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Effect of Temperature on Air Adsorption onto Alkali Metal Ion-Exchanged ZSM-5 Zeolites

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ABSTRACT

Alkali metal ion-exchanged ZSM-5 zeolites, M-ZSM-5 (M = Li, Na, K, Rb, and Cs), were prepared from Na-ZSM-5 by a conventional ion-exchange method, and their abilities to adsorb air were investigated through measurements of the amount of gases adsorbed as determined from elution curves on chromatography. The interaction of adsorbed gases and cations of M-ZSM-5 were examined from IR spectra of the adsorbed gases. It was found that the nitrogen in air was adsorbed selectively on M-ZSM-5 adsorbents, particularly Li-ZSM-5 and Na-ZSM-5 at room temperature. IR spectra indicated that nitrogen in air was adsorbed predominantly on cation sites in M-ZSM-5 zeolites owing to their strong interactions with these sites.

Key Words. Adsorption; ZSM-5 Zeolite; Air; Temperature

INTRODUCTION

Zeolites are microporous adsorbents with SiO_4 and AlO_4 tetrahedra as their fundamental structural units, and they have exchangeable cations in their pores. The cations, the source of the electric field in the pores, behave as ad-

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sorption sites for molecules as also does the pore wall. Since a report (1) on the catalytic activity of ZSM-5 in methanol conversion, extensive studies on the catalysis of various ZSM-5-type zeolites have been made (2), but there have been few reports on the adsorptive properties of ZSM-5 zeolites (3, 4).

One of the authors has studied the adsorption of several pure gases on ZSM-5 zeolites (5–7). These studies showed that the exchanged cation in a ZSM-5 zeolite significantly influences its ability to adsorb gases.

In the present study, alkali metal ion-exchanged ZSM-5 zeolites were used as adsorbents, and the effects of the exchanged cation on the adsorption of nitrogen and/or oxygen from air were studied at several temperatures. Measurements of both the amounts of adsorbed gases and the IR spectra of the adsorbed molecules have been made.

EXPERIMENTAL

The ZSM-5 adsorbents used were prepared by a conventional ion-exchange method (3, 4) from Na-ZSM-5 ($SiO_2/Al_2O_3 = 23.8$: supplied by Tosoh Co., Ltd.). Ion-exchange rates were confirmed to be about 100% by x-ray photoelectron spectroscopy. Pure air ($CO_2 < 0.1$ ppm, dew point of $H_2O < 193$ K) was obtained commercially. At the factory the atmosphere was dried and carbon dioxide was removed from the atmosphere. N_2 (purity $> 99.999\%$) and O_2 (purity $> 99.99\%$) were also obtained commercially. These gases were used after purification by passing them through cold traps at 77 K before IR measurements.

The amounts of gases adsorbed on M-ZSM-5 zeolites were determined from the elution curves on chromatography. The apparatus for measurements is shown in Fig. 1. A 2-g portion of zeolite sample was packed in a tubular column of stainless steel with a 3-mm inner diameter. The packing length was 500 mm. The adsorbent zeolites were conditioned at 573 K by passing a He carrier gas through them for 2 h before adsorption measurements commenced. Adsorption temperatures from room temperature to 373 K and a pressure of 0.12 MPa were used.

A typical profile for gas concentration is illustrated in Fig. 2. The adsorption gas is introduced in a step-function manner at time t_i. The breakthrough of gas concentration is detected at time t_b. After the reflection of the detector is saturated, the adsorption gas supply is stopped at time t_s. Helium is then introduced, and adsorbed gases elution is allowed to continue. In this experiment the outlet flow rate was decreased by adsorption. Therefore, the amounts of adsorption were determined by the elution curves (diagonal lines in Fig. 2). The correction for dead space of the flow pass was obtained by a blank test.

