for analyses on pore structure of our samples.

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(Received August 30, 1993)