[April, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 1039—1044 (1988)* 1039

Infrared Spectra of Nitrogen Adsorbed on Ion-Exchanged ZSM-5 Zeolite

Tatsuya Yamazaki,* Isao Watanuki, Sentaro Ozawa, and Yoshisada Ogino
Department of Chemical Engineering, Faculty of Engineering, Tohoku University, Aramaki-Aoba, Sendai 980

(Received August 11, 1987)

Amounts of nitrogen adsorbed by ion-exchanged ZSM-5 zeolites (H^+, Li^+, Na^+, K^+, Rb^+, and Cs^+) and silicalite have been measured under various conditions; pressure=6.7×10^2—6.7×10^4 Pa, temperature=196—273 K. IR spectra of adsorbed nitrogen have also been measured at 226 K under various nitrogen pressures (1.3×10^2—4.0×10^4 Pa). The adsorption capacity, the specific surface area, and the heat of adsorption have been evaluated from the adsorption data. These quantities coupled with the IR peak shifts observed have revealed that the nitrogen molecule adsorbed on a small and strong cationic site (Li^+, Na^+) has an orientation in which the longer molecular axis lies in parallel with the direction of the electric field of the cation site. It has also been revealed that the nitrogen molecule adsorbed on a large (K^+, Rb^+, Cs^+) or weak (H^+) cationic site takes on no special orientation. The electric field evaluated by analyzing the IR intensity is consistent with the adsorption model obtained.

ZSM-5 type zeolites have been studied extensively[1] as molecular shape selective catalysts and catalyst carriers. The adsorptive properties of the zeolites have also been studied by many researchers.[2—5] Nevertheless details of the molecular behavior of adsorbates in the zeolite pore still remain to be discovered. The present authors[6—8] have attempted to clarify the nature of the adsorption site over the ZSM-5 zeolite surface using an infrared spectroscopic technique developed by Cohen de Lara et al.[9—12] As reported in earlier papers,[6—8] this technique has yielded valuable information about the behavior of methane adsorbed on ZSM-5 zeolites. Nitrogen adsorption has been studied by the same technique in the present work, in order to accumulate further information about the adsorptive properties of the zeolites. Interesting results concerning interaction between the nitrogen molecule and the cationic adsorption site have been obtained. The purpose of this paper is to describe the experimental results and discuss the adsorption model.

Experimental

Materials. The zeolites used as adsorbents are listed in Table 1, which also summarizes adsorptive properties of these zeolites. The zeolites other than silicalite and NaZSM-5 were prepared by a conventional ion exchange method using 0.3—1.0 mol dm^{-3} solution containing a desired cation. A chemical analysis of the sample prepared proved that the ion exchange had been completed.

Commercial high purity nitrogen was used as an adsorbate gas after passage through a cold trap immersed in liquid nitrogen.

Methods. Details of the experimental methods have already been reported[6] and only important points are described below.

The amount of adsorption was measured using a conventional constant pressure type adsorption apparatus. The adsorbent was degassed at 573 K for 12 h at 1.3×10^{-3} Pa. The temperature range of the adsorption measurement was 196—273 K and the pressure range was 6.7×10^2—6.7×10^4 Pa. Part of the adsorption data was obtained at 77 K and used for the surface area (A_s) calculation; a finite layer BET theory (1.2—1.6 layers depending on the sample) was applied.

A cell reported in the previous paper[6] was used in the infrared (IR) spectroscopic study. A sample disk with a thickness of ca. 100 μm was degassed in the cell at 573 K for 12 h at 1.3×10^{-3} Pa. The IR spectra were recorded on a JEOL-JIR-100 FTIR spectrometer at a resolution of 2 cm^{-1} by averaging 200 scans. The temperature of the IR