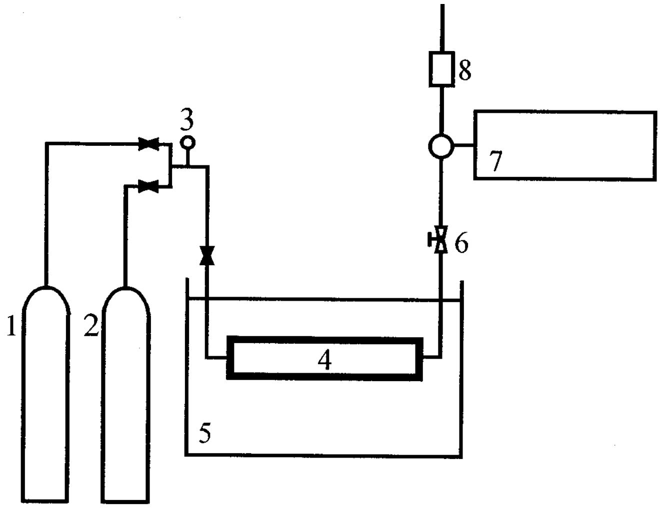

FIG. 1 Schematic diagram of experimental apparatus. (1) He gas cylinder; (2) adsorption gas cylinder; (3) pressure gauge; (4) adsorption column; (5) electric furnace; (6) flow control valve; (7) gas chromatograph; (8) soap film flowmeter.

The IR spectra of air adsorbed on the zeolites at room temperature under an air pressure of about 0.1 MPa were obtained using the cell designed by Yamazaki et al. (3). A self-supporting wafer (100–300 μm thickness) of the adsorbent was degassed in the cell at 573 K under 1.0×10^{-2} Pa for 2 h. Spectra were recorded using a JASCO VALOR-IIIFTIR spectrometer with 4 cm^{-1} resolution.

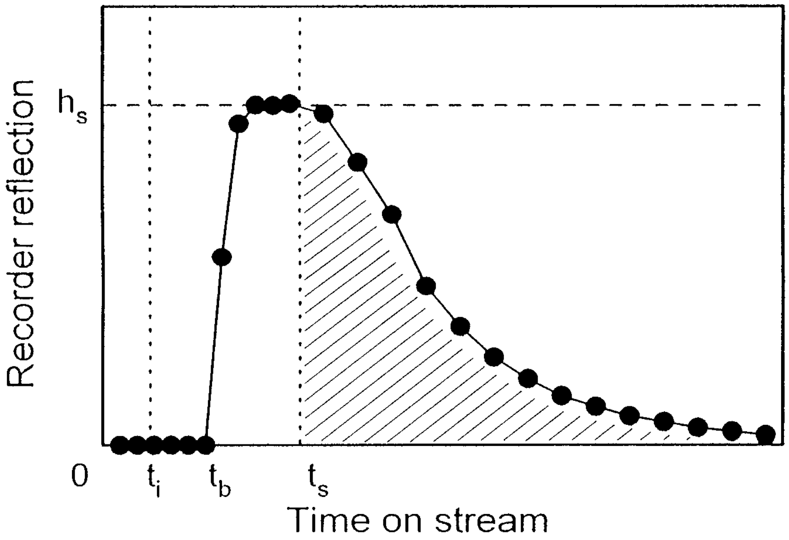

FIG. 2 Illustrative gas chromatograph of the adsorption measurements.

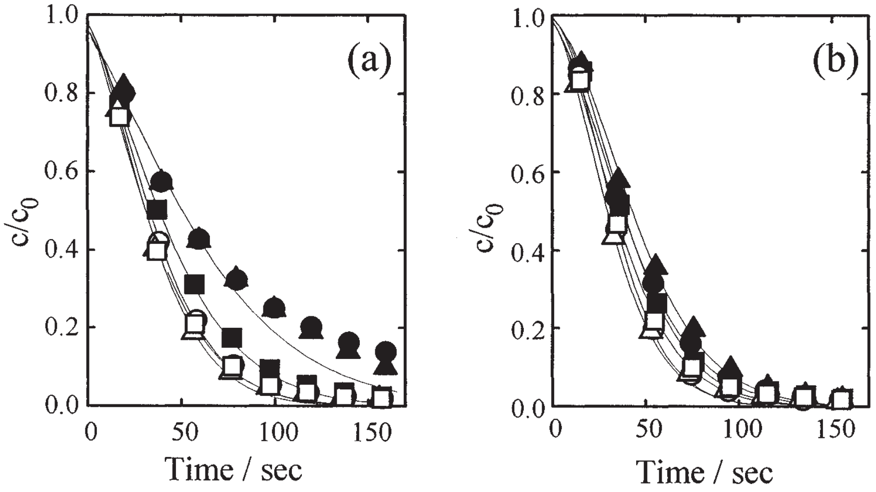

FIG. 3 Elution curves of N_2 (a) and O_2 (b) over alkali metal ion-exchanged ZSM-5 zeolites: (●) Li-ZSM-5, (▲) Na-ZSM-5, (■) K-ZSM-5, (○) Rb-ZSM-5, (△) Cs-ZSM-5, (□) H-ZSM-5. Lines: calculated.

