Analyses of ν_1-Band of Methane Adsorbed on Ion-exchanged L-Zeolites

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To clarify the nature of cation sites in L-zeolite, an analysis of ν_1-IR band of adsorbed methane was carried out. The relation between the peak shift, $\Delta\nu_1$, and the strength of electric filed, E, and that between $\Delta\nu_1$ and the molar extinction coefficient of induced band, A, were derived on the basis of perturbation theory. Estimating the maximum IR absorption intensity expermentally, the numbers of cations available for methane adsorption in both K- and Rb-exchanged L-zeolites are estimated to be 3 atom/unit cell.

It is important to characterize cations in zeolite because they frequently act as active sites for many catalytic reactions and adsorption processes. Among various technique used to characterize a zeolite, molecular probe IR spectroscopy is a promising one since this method only detects sites accessible by gaseous molecules.[1,2] The purpose of the present study is to develop an analysis of the induced ν_1-band of adsorbed methane, and to apply the method to the characterization of the cation sites incorporated in ion exchanged L-zeolites.

Samples (Table 1) were prepared by ion- exchanging K-L zeolite (Tosoh; Si/Al = 3.1). The rates of ion exchange on surface was generally higher than that of the bulk, it showed that the ion exchange on the L-zeolites were rather heterogenious. The pelletized sample was evacuated in IR cell at 350℃ for 12h before IR measurement. IR spectra were obtained by transmission method using JEOL-JIR100 spectrometer with TGS detector and resolution of 4cm^{-1}.

Table 1. Ion exchanging rate and ν_1-peak position and $S_{1,\max}$ of adsorbed methane on L-zeolites

	Ion exchanging rate (%)		ν_1-peak position	$S_{1,\max}$ [c]
	surface[a]	bulk[b]	cm^{-1}	cm•g^{-1}
KL	--	--	2896	313.7
HL	83	73	2904	-
NaL	67	32	2894	-
RbL	79	79	2897	213.2
CsL	75	50	2897	-
MgL	34	28	2867	-
CaL	41	29	2873	-
SrL	31	33	2887	-
BaL	58	38	2885	-

[a] Estimated from the reduction of K 2p peak in XPS.
[b] Estimated from the reduction of K ($K\alpha_{1,2}$) peak in XRF.
[c] $S_{1,\max}$ is the maxima of ν_1-band intensity

The ν_1-band of methane induced by the electric field of adsorption site appeared on every samples. Furthermore, in cases of H- and divalent cation exchanged samples, the peak could be deconvoluted into two peaks, i.e. ones for adspecies on the exchanged cation site and the residual K$^+$ site. The ν_1-peak positions of interacting species on the exchanged cation sites were listed in Table 1. In every case, the peak was shifted to a lower frequency than that of gaseous methane (Raman; 2914 cm^{-1}),[3] and they were plotted in Fig.1 as a function of the polarizing power of cations (Z/r),[4] where Z and r are the formal charge and the ionic radius. The figure also involves data for ion-exchanged mordenites[5] and ZSM-5 zeolites[2,6] for comparison. Similarly to mordenite and ZSM-5 zeolite, the plots for L-zeolite gave a linear relationship. This result suggests the ion-exchange of accessible site by methane, i.e. the main channel sites of L-zeolite. The smaller slope of the plot for L-zeolites may be the result of lower Si/Al ratio in the L-zeolites than those of mordenite or ZSM-5 zeolite.[7]

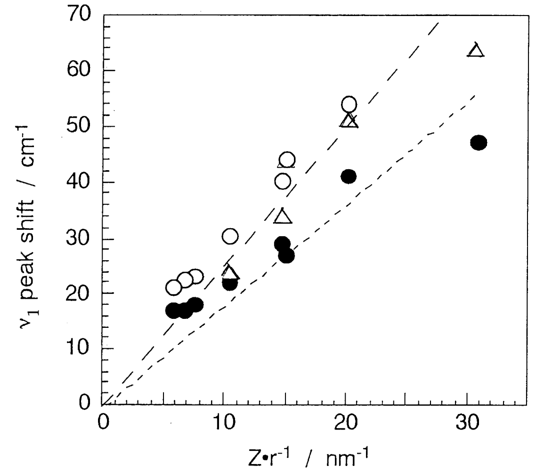

Figure 1. Correlation between ν_1-peak shift and polarizing power (Z/r) of the exchanged cation;
●: L-zeolite, ○: ZSM-5, △: Mordenite.