Table 1. Adsorptive Properties of Ion-Exchanged ZSM-5 Zeolites and Silicalite

Zeolite	Ionic radius[a] of cation, r_0	Surface[b] area, A_s	Adsorption capacity, V_m	Heat of adsorption, q°_{st}	Number of cationic sites, b_c
	Å	m^2 g^{-1}	10^{-6} m^3-NTP/g	kJ mol^{-1}	10^{-3} mol g^{-1}
HZSM-5	−0.04[c]	442 (1.58)	44.3	16.6	1.32
LiZSM-5	0.60	439 (1.41)	45.9	36.3	0.94
NaZSM-5[d]	0.95	414 (1.23)	48.8	27.9	1.28
KZSM-5	1.33	390 (1.29)	44.9	23.7	1.25
RbZSM-5	1.48	359 (1.29)	38.7	21.6	1.18
CsZSM-5	1.69	310 (1.24)	29.6	20.8	1.12
Silicalite[e]	—	337 (1.55)	42.0	16.2	0.02

a) Except for the value of H^+, the values reported by L. Pauling in "The Nature of The Chemical Bond," 3rd ed, p. 518, Cornell University Press (1960) are shown. b) Values in parenthesis are the number of layers. c) The value reported by R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B,* **25**, 925 (1969). d) Original zeolite kindly provided by Mr. K. Igawa, Chem. Res. Lab., Toyo Soda Manufacturing, Co. Ltd.. SiO_2/Al_2O_3=23.3 in molar ratio. e) Kindly provided by Prof. T. Yashima, Tokyo Inst. Techn. SiO_2/Al_2O_3=2000 in molar ratio.

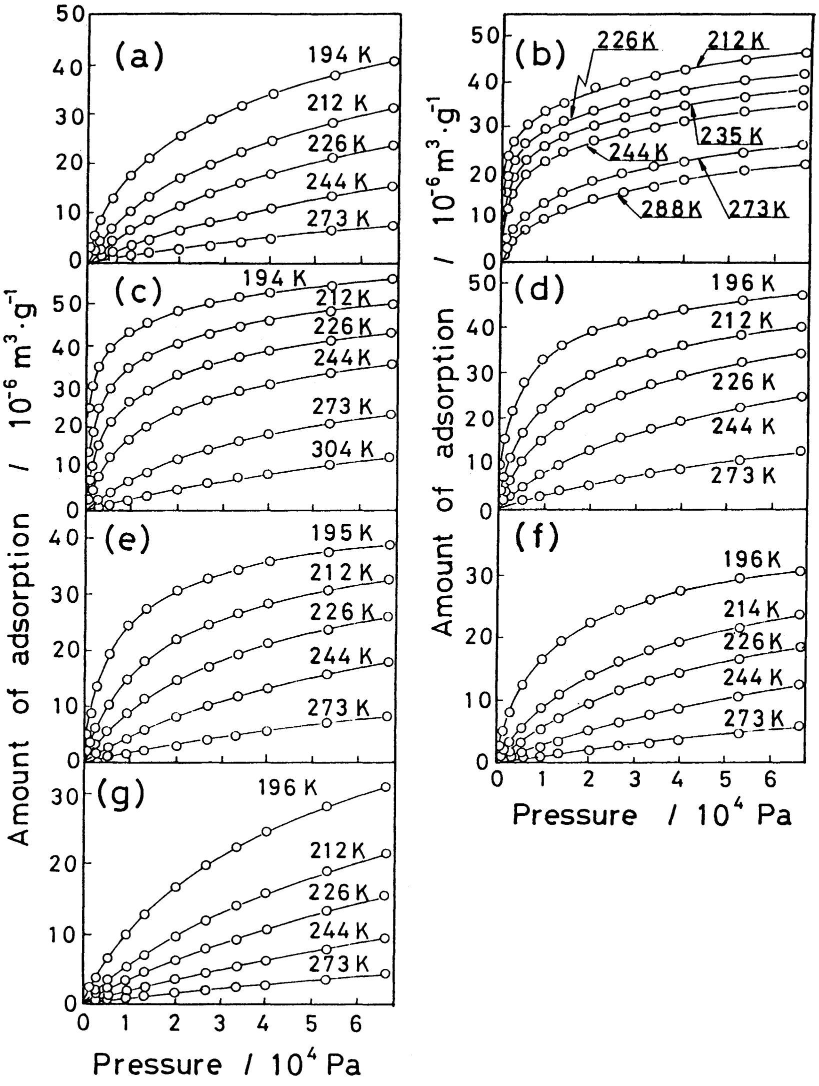

Fig. 1. Isotherms for nitrogen adsorption on ion-exchanged ZSM-5 zeolites and silicalite. a: HZSM-5, b: LiZSM-5, c: NaZSM-5, d: KZSM-5, e: RbZSM-5, f: CsZSM-5, g: silicalite.