RESULTS AND DISCUSSION

Adsorption in a Single-Component System

Figure 3 illustrates the experimental elution curves for nitrogen and oxygen from M-ZSM-5 zeolites at room temperature under a pressure of 0.12 MPa and also the calculated elution curves. The calculated values were obtained from

$$\frac{c}{c_0} = 1 - \left\{ e^{-X-T} I_0 \, (2\sqrt{XT}) + \int_0^T e^{-X-T} I_0 \, (2\sqrt{XT}) \, dT \right\} \tag{1}$$

Equation (1) can be derived (8) by assuming a Henry-type adsorption equilibrium where X and T are defined by Eqs. (2) and (3), respectively.

$$X = \frac{K_F a_v L}{u} \tag{2}$$

$$T = \frac{K_F a_v t}{\beta\gamma} \tag{3}$$

The calculated line agreed reasonably well with experimental results, although the adsorption behavior conformed to the Langmuir isotherm in this system. Although the adopted model is very simple, the model represented the experimental elution curves. This is because experiments have been performed in the low pressure range, that is, the range of Henry. Overall volumetric mass transfer coefficients and adsorption equilibrium constants determined by matching elution curves for nitrogen and oxygen at room temperature are listed in Table 1. The overall volumetric mass transfer coefficients of nitrogen are close to those of oxygen for all ZSM-5 examined. In these experiments the same types of zeolites were used, and because these zeolites have the same framework, the elution rates have the same values. The order of adsorption equilibrium constants decreased for both nitrogen and oxygen with an increase in cation (M) size except in the case of H-ZSM-5. These results indicate that the interaction between nitrogen and small cations (Li^+, Na^+) is more effective than that of oxygen. Therefore, at the first stage of adsorption, small cations are expected to play an important role for selective adsorption.

The amounts of nitrogen and oxygen adsorbed on the zeolites at room temperature were determined from the elution curves. They are shown in Fig. 4 with the BET surface areas. The different ion-exchanged cations cause a large difference of BET surface areas. A cation site model was reported in an earlier study (4). The difference of ion-exchanged cation affects the pore structure for gas adsorption. The order of the amounts of adsorption were consistent with the BET surface areas except in the case of H-ZSM-5: the amounts of adsorption by H-ZSM-5 were less than by Li-ZSM-5 and Na-ZSM-5, although their BET surface areas were similar. The electric field of the cation in H-ZSM-5 is weaker than those in other M-ZSM-5 zeolites (3). These results indicate that the amounts of adsorption of gases are governed not only by the pore structure of the ZSM-5 zeolites but also by the electric field of the cation. The amounts of nitrogen adsorbed were much more than of oxygen. For gas separation, the greater the difference of adsorption interaction and capacity, the higher is the separation ability. Therefore, on Li-ZSM-5 and Na-ZSM-5,

TABLE 1
Overall Volumetric Mass Transfer Coefficients ($K_F a_v$) and Adsorption Equilibrium Constants (β)

	$K_F a_v$ (s^{-1})		β ($cm^3 \cdot g^{-1}$)	
Zeolite	N_2	O_2	N_2	O_2
Li-ZSM-5	1.6	1.7	54	32
Na-ZSM-5	1.5	2.0	50	34
K-ZSM-5	1.5	2.1	32	29
Rb-ZSM-5	1.6	2.2	29	27
Cs-ZSM-5	1.6	1.8	25	23
H-ZSM-5	1.5	1.8	27	27

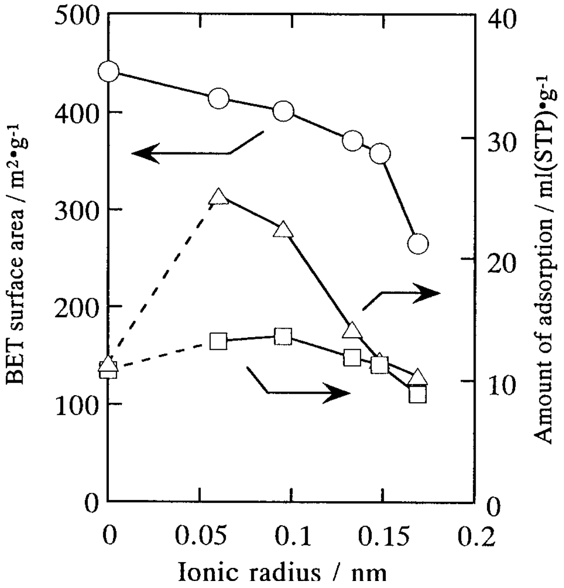

FIG. 4 BET surface areas and amount of adsorption as a function of ionic radius of cation incorporated. (○) BET surface area, (△) amount of N_2 adsorption, (□) amount of O_2 adsorption.

because the difference of adsorption capacity between nitrogen and oxygen is large, these ZSM-5 should be useful for separations of oxygen and/or nitrogen from their mixtures.

