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Infrared Spectroscopic Study on Methane Adsorption Sites on Mesoporous Silicates

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Some MCM-41 materials substituted by trivalent metal ion (Met–MCM-41; Met = Al, Fe, and Ga) were prepared, and their methane adsorption sites were investigated by IR spectroscopy. Three adsorption sites on Met–MCM-41 with different strengths of electric field were observed. They were assigned to pore wall site (0 V m^{-1}), silanol site (ca. 4×10^9 V m^{-1}), and Na$^+$ site (ca. 6×10^9 V m^{-1}), respectively. The amounts of silanol site in Met–MCM-41 were estimated to 2—3 mmol g^{-1}, while the amounts of the Na$^+$ site were 0.1—0.2 mol g^{-1}. Methane molecules were preferentially adsorbed on the electrostatic sites (silanols and Na$^+$sites) at low methane pressures, but as methane pressure increased, the amount of adsorption on the pore wall site became comparable to that on the silanol sites. Since the amounts of Na$^+$ site estimated from methane adsorption on the Met–MCM-41 samples were less than the theoretical ones calculated from the compositions of starting materials, most of the Na$^+$ sites were thought to be inaccessible for methane molecules.

An ordered mesoporous silica such as MCM-41[1] or FSM-16[2] is a promising material as adsorbent or catalyst support because of adjustable mesopore size and high surface area. Both MCM-41 and FSM-16 are built up of a hexagonal array of tubular mesopores (2—10 nm diameter) like a honeycomb with narrow pore size distribution. The surfaces of mesoporous silicas have silanol sites, which are correlated with surface acidity.[3] In order to functionalize the surface, various modifications of the surface have been investigated. For example, to create strong acid sites and/or to generate ion exchangeability, introduction of a trivalentcation such as Al, Ga, and Fe into MCM-41 skeleton (Met–MCM-41) has been often carried out.

Reddy et al.[4] discussed the acid properties of mesoporous alminosilicates (Al–MCM-41) prepared from various Al sources by means of TPD (Temperature Programmed Desorption) of *n*-butylamine and hydrocracking reaction test of 1,3,5-triisopropylbenzene. Okumura et al.[5] analyzed acid strength of Ga–MCM-41 surface by ammonia TPD and cracking reaction of octane, and they reported that the acid site in Ga–MCM-41 is stronger than that of Al–MCM-41. Jentys et al.[6] showed that the amount of the surface hydroxide was obtained by pyridine TPD spectra for various Al–MCM-41 with different Si/Al ratios.

In spite of a number of the studies on acidic properties, few studies on the cation incorporated in Met–MCM-41 have carried out, probably due to the difficulty of analysis of the pore wall made of amorphous silica. It is well known that a cation in zeolite pores is one of the factors dominating adsorption performance, and such a cation often acts as a catalytic active center or an adsorption site. Thus, fundamental questions for application of the MCM-41 materials, for example location of ion exchange site and the interaction of admolecules with the cation, still remain. In this work, the adsorption of methane in MCM-41 including trivalent metal was observed by using IR spectroscopy, and their surface properties were investigated by analyzing the adsorption interaction of methane with the surface. In addition, the role of the metal in MCM-41 skeleton in the nature of the surface sites was discussed by comparing with that of zeolites.

Experimental

1 Materials. MCM-41 samples were prepared by referring to the report of Beck et al.[1,7] Namely, sodium silicate (SiO_2/Na_2O = 2.5, Wako Co., Ltd., CP grade) was used as silica source and aluminum nitrate nonahydrate (Wako Co., Ltd., S grade), gallium(III) nitrate *n*-hydrate (*n* = 7—9 Wako Co., Ltd., 99.9% purity), and iron(III) nitrate nonahydrate (Wako Co., Ltd., S grade) were selected as metal sources. Cetyltrimetylammonium chloride (Tokyo Kasei Ind., extra pure grade) was used as template reagent. The metal contents were adjusted to Si/Met = 20 (atom ratio, Met = Al, Ga, and Fe). The synthesized samples were calcined at 823 K for 24 h in air flow to remove any templates in the pores before measurements. The hexagonal structure of the samples used was confirmed by appearance of (100), (110), (200), and (210) peaks in X-ray diffraction spectra. The fundamental data of synthesized samples were listed in Table 1. The high surface area and the sharp distribution (Full width at half maximum = ca. 0.5 nm) of pore diameter around 3 nm for all of samples used mean the high quality of MCM-41 structure.