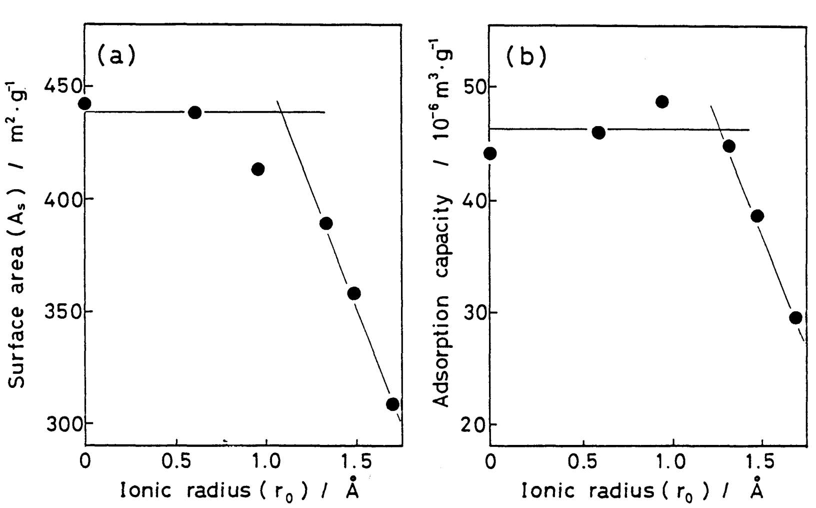

Fig. 2. Surface area and adsorption capacity of ion-exchanged ZSM-5 zeolites as a function of ionic radius of cation incorporated. a: surface area, b: adsorption capacity.

measurement was 226 K and the pressure range was 1.3×10^2—4.0×10^4 Pa.

Results and Discussion

Amount of Adsorption. Adsorption isotherms obtained are shown in Fig. 1 (a—g). The shapes of all the isotherms are analogous. It must be pointed out, however, that even silicalite, which contains few cationic adsorption sites, adsorbs a significant amount of nitrogen. This suggests that the pore wall itself provides nitrogen with adsorption sites and the ZSM-5 zeolite would have two kinds of adsorption sites, i.e. cationic sites and silicalite-like sites.

Although the full range of the adsorption isotherm could not be expressed by a Langmuir adsorption equation, part of the isotherm ranging from 1.3×10^4 to 6.7×10^4 Pa could be approximated by this adsorption equation and enabled us to estimate the maximum adsorption capacity V_m of the adsorbent. The V_m values thus obtained and the specific surface area A_s are shown in Fig. 2(a,b) as a function of the ionic radius (r_0)[13] of the cation incorporated into the zeolite. It is interesting that, both for RbZSM-5 and for CsZSM-5, the V_m value as well as the A_s value are remarkably small compared with the values for other zeolites.

The above mentioned relationships between V_m (or A_s) and r_0 have led the authors to draw the adsorption model illustrated in Fig. 3(a,b). The model assumes that pentagonal oxide ion rings[14] constitute the pore wall and the oxide ion has an ionic radius of 1.4 Å.[13] As shown in Fig. 3a, the void surrounded by five oxide ions can accept the whole body of a cation with a small radius; H^+, Li^+, and Na^+. On the other hand, as shown in Fig. 3b, the void can accept only part of the body of a large cation and a considerable part of the pore space over the pentagonal site is occupied by the cation itself; Rb^+ and Cs^+. The situation of K^+ is somewhat similar to that shown in Fig. 3b, though the extent of occupation of the pore space by the cation is small. It is thus obvious that an incorporation of such a small cation as H^+, Li^+, or Na^+ has little effect on the adsorption capacity as well as the specific surface area of the zeolite. The same situation is expected for K^+. On the other hand, the incorporation of Rb^+ or Cs^+ is expected to reduce V_m and A_s.