Adsorption of Nitrogen and Oxygen in Air

The separation factor α at a fixed temperature was calculated by the following equation:

$$\alpha = \frac{X_1 Y_2}{X_2 Y_1} \tag{4}$$

where X and Y respectively represent the adsorbed- and gas-phase molar fractions of binary N_2 (Component 1) and O_2 (Component 2) mixtures ($Y_1 = 0.79$, $Y_2 = 0.21$).

Figure 5 shows α of the various M-ZSM-5 zeolites for nitrogen in N_2/O_2 mixtures as a function of the adsorption temperature. The separation factors for nitrogen of all the M-ZSM-5 samples used were more than 1, indicating that they selectively adsorbed nitrogen molecules. The separation factors of the M-ZSM-5 zeolites tended to decrease with an increase in temperature and with an increase in cation (M) size, except in the case of H-ZSM-5. Li-ZSM-5 and Na-ZSM-5 particularly adsorbed nitrogen molecules selectively. These results show that the electric field of the cation significantly influences the selectivity of adsorption.

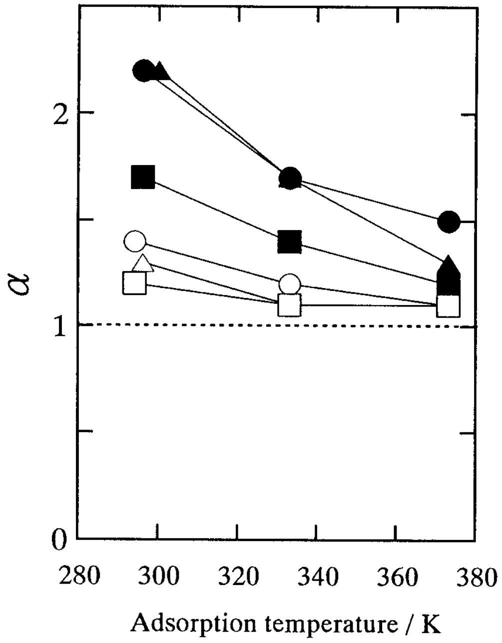

FIG. 5 Temperature dependence of separation factor, *a*, calculated from elution curves of air adsorbed on ion-exchanged ZSM-5 zeolites: (●) Li-ZSM-5, (▲) Na-ZSM-5, (■) K-ZSM-5, (○) Rb-ZSM-5, (△) Cs-ZSM-5, (□) H-ZSM-5.

In a manner similar to single-component adsorption, adsorption equilibrium constants were estimated by mixture adsorption at several temperatures. Figure 6 shows the adsorption equilibrium constants of mixture adsorption as a function of the ionic radius of a cation with the adsorption equilibrium of single-component adsorption.

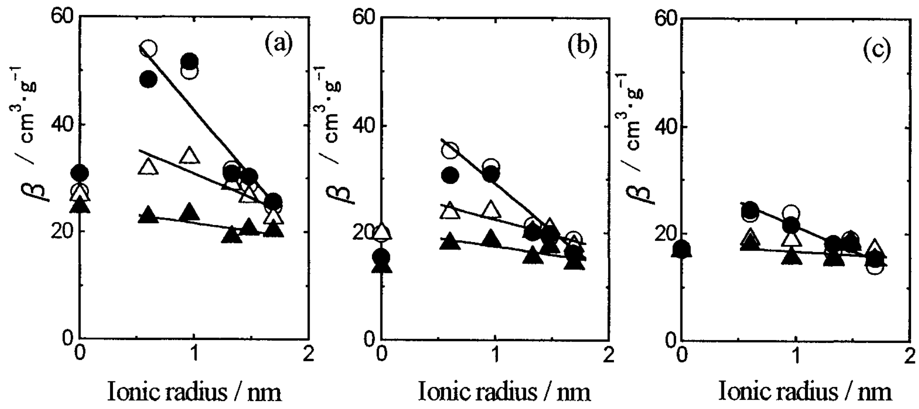

FIG. 6 Correlation between the ionic radius of cation and adsorption equilibrium constant, β. (a) Room temperature, (b) 333 K, (c) 373 K. (○) Pure N_2, (●) N_2 in air, (△) pure O_2, (▲) O_2 in air.