Assuming all of the cations in the main channel of L-zeolite (n_1 = 3 atom/unit cell)[8] is effective for methane adsorption, the integrated molar extinction coefficient, A, of adsorbed methane on K-L and Rb-L zeolite were estimated from the maxima of ν_1-band intensity normalized by the sample density, $S_{1,\max}$ in Table 1, to be 2.6×10^3 m/mol and 2.3×10^3 m/mol, respectively. Then, the strength of the electric field, E, is evaluated by following equations,[9]

$$A = S_{1,\max} / n_1 \tag{1}$$

$$A = \frac{\pi\cdot N}{2.303\cdot 3\cdot c^2}\left(\frac{\partial\alpha_M}{\partial Q_1}\right)^2 E^2 \tag{2}$$

where N, c, α_M, Q_1 are Avogadro's number, the velocity of light, the mean polarizability, and the normal coordinate of ν_1-vibration, respectively. Adopting the value $(2.27\times10^{-16}\mathrm{cm}^2\cdot\mathrm{g}^{-1/2}\cdot\mathrm{N}^{1/2})$[10] of $\partial\alpha_M/\partial Q_1$ for gaseous methane, the resultant valuses of E for cations in the main chanel of K-L and Rb-L zeolite were 1.66×10^5esu and 1.57×10^5esu, respectively. The electric fields in L- zeolites are weaker than those in ZSM-5 zeolites,[11] and this fact coincides with the smaller ν_1-peak shift on L-zeolites.

The integrated molar extinction coefficients of ν_1-band of adsorbed methane on the cation site were plotted in Fig.2 as a

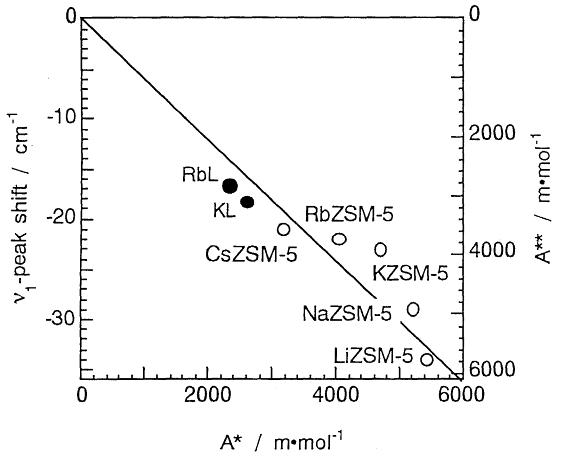

Figure 2 Correlation between ν_1 peak shift and an integrated molar extinction coefficient ; ●: L-zeolite, ○:ZSM-5 zeolites. A* and A** are integrated molar extinction coefficients estimated from ν_1 intensity and ν_1 peak shift, respectively.

function of the magnitude of the peak shift. The earlier results for ZSM-5 zeolites[2] were also included. As seen, the figure shows a linear relationship including the plots for ZSM-5 zeolites.

According to Backingham's studies,[12] the peak shift of vibration band for an interacting system was estimated using the first and second derivatives of the interaction potential (U) with respect to the normal coordinate (Q_i). The peak shift ($\Delta\nu_1$) for ν_1-vibration of T_d symmetrical molecule like methane was represented as follows;

$$\Delta\nu_1 = \frac{1}{8\pi^2 c^2\omega_1}\left\{ U'' - \frac{3V_{111}}{2\pi^2 c^2 \omega_1^2} U' \right\} \tag{3}$$

where ω_1 and V_{111} are the frequency of harmonic oscillation of ν_1-vibration and the anharmonicity of the vibration potential, respectively. The other anharmonicity terms (V_{112}, V_{113}, and V_{114}) were neglected because of the symmetry of ν_1-vibration.[13] Considering that the electrostatic interaction mainly governs adsorption interaction between a cation and methane molecule, eq. (3) is rewrited to