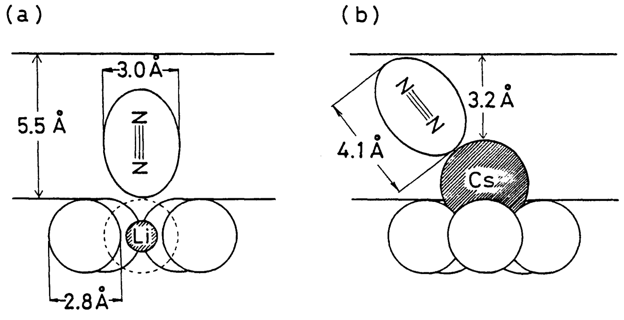

Fig. 3. Model for nitrogen adsorption on the cationic site. a: N_2 on Li^+ site, b: N_2 on Cs^+ site. (molecular size of nitrogen was taken from Ref. 15; pore size was taken from Ref. 14; O^{2-} size was taken from Ref. 13).

The model shown in Fig. 3 induces a discussion on the orientation of the nitrogen molecule adsorbed on the cationic site. As shown in Fig. 3a, the nitrogen molecule adsorbed on a small cationic site can take an orientation wherein the longer molecular axis is parallel with the direction of the electric field of the cation (perpendicular to the pore surface). On the other hand, as shown in Fig. 3b, the nitrogen molecule adsorbed on a large cation would find it difficult to assume such an orientation. Here, the discussion is rather speculative but its importance becomes clear in the later section of this discussion.

Heat of Adsorption. The adsorption isotherms shown in Fig. 1 enabled us to evaluated the isosteric heat of adsorption q_{st} using the Clausius-Clapeyron equation. An extrapolation of the q_{st} values obtained at different coverages to zero-coverage was carried out, in order to evaluate the heat of adsorption q°_{st} at zero coverage. The q°_{st} values thus obtained are also listed in Table 1. The decreasing order of the q°_{st} value is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > H^+ >$ silicalite. The larger q°_{st} value for ion-exchanged zeolites than that for silicalite strongly suggests that the adsorptive forces of all the cations are stronger than that of the pore wall (silicalite-like site). The adsorptive force of a cation consists of a dispersion force, an attractive force exerted upon the induced dipole on the adsorbed nitrogen, and an attractive force exerted upon the quadrupole of the adsorbed nitrogen molecule,[15] except for the repulsive force. The attractive forces mostly increase when the ionic radius of the cation becomes small. Thus the above sequence of q°_{st} values is reasonable, except for the small q°_{st} value for HZSM-5. Since the size of H^+ is very small (−0.04 Å),[16] oxide ions surrounding it would hinder the adsorbed nitrogen molecule from contacting with H^+. Namely, the steric hindrance of the oxide ions would separete the admolecule far from H^+, resulting in a weak adsorptive force and hence a small q°_{st}. A small ionic character[17] of H^+ might also be the cause of the small q°_{st} value of the HZSM-5 zeolite.

IR Spectra of Adsorbed Nitrogen. IR spectra of nitrogen-ion-exchanged zeolite adsorption systems are shown in Fig. 4(a—f). The observed spectra (dotted line) were found to be well simulated by a Lorentzian function as shown in the figure (solid line). According to the literature,[18] the IR band observed is assigned to the nitrogen stretching vibration ν_{N-N} which is usually IR inactive. An electric field of the cationic site probably has induced an IR active state of the adsorbed nitrogen.[18] This view has been supported by the fact that no absorption band has been observed for the silicalite-N_2 system. It is thus expected that the IR spectra shown in Fig. 4 would contain much informa-