2 Measurement. The adsorption isotherms of methane on MCM-41 samples were obtained by volumetric method after evacuation at 623 K for 8 h. IR spectra of adsorbed methane were obtained using Bio-rad FTS165 with a Mercury Cadmium Tellurium (MCT) detector (resolution = 2 cm^{-1}, repeat times = 200, temperature = 183 K) by transmission method. The sample powder was pelletized at 220 MPa before calcination to avoid destroying MCM-41 structure. The calcined sample disk was placed in the IR

Table 1. Basal Spacing (d_{100}), Specific Surface Area (Σ), and Mean Pore Diameter (D)[a]

Sample	d_{100}/nm	Σ/m^2 g^{-1}	D/nm
Si–MCM-41	3.60	1190	2.8
Al–MCM-41	4.00	870	3.1
Ga–MCM-41	3.63	1080	3.0
Fe–MCM-41	3.60	1000	2.9

a) Estimated from N_2 adsorption isotherms at 77 K.

cell and evacuated at 623 K for 8 h before methane adsorption.

Results and Discussion

1 Methane Adsorption Isotherms and Isosteric Heat of Adsorption.

The adsorption isotherms of methane on the MCM-41 samples are shown in Fig. 1. All of the isotherms in the pressure ranges observed can be classified as Henry-type, and this means small adsorption interactions. The amounts of adsorption on MCM-41 samples including the trivalent metals were similar to that of Si–MCM-41. The isosteric heats of adsorption obtained from the isotherms using Clausius–Clapeyron equation are shown in Fig. 2 as a function of the amount of adsorption. The heats were smaller than those (for example Na-mordenite = 23—26 kJ mol^{-1})[8] of zeolite adsorbents. The small interaction was responsible for a large pore size, because only the nearest pore wall was capable of interacting with methane molecule. The heats of adsorption decreased with the increase in the amount of adsorption. It shows that the surface sites are energetically heterogeneous. Such surface heterogeneity was often caused by a cation and/or surface group. Since even Si–MCM-41

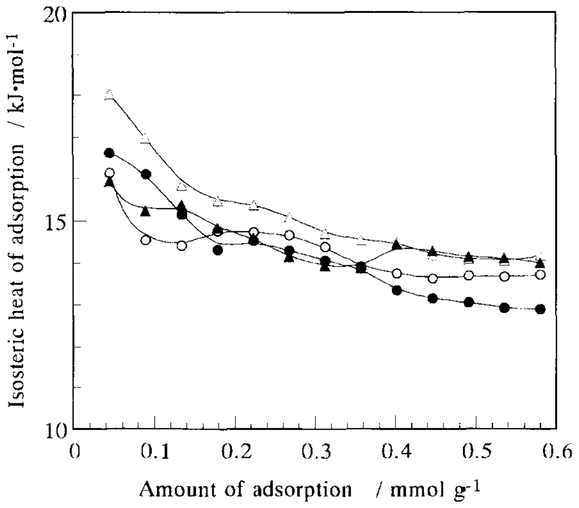

Fig. 2. Isosteric heats of methane adsorbed; ○: Si–MCM-41, ●: Al–MCM-41, △: Fe–MCM-41, ▲: Ga–MCM-41.