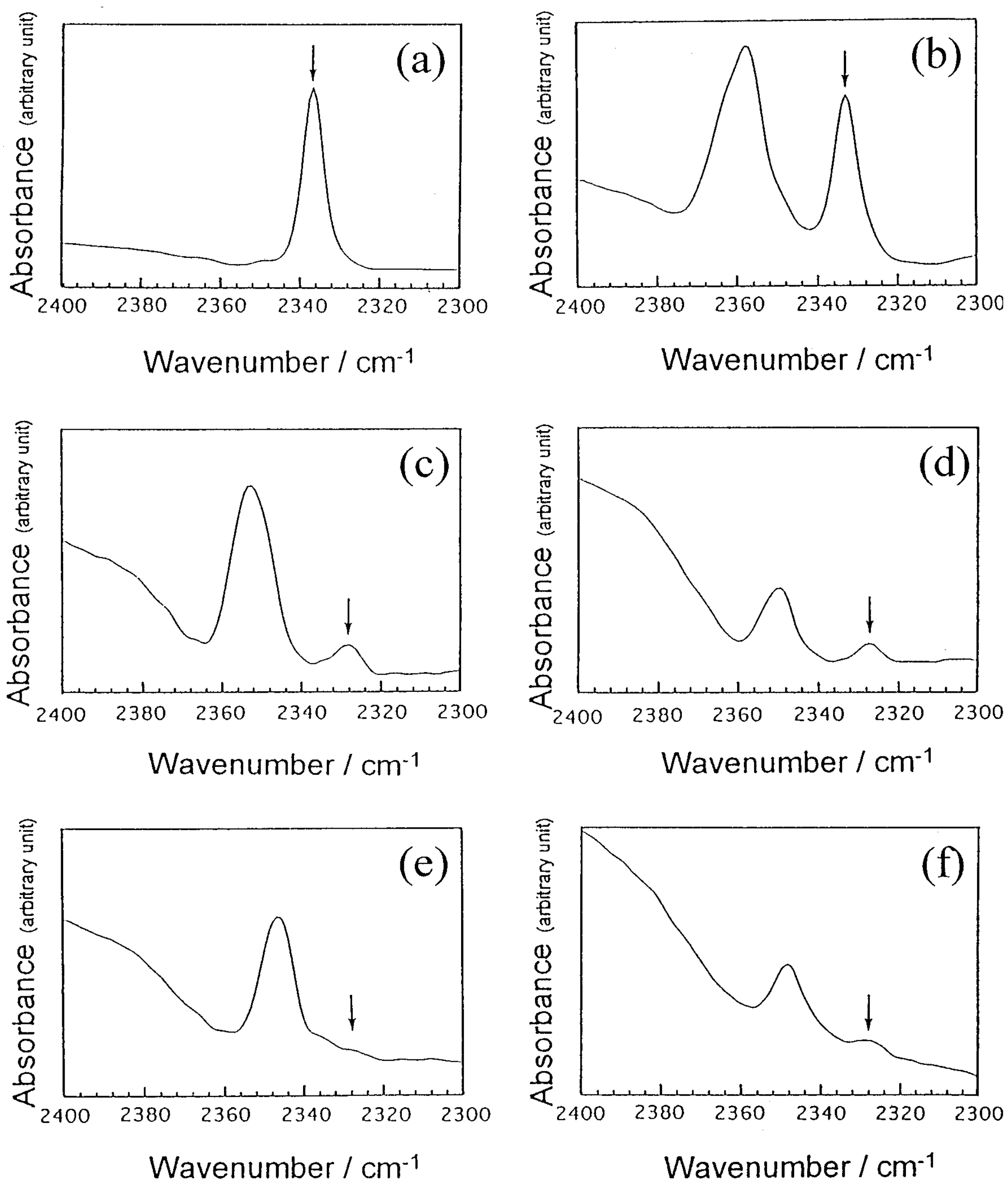

FIG. 7 IR spectra for air adsorbed by (a) Li-ZSM-5, (b) Na-ZSM-5, (c) K-ZSM-5, (d) Rb-ZSM-5, (e) Cs-ZSM-5, (f) H-ZSM-5.