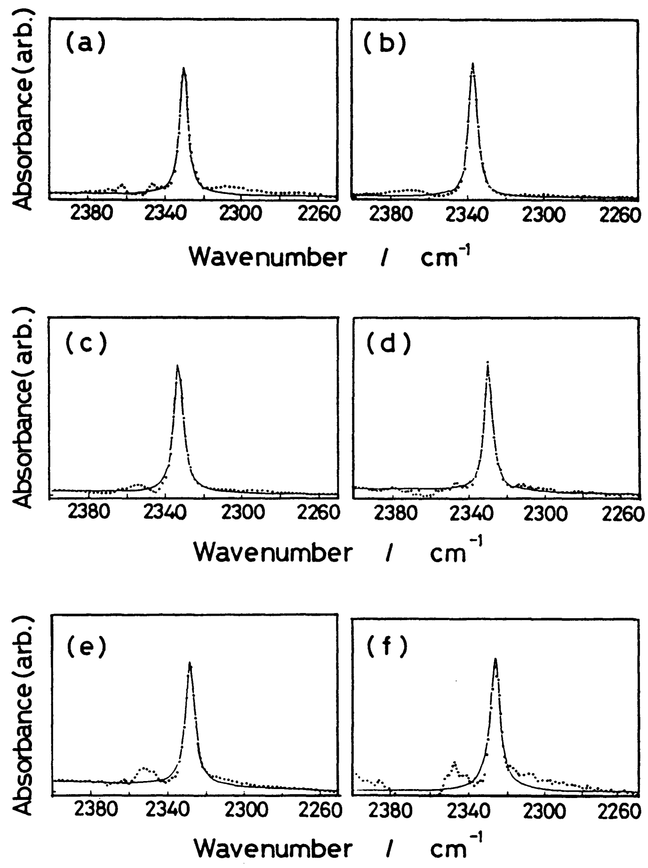

Fig. 4. IR absorption spectra for N_2– ion-exchanged ZSM-5 adsorption systems. a: HZSM-5, b: LiZSM-5, c: NaZSM-5, d: KZSM-5, e: RbZSM-5, f: CsZSM-5. (……) observed, (----) simulated.

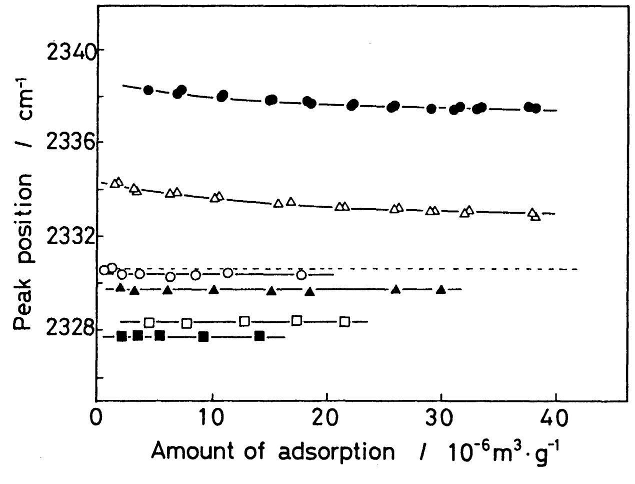

Fig. 5. Peak positions of IR bands for nitrogen adsorbed on ion-exchanged ZSM-5 zeolites. ●: N_2-LiZSM-5, △: N_2-NaZSM-5, ○: N_2-HZSM-5, ▲: N_2-KZSM-5, □: N_2-RbZSM-5, ■: N_2-CsZSM-5, ----: N_2-gas.

tion about the interaction between the adsorbed nitrogen molecule and the cationic site. On account of the IR data, the adsorption characteristics suggested by the preceding discussion are expected to be further clarified.

IR Peak Position. IR peak positions for all the ZSM-5-N_2 adsorption systems are shown in Fig. 5 as a function of the amount of adsorption. The peak position varied little with the change in the amount of adsorption. The peak for the LiZSM-5-N_2 system was found at the highest wavenumber position and was followed by those for the other adsorption systems. The descending order of the peak position was $Li^+ > Na^+ > K^+ \simeq H^+ > Rb^+ \simeq Cs^+$. It must be pointed out, in addition, that the peak positions both for the LiZSM-5-N_2 system and for the NaZSM-5-N_2 system are located at considerably higher wavenumber than the gaseous nitrogen peak expressed by a dotted line (2330.7 cm^{-1}; Raman spectral value).[19]