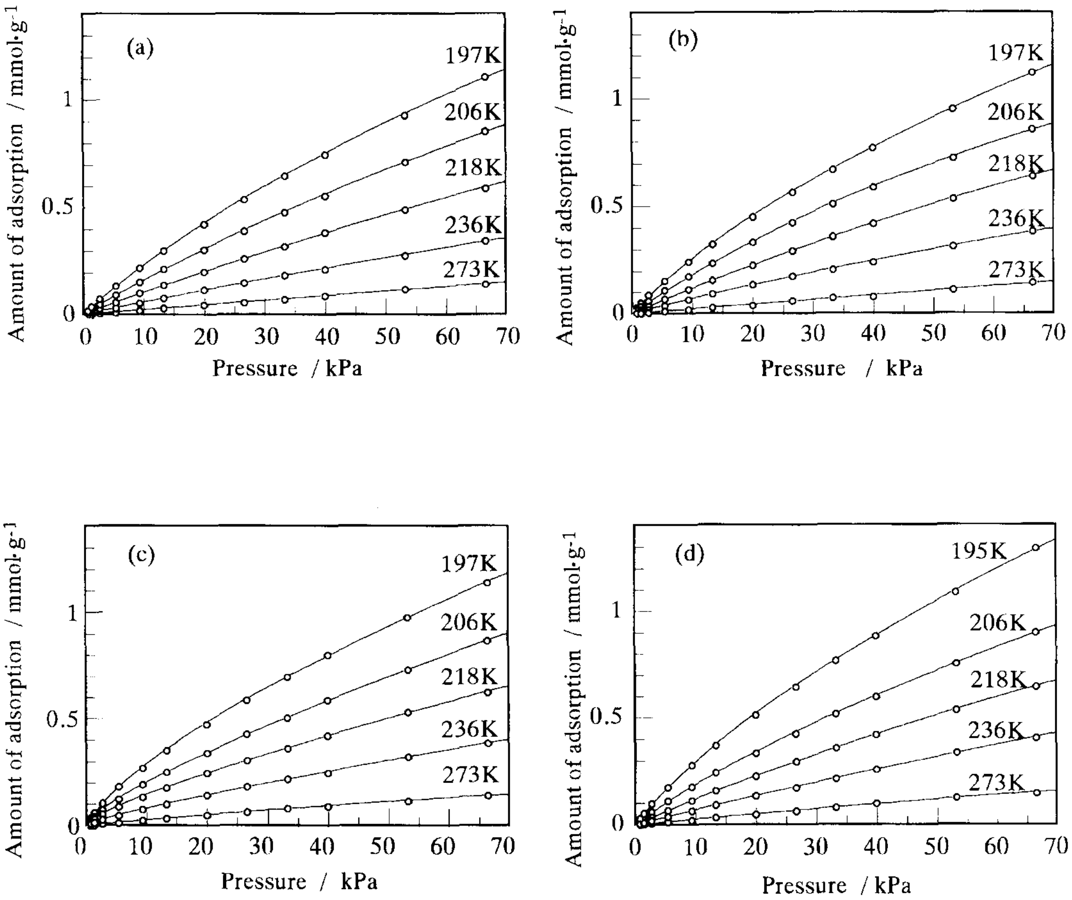

Fig. 1. Adsorption isotherms of methane on several MCM-41; (a): Si–MCM-41, (b): Al–MCM-41, (c): Fe–MCM-41, and (d): Ga–MCM-41.

without trivalent metals were heterogeneous, the silanol sites in MCM-41 surface were suggested to act as preferential adsorption sites of methane, and then this should cause surface heterogeneity. On the other hand, for Met–MCM-41 (Met = Al, Ga, and Fe), the cation may also play the role of strong adsorption site, but the degree of surface heterogeneity was almost equal to that of Si–MCM-41. The effects of the cation are too small to be detected in heat of adsorption because of the low contents of the cations.

2 Electric Field on Si–MCM-41 Surface. IR spectra of methane adsorbed on Si–MCM-41 surface are shown in Fig. 3. A broad band around 3000 cm^{-1} was assigned to ν_3-band, which is the antisymmetrical C–H stretching vibration (3018 cm^{-1}; position of Q-branch of gaseous methane), and the small peak at 2900 cm^{-1} was assigned to ν_1-band, which is the symmetrical C–H vibration (inherently IR-inactive, 2914 cm^{-1}; Raman line for gaseous methane) induced by an electric field on adsorption sites.[9] The ν_1-peak is shifted to low wavenumber side by imposing an electric field on the adsorption site as in the following equation:

$$\Delta\omega_1 = -6.139\times 10^{-19}\times E^2, \qquad (1)^{10)}$$

where $\Delta\omega_1$ and E are the ν_1-peak shift (cm^{-1}) and the electric field (V m^{-1}) on adsorption site. The electric field in Si–MCM-41 pore was estimated to be 4.23×10^9 V m^{-1}, which was similar to those of silicagel (4.5×10^9 V m^{-1})[11] and FSM-16 (4.2×10^9 V m^{-1})[12] rather than Na-zeolites (ca. 6.0×10^9 V m^{-1}).[8] Therefore, silanol sites on Si–MCM-41 are suggested to be one source of electric field; this is also confirmed by the change in IR spectra of O–H stretching vibration of surface silanols after methane adsorption. Namely, the negative peak (ca. 3740 cm^{-1}) in OH vibration region after adsorption (Fig. 4) means the diminishing of free-silanol sites, and the appearing of a new peak around 3720 cm^{-1} means formation of silanols perturbed by methane adsorption. Both areas of the negative peak (ν_{OH}^-) and the perturbed peak (ν_{OH}^+) should be correlated with the amount of methane adsorbed on the silanol site. On the other hand, the area of the ν_1-peak induced by the electric field should be correlated with the amounts of methane adsorbed on sites bearing electric field when the electric field is homogeneous, but not with the total adsorption on all of the surface. The linear relationship (Fig. 5) between the intensity of ν_1-band and the IR intensity (ν_{OH}^+) of the perturbed silanol site supports the conclusion that the silanol site is the source of electric field. Nevertheless the non-linear relationships between ν_3-band and the ν_{OH}^+ band shows that the adsorbed methane is not distributed only on silanol sites but also on non-electric sites.

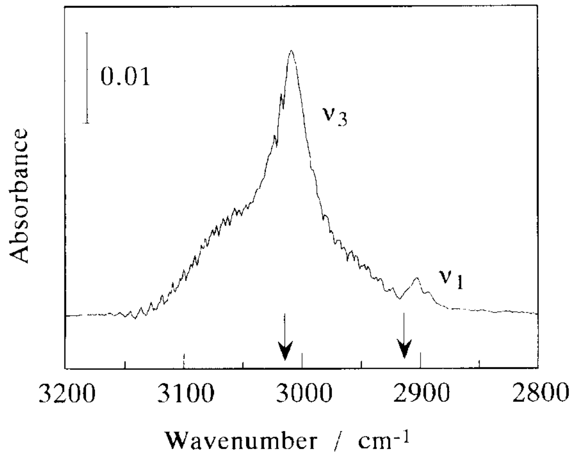

Fig. 3. IR spectra for methane adsorbed on Si–MCM-41 at 0.7 kPa at 203 K, the arrows in the figure denote ν_1 and ν_3-peak positions of gaseous methane.

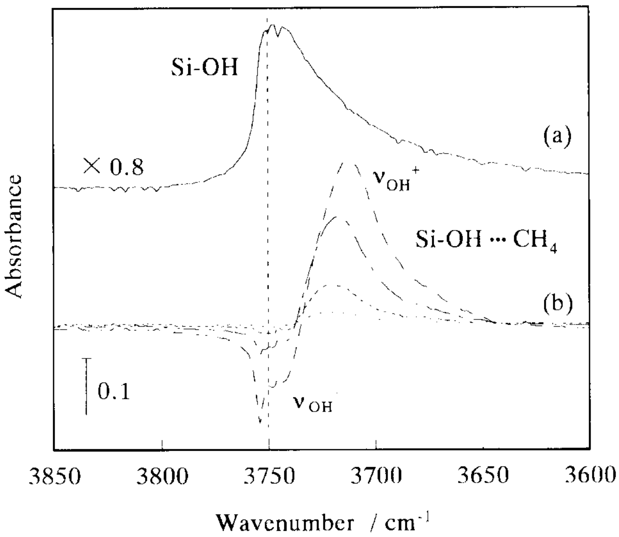

Fig. 4. (a): IR spectra of silanol on Si–MCM-41 surface, (b): difference spectra from before methane adsorption; ····: 0.7 kPa, - - -: 2.7 kPa, – • — • –: 9.3 kPa, — —: 21.3 kPa.