At room temperature, on alkali metal ion-exchanged ZSM-5 zeolites, the adsorption equilibrium constants of nitrogen in air agreed with that of pure nitrogen. On the other hand, β of oxygen in air was smaller than that of pure oxygen. Furthermore, that of oxygen in air doesn't depend on cation species. This shows that the adsorption of nitrogen isn't affected by oxygen, but the adsorption of oxygen is affected by nitrogen, and oxygen can't adsorb on the cationic site.

TABLE 2
IR Peak Positions of Adsorbed N_2

Zeolite	Peak position (cm^{-1}) N_2 in air	 Pure N_2 (4)
Li-ZSM-5	2337	2338
Na-ZSM-5	2333	2334
K-ZSM-5	2329	2330
Rb-ZSM-5	2327	2328
Cs-ZSM-5	2327	2328
H-ZSM-5	2330	2330

The difference in the adsorption equilibrium constants between oxygen in air and pure oxygen decreased with an increase in temperature. This means that the influence of nitrogen on oxygen adsorption decreases. There are large difference in the adsorption equilibrium constants between nitrogen and oxygen at room temperature. This result corresponds to a large separation factor at room temperature.

The infrared (IR) spectra were measured for M-ZSM-5 zeolites treated in air at room temperature. IR peak profiles are shown in Fig. 7. The observed IR band of air adsorbed on M-ZSM-5 zeolites, shown by arrows, can be assigned to the nitrogen stretching vibration $\nu_{\text{N-N}}$ induced by the electric field of the adsorption site (9) because the IR spectra were similar to that of pure nitrogen adsorbed on M-ZSM-5 zeolites. However, on M-ZSM-5, except in the case of Li-ZSM-5 at ca. 2350 cm^{-1}, gaseous carbon dioxide not adsorbed on M-ZSM-5 (5) is observed. The absorption coefficient of carbon dioxide is much larger than that of nitrogen and oxygen. Trace amounts of gaseous carbon dioxide were detected. Therefore, gaseous carbon dioxide was neglected in this discussion. The peak positions of adsorbed nitrogen are listed in Table 2 where they are compared with the peak positions of pure nitrogen as reported by Yamazaki et al. (4). The peak position of adsorbed nitrogen in air was similar to that of adsorbed pure nitrogen. Therefore, we conclude that adsorption of nitrogen onto the cation site was not appreciably affected by oxygen, and that nitrogen may be adsorbed predominantly at the cation sites in M-ZSM-5 zeolites.

CONCLUSIONS

Studies on the adsorption of nitrogen and oxygen in air showed that nitrogen is adsorbed selectively by Li-ZSM-5 and Na-ZSM-5, in particular at room temperature. This suggests that nitrogen interacts more strongly with smaller cations.

The IR spectra were compatible with results on the amounts of air adsorbed. We conclude that the adsorption selectivity of M-ZSM-5 zeolites depends on their exchanged cation, which would affect the pore structure and electric field.

NOMENCLATURE

c	concentration ($g \cdot cm^{-3}$)
c_0	initial concentration ($g \cdot cm^{-3}$)
I_0	Bessel function of first degree
$K_F a_V$	overall volumetric mass transfer coefficient (s^{-1})
L	column length (cm)
t	time (s)
u	velocity of gases ($cm \cdot s^{-1}$)

Greek

β	adsorption equilibrium constant ($cm^3 \cdot g^{-1}$)
γ	bed density ($g \cdot cm^{-3}$)

REFERENCES

1. R. J. Argauer and G. R. Landolt, US Patent 3,702,886 (1972).
2. For instance, see *Proceedings of the 8th International Congress on Catalysis, July 2–6, 1984, West Berlin*, Verlag Chemie, Weinheim, 1984.
3. T. Yamazaki, I. Watanuki, S. Ozawa, and Y. Ogino, *Langmuir*, *4*, 433 (1988).
4. T. Yamazaki, I. Watanuki, S. Ozawa, and Y. Ogino, *Bull. Chem. Soc. Jpn.*, *61*, 1039 (1988).
5. T. Yamazaki, M. Katoh, S. Ozawa, and Y. Ogino, *Mol. Phys.*, *80*, 313 (1993).
6. M. Katoh, T. Yamazaki, and S. Ozawa, *Bull. Chem. Soc. Jpn.*, *67*, 1246 (1994).
7. M. Katoh, T. Yamazaki, H. Kamijo, and S. Ozawa, *Zeolites*, *15*, 591 (1995).
8. K. Suzuki and H. Kitagawa, *Kyuchaku no kiso to sekkei*, Makishoten (1976, in Japanese).
9. H. Förster and M. Schuldt, *J. Chem. Phys.*, *66*, 5237 (1977).

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