The high frequency shifts observed (LiZSM-5-N_2, NaZSM-5-N_2) suggest that the adsorbed nitrogen molecule takes on an orientation as exemplified in Fig. 3a. According to the theoretical calculation of Cohen de Lara et al.,[10] a high frequency shift of the nitrogen IR band results from the orientation of the nitrogen molecule toward the direction of the electric field of the cationic site. The ionic radii of Li^+ and Na^+ are small and hence there are little geometrical restriction for the molecule to take such an orientation as mentioned above and illustrated in Fig. 3a. In addition, the strong attractive forces of these cations would be favorable to maintaining this orientation. On the other hand, a weak adsorptive force at the H^+ site probable can not maintain the orientation, though there is little geometrical restriction. The adsorptive force of the K^+ site is not so strong and, in addition, a small geometrical restriction due to the somewhat large ionic radius of this cation may exist. Thus the molecular orientation mentioned above would not persist on the K^+ site, though it might momentarily be induced. Both for the Rb^+-N_2 system and for the Cs^+-N_2 system, the adsorptive forces are weak and the Li^+-N_2 like orientation of adsorbed nitrogen is geometrically hindered as shown in Fig. 3b. Approximately speaking, therefore, nitrogen molecules on H^+, K^+, Rb^+, Cs^+ cationic sites would be in a random orientation state. This view is supported by the experimental observation that the IR peak positions for these systems are located close to that of the gaseous nitrogen (Fig. 5).

IR Peak Intensity. The integral molar extinction coefficient A needed to discribe the intensity of IR spectra of an adsorbed species is defined by[9]

$$A=(1/n\cdot l)\int\log(I_0/I)\,\mathrm{d}\tilde{\nu}, \qquad (1)$$

where I_0 is the intensity of incident light, I is the intensity of transmitted light, $\tilde{\nu}$ is the wavenumber, n is the number of moles of the vibrator in unit volume of the sample, and l is the thickness of the sample.

If we express the sample weight, the total amount of admolecules on the cationic sites of the sample, and the cross-sectional area of the sample by W (g), m_c (mol), and a (cm^2), respectively, Eq. 1 can be rewritten as follows;

$$A=[1/(m_c/W)(W/a)]\int\log(I_0/I)\,\mathrm{d}\tilde{\nu}, \qquad (2)$$

or more concisely

$$AM_c=S, \qquad (3)$$

where $M_c=m_c/W$, and $S=[1/(W/a)]\int\log(I_0/I)\mathrm{d}\tilde{\nu}$. Since the right hand side of Eq. 3 can be evaluated from the experimental data, the molar extinction coefficient A is obtainable if we know the value of M_c. It must be pointed out here that the experimentally measured amount of adsorption M involves the amount of adsorption onto the pore wall (silicalite-like adsorption; M_s). Thus we can not use the adsorption isotherms shown in Fig. 1 to obtain the M_c value.

The evaluation of A can, however, be carried out in the following manner. Namely, if we assume that a Langmuir type adsorption equation is applicable to the nitrogen adsorption onto the cationic sites, the following relation should hold;

$$S=AM_c=AK_cb_cP/(1+K_cP), \qquad (4)$$

where K_c, b_c, and P denote the adsorption equilibrium constant, the number of moles of the cation sites in unit weight of the zeolite sample, and the equilibrium nitrogen pressure, respectively. This equation (Eq. 4) enables us to evaluate A from the IR peak areas obtained under varying pressures.

According to Eq. 4, plots of P/S against P should be linear because

$$P/S=1/(AK_cb_c)+P/Ab_c. \qquad (5)$$

Indeed, as we can see in Fig. 6, the straight line relationship between P/S and P has been found for all the adsorption systems. Since the value of b_c is known (Table 1), we can obtain A from the slope of the straight line. Values of A obtained in the present study are listed in Table 2. The decreasing order of the A value is $A_{\mathrm{Li}^+}>A_{\mathrm{Na}^+}>A_{\mathrm{K}^+}>A_{\mathrm{Rb}^+}>A_{\mathrm{Cs}^+}>A_{\mathrm{H}^+}$. This is parallel with the decreasing order of the heat of adsorption q°_{st} and very reasonable.

Electric Field of the Cationic Site. The electric field E of the cationic site in the ZSM-5 zeolite has already been determined[8] using methane as a probing molecule. Since the average size of the nitrogen molecule is almost the same as that of methane, the electric field determined by nitrogen should be identical with that obtained by methane. Thus we can examine the validity of the preceding discussion by comparing the E value obtained for nitrogen with that obtained for methane.