3 Amount of Silanol Sites on Si–MCM-41. The intensity of ν_1-vibration band induced is also correlated with the electric field (E) on adsorption sites as seen in the following equation:

$$S_1 = A\cdot n_1 = \pi\cdot N_A\cdot n_1/(2.303\cdot 3c^2)\cdot(\partial\alpha/\partial Q_1)^2\cdot E^2, \qquad (2)^{10)}$$

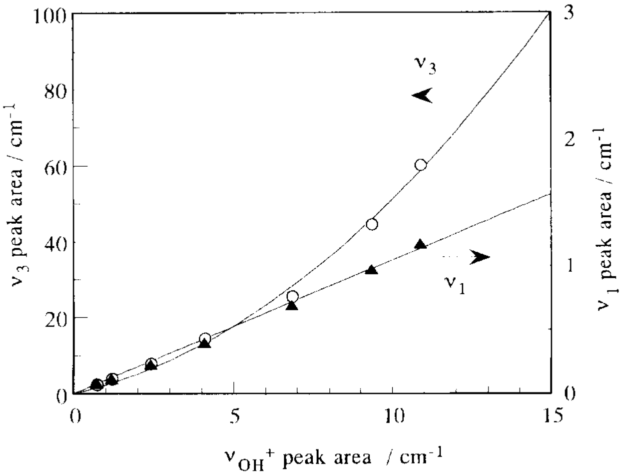

Fig. 5. Integrated intensities of ν_1-peak (▲) and ν_3-peak (○) as a function of intensity of interacted OH peak for Si–MCM-41.

where n_1 (mol g^{-1}), A (m mol^{-1}), N_A, c, α, and Q_1 were the amount of adsorption on the silanol site, the integrated molar extinction coefficient, Avogadro's number, the velocity of light, the molecular polarizability of methane, and the normal coordinate of ν_1-vibration, respectively. Since the extinction coefficient of ν_1-band induced is estimated as 1865 m mol^{-1} from Eq. 1 using the magnitude of ν_1-peak shift, the amount of adsorption on the silanol sites can be estimated from ν_1 peak intensity (Fig. 6). On the other hand, the total amount of adsorption was estimated from the observed ν_3-peak intensity using the molar extinction coefficient (2.92×10^4 m mol^{-1})[13] of ν_3-band of gaseous methane. Since the amount of adsorption on silanol sites was less than the total amount of adsorption, it is clear that sites distinct from the silanol exist in MCM-41 surfaces. The relative amount of adsorption on silanol sites was high at low coverage. Such preferred adsorption on silanol sites may be caused by the weak electric field (4.23×10^9 V m^{-1}). The saturated amount of adsorption on silanol sites can be estimated from a Langmuir plot of the isotherm in Fig. 6 to be 1.72 mmol g^{-1}, which is almost equal to that of FSM-16 reported by Ishikawa et al.[14] However, the amount of silanols ($\nu_{OH}{}^{-}$) which interact with methane molecules is less than that of inherent silanols before methane adsorption (almost 1/10 at 21 kPa). Therefore there may be a large amount of inaccessible silanol sites for methane molecules in the MCM-41 structure. The surface density of the accessible silanol sites was estimated to be 0.87 site/nm^2, which means that some surface sites other than the silanol can adsorb methane molecules.

4 Electric Field on Met–MCM-41 Surface. IR spectra of methane adsorbed on Met–MCM-41 samples are shown in Fig. 7. The induced ν_1-peak positions were similar to that of Si–MCM-41, but the intensities and the widths increased slightly. The results suggested that electrostatic sites other than the silanol site were created on Met–MCM-41 surfaces. To remove contribution of silanol site in the ν_1-bands, we subtracted the ν_1-band of Si–MCM-41 from those of Met–MCM-41 samples (Fig. 8). The figure shows small peaks around 2893 cm^{-1} for all the samples. For Ga–MCM-41, another peak was also recognized on the lower side.

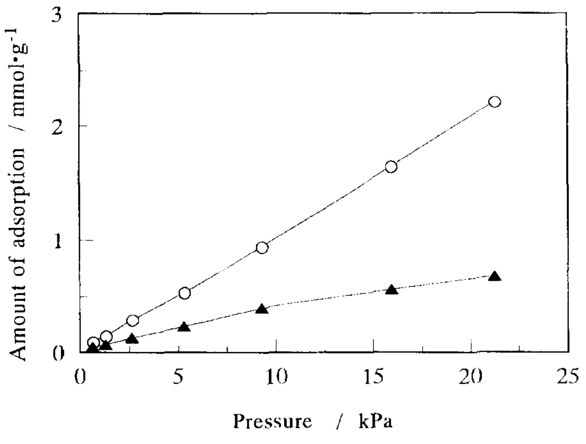

Fig. 6. Total amount of adsorption (○) and amount of adsorption on silanol site (▲).

