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Separation of Oxygen and Nitrogen Due to the Controlled Pore-opening Size of CVD Zeolite A

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We modified zeolite A by the CVD (chemical vapor deposition) method using silicon methoxide ; the CVD zeolite A adsorbs oxygen in preference to nitrogen because of the controlled pore-opening size. This behavior for the adsorption of oxygen and nitrogen is inverse to that usually observed on zeolite A.

Nitrogen is adsorbed on zeolite A preferentially to oxygen; nitrogen and oxygen thereby can be separated by using zeolite A. The principle of molecular sieving is not based on the molecular size but on the chemical property, because the molecular size of nitrogen is larger than that of oxygen. On the other hand, we modified zeolite A by the CVD method; the CVD zeolite A adsorbs oxygen in preference to nitrogen because of the controlled pore-opening size. In this communication, therefore, sorption behaviors of the newly-developed CVD zeolite A will be described.

The CVD method has been developed by us to finely control the pore-opening size of zeolites. Findings on mordenite[1)] and ZSM-5[2)] which showed enhanced shape-selectivity have already been published. In this method, silicon methoxide is deposited on the external surface of zeolites only, and the deposited silica controls the pore-opening size precisely.

The experimental method of CVD was described elsewhere.[3)] After the zeolite NaA (supplied from Tosoh Ltd.; no other alkali cation was included.) was evacuated at 673 K, silicon methoxide vapor (2.5 Torr; 1 Torr=133.3 Pa) was deposited at 673 K. Water vapor was then admitted to the obtained sample at 673 K; remaining methoxide was removed by the reaction with water. By repeating the deposition, we prepared samples with various degrees of deposition. Sorption experiments were carried out gravimetrically by the McBain method in the static system. In addition, the elution chromatogram was measured to know sorption behaviors on the zeolites.

Sorption behavior of NaA and SiNaA (CVD-NaA zeolite) was shown in Fig. 1 (a) - (e). On NaA, amount of nitrogen sorbed was larger than that of oxygen. On SiNaA, sorptions of these gases became suppressed as silicon was deposited; however, its extent for nitrogen was severer than for oxygen. On 0.57 wt% (weight gain by the CVD) SiNaA, finally, only oxygen was adsorbed (Fig.1-e).

Figure 2 shows chromatograms of oxygen, nitrogen, and the 1:1 mixture on 0.21 wt% SiNaA. By comparison between them, the first peak of the mixture was assigned to nitrogen, and the second one oxygen. The sequence of this elution was reverse to that on the NaA. These chromatograms thus supported above findings of sorptions.

As shown by these sorption experiments, the CVD zeolite A adsorbs oxygen in preference to nitrogen. This property can be ascribed to the controlled pore-opening size of the CVD zeolite A. Sorption of nitrogen, which is larger than oxygen, is suppressed in a higher degree. Accuracy of controlling the pore-opening size is extremely high, because the molecular sizes of both molecules differ by 0.18 angstrom only.

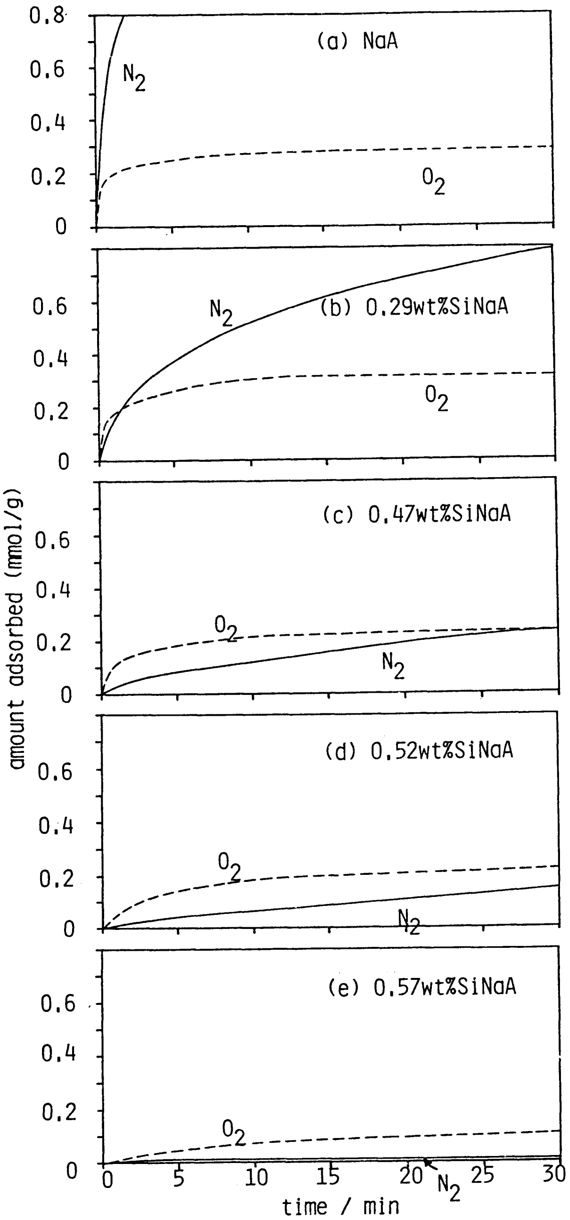

Fig. 1. Sorption of oxygen and nitrogen on NaA and SiNaA.

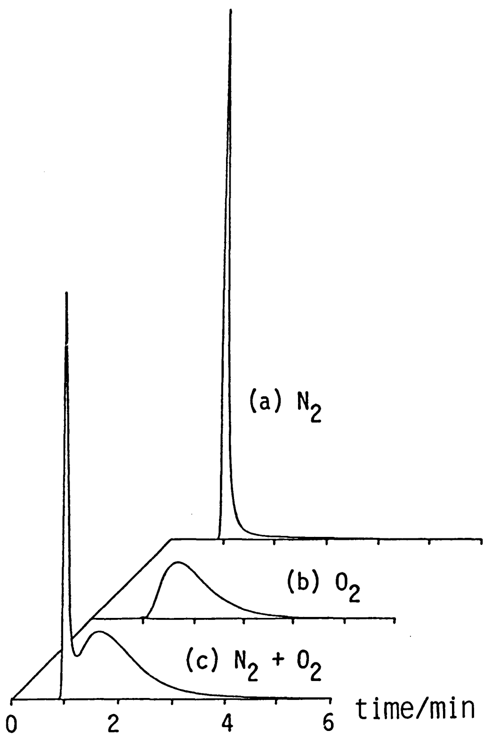

Fig. 2. Elution chromatograms on 0.21 wt% CVD A at 195 K: zeolite, 1 g; pulse size, 0.2 ml; He, 36 ml/min

References

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