The relation between the electric field E and the IR extinction coefficient A varies, depending on the orientation of the probe molecule at the adsorption site. According to the preceding discussion, nitrogen molecules adsorbed on any of H^+, K^+, Rb^+, and Cs^+ site are considered to be almost randomly oriented. Thus the following relation[9] would be applicable;

$$A=(\pi/3c^2)E^2[(\partial\bar{\alpha}/\partial q)^2+(2/9)(\partial\gamma/\partial q)^2], \qquad (6)$$

where c is the velocity of light, $\bar{\alpha}$ is the average polarizability defined from the polarizability ($\alpha_{\parallel}$) along the direction of the electric field and that ($\alpha_{\perp}$) perpendicular to the direction of the electric field by $(1/3)(\alpha_{\parallel}+2\alpha_{\perp})$, γ is defined by $(\alpha_{\parallel}-\alpha_{\perp})$ to express an anisotropy in the polarizability, and q is the normal coordinate of vibration.

On the other hand, the following relation[9] would be applicable in evaluating the electric fields of the Li^+ site and the Na^+ site, because the nitrogen molecules on these sites are expected to take an orientation such

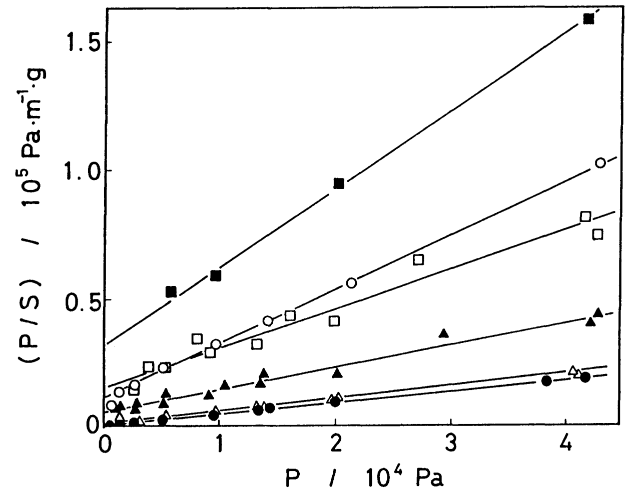

Fig. 6. Plots showing linear relationships between P/S and P. ●: N_2-LiZSM-5, △: N_2-NaZSM-5, ▲: N_2-KZSM-5, □: N_2-RbZSM-5, ○: N_2-HZSM-5, ■: N_2-CsZSM-5.

Table 2. IR Spectroscopic Data for Nitrogen Adsorbed on Ion-Exchanged ZSM-5 Zeolites

Zeolite	Peak position[a)]	Extinction coefficient, A	Electric field of cation, $E^{\mathrm{b,c)}}$
	cm^{-1}	$\mathrm{m\ mol}^{-1}$	10^5 esu
HZSM-5	2330	351	1.19 (0.80)
LiZSM-5	2338	2457	2.00 (1.58)
NaZSM-5	2334	1602	1.62 (1.55)
KZSM-5	2330	897	1.91 (1.47)
RbZSM-5	2328	552	1.50 (1.36)
CsZSM-5	2328	297	1.10 (1.21)

a) Values at $M=10\times10^{-6}$ $\mathrm{m^3}$-NTP/g are listed; M denotes the amount of adsorption. b) Values in parenthesis are the electric fields measured with methane. c) 1 esu=3×10^4 V m^{-1}.

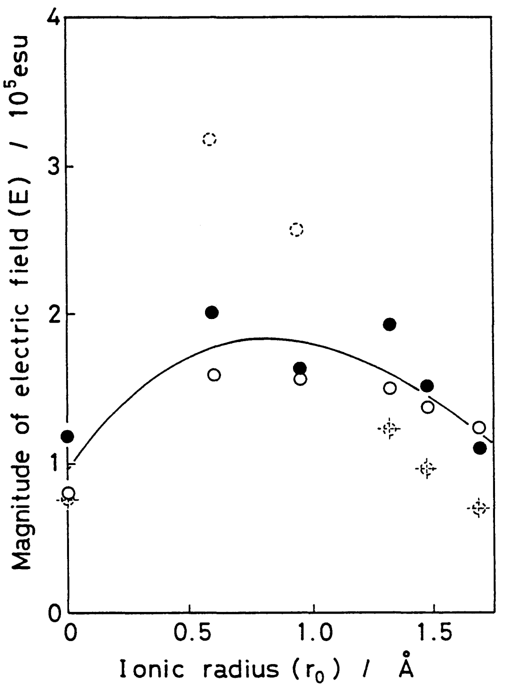

Fig. 7. Electric fields of cationic sites. ●: obtained from nitrogen IR data, ○: obtained from methane IR data, ◌: values for random orientation (N_2-Li^+, and N_2-Na^+), ⊕: values with orientation (N_2-H^+, N_2-K^+, N_2-Rb^+, and N_2-Cs^+).