$$\begin{aligned}\Delta\nu_1 = \frac{1}{8\pi^2 c^2\omega_1}\Big\{ &\frac{\partial^2}{\partial Q_1^2}\Big[-\frac{q\mu\cos\varphi}{d^2} + \frac{q\cdot Q\cdot(3\cos^2\varphi - 1)}{2d^3} \\ &- \frac{q^2(\alpha_M + \gamma(3\cos^2\varphi - 1)/3)}{2d^4} \Big] \\ &- \frac{3V_{111}}{2\pi^2 c^2 \omega_1^2}\frac{\partial}{\partial Q_1}\Big[-\frac{q\mu\cos\varphi}{d^2} \\ &+ \frac{q\cdot Q\cdot(3\cos^2\varphi - 1)}{2d^3} - \frac{q^2(\alpha_M + \gamma(3\cos^2\varphi - 1)/3)}{2d^4}\Big]\Big\}\end{aligned} \tag{4}$$

where q, μ, φ, d, *Q*, and γ are the charge of the cation, the dipole moment, the orientation angle between the electric field and molecular axis, the distance between a cation and methane, the quadrupole moment, and the anisotropy of the polarizability, respectively. Since the ν_1-vibration of methane is totally symmetric, it seems rasonable to set $(\partial\mu/\partial Q_1) = (\partial Q/\partial Q_1) = (\partial\gamma/\partial Q_1) = (\partial^2\mu/\partial Q_1^2) = (\partial^2 Q/\partial Q_1^2) = (\partial^2\gamma/\partial Q_1^2) = 0$. In addition, approximating the other parameters by those of unperturbed (gaseous) methane as; $(\partial^2\alpha_M/\partial Q_1^2) = 8.603\times10^{15}\,g^{-1}\cdot cm$, $(\partial\alpha_M/\partial Q_1) = 1.755\times10^{4}\,g^{-1/2}\cdot cm^2$, and $V_{111} = -7.073\times10^{49}\,g^{-1/2}\cdot cm^{-1}\cdot s^{-2}$,[14] and substituting E by q/d^2, we get

$$(\Delta\nu_1/\mathrm{cm}^{-1}) = -5.525 \times 10^{-10}\cdot(E/\mathrm{esu})^2 \tag{5}$$

Eq. (5) shows that the magnitude of ν_1-peak shift is proportional to the squared electric field, and that the peak will shift to lower frequency side with the increase in the strength of electric field. Furthermore, since the correlation between the electric field and the molar extinction coefficient was represented by eq. (2), the linear relationship in Figure 2 is reasonable. Namely, the following relation can be drived;

$$(A/\mathrm{m}\cdot\mathrm{mol}^{-1}) = -169.5\cdot(\Delta\nu_1/\mathrm{cm}^{-1}) \tag{6}$$

Eq. (6) gives the integrated molar extinction coefficient without assumption of the number of adsorption sites. Therefore, the amount of adsorption on each of the cationic sites can be selectively estimated if the ν_1-peak shift and the IR absorption intensity are measured separately. In addition, the good agreement of the integrated molar extinction coefficients from peak shift to those from peak intensity supports the view that the number of available cationic adsorption site in L-zeolite is about 3 atom/unit cell, as assumed before.

The strength of electric field on Na^+ site in Na-L zeolite was estimated to be 1.9×10^5esu from $\Delta\nu_1$ value and eq. (5), even the ν_1-band could only be incompletely deconvoluted. On the basis of eq. (6) and $S_{1,max}$ (the initial slope of P/S_1 vs. P plots)[6], the number of Na^+ site in the main channel was estimated to be about 0.7 atom/unit cell. Although this value was slightly smaller than that expected from XRF measurement (1 atom/unit cell), this value seems to be in reasonable range because Na^+ may also be exchanged in deep sites (unaccesible site by methane, such as ones in the cancrinite cage or the D6R) . [8]

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