as is exemplified in Fig. 3a;

$$A=(\pi/3c^2)E^2[(\partial\bar{\alpha}/\partial q)+(2/3)(\partial\gamma/\partial q)]^2. \qquad (7)$$

The results of the calculation are shown in Fig. 7. A close agreement between the E values obtained from the nitrogen IR data and those obtained from the methane IR data (Table 2) proves the validity of the adsorption model hitherto discussed. It must finally be noted that the following literature values[9)] have been used in the above mentioned calculation of E;

$$|\partial\bar{\alpha}/\partial q|=0.66\ N^{1/2}\ 10^{-16}\ \mathrm{cm^2\,g^{-1/2}},$$

$$|\partial\bar{\gamma}/\partial q|=0.82\ N^{1/2}\ 10^{-16}\ \mathrm{cm^2\,g^{-1/2}},$$

where N is the Avogadro number.

Both derivatives have been assumed to be positive, in the present study. It is reported in the literature[9)] that the positive value for $\partial\bar{\alpha}/\partial q$ appears pertinent. The use of negative value for $\partial\gamma/\partial q$ with positive value of $\partial\bar{\alpha}/\partial q$ in the calculation of Eq. 7 results in anomalously large values of E for every cation examined in the present study.

References

1) For instance; P. B. Weitze, "Proc. of the 7th Intern. Congr. on Catal.," ed by T. Seiyama and K. Tanabe, Kodansha Tokyo (1981), p. 3.

2) P. A. Jacobs, H. K. Beyer, and J. Valyon, *Zeolites,* **1**, 161 (1981).

3) S. Furuyama, M. Miyazaki, and H. Inoue, *J. Phys. Chem.,* **88**, 1741 (1984).

4) P. Wu and Y. H. Ma, "Proc. of the 6th Intern. Zeolite Coference," ed by D. Olsen and A. Bisio, Butterworths Guildford (1984), p. 251

5) R. E. Richards and L. V. C. Rees, *Langmuire,* **3**, 335 (1987).

6) T. Yamazaki, I. Watanuki, S. Ozawa, and Y. Ogino, *Nippon Kagaku Kaishi,* **1987**, 1535.

7) T. Yamazaki, Y. Abe, I. Watanuki, T. F. Ding, S. Ozawa, and Y. Ogino, *Chem. Lett.,* **1987**, 1457.

8) T. Yamazaki, I. Watanuki, S. Ozawa, and Y. Ogino, *Langmuire,* submitted.

9) E. Cohen de Lara and Y. Delaval, *J. Chem. Soc., Faraday Trans. 2,* **74**, 790 (1978).

10) E. Cohen de Lara, *J. Chem. Soc., Faraday Trans. 2,* **77**, 355 (1981).

11) E. Cohen de Lara, R. Kahn, and R. Seloudoux, *J. Chem. Phys.,* **83**, 2646 (1985).

12) B. Barrachin and E. Cohen de Lara, *J. Chem. Soc., Faraday Trans. 2,* **82**, 1953 (1986).

13) L. Pauling, "The Nature of The Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York (1960), p. 514.

14) G. T. Kokotailo, S. L. Lawton, D. H. Olsen, and W. M. Meier, *Nature (London),* **272**, 437 (1978).

15) R. M. Barrer and W. I. Stuart, *Proc. R. Soc. London, Ser. A,* **237**, 439 (1959).

16) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B,* **25**, 925 (1969).

17) L. Pauling, "The Nature of The Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York (1960), p. 97.

18) H. Föster and M. Schuldt, *J. Chem. Phys.,* **66**, 5237 (1977).

19) F. Rasetti, *Phys. Rev.,* **34**, 367 (1929).