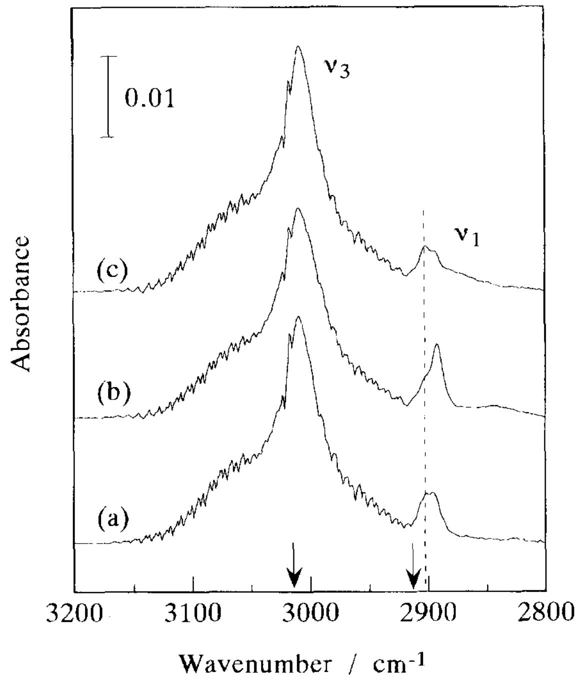

Fig. 7. IR spectra at 183 K at 0.7 kPa for methane adsorbed on (a): Al–MCM-41, (b): Fe–MCM-41, (c): Ga–MCM-41, the broken line in the figure denotes ν_1-position of methane adsorbed on Si–MCM-41, and the arrows in the figure denote ν_1 and ν_3-peak positions of gaseous methane.

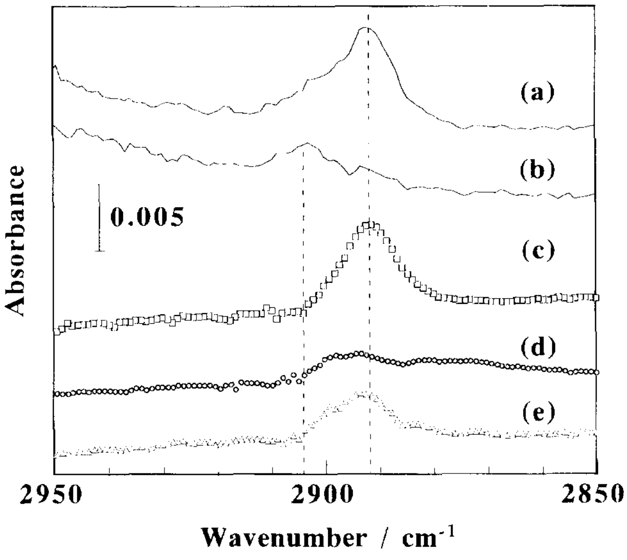

Fig. 8. IR spectra of ν_1-band for adsorbed methane; (a) on Fe–MCM-41, (b): on Si–MCM-41, subtracted spectra of those of (c): Fe–MCM-41, (d): Ga–MCM-41, and (e): Al–MCM-41 by that of Si–MCM-41.

The electric fields on Met–MCM-41 surface estimated from the position of the subtracted ν_1-peaks are listed in Table 2. Since the electric fields for Al–MCM-41, Fe–MCM-41 and one of peaks in Ga–MCM-41 were between those of Na-mordenite (6.75×10^9 V m^{-1})[8] and Na–L zeolite (5.70×10^9 V m^{-1}),[10] the IR peaks may be assigned to Na$^+$ site in MCM-41. It is known that the electric field of the cation incorporated in some zeolites increased with the increase in

Table 2. IR Peak Shift of ν_1-Band Subtracted and Electric Field Estimated from the Peak Shift

Sample	Peak shift	Electric field
	cm^{-1}	10^9 V m^{-1}
Al–MCM-41	−21	5.85
Ga–MCM-41	−20	5.70
	−32	7.23
Fe–MCM-41	−22	6.00
Na–Mordenite	−28	6.75
Na–L	−20	5.70
Na–ZSM-5	−29	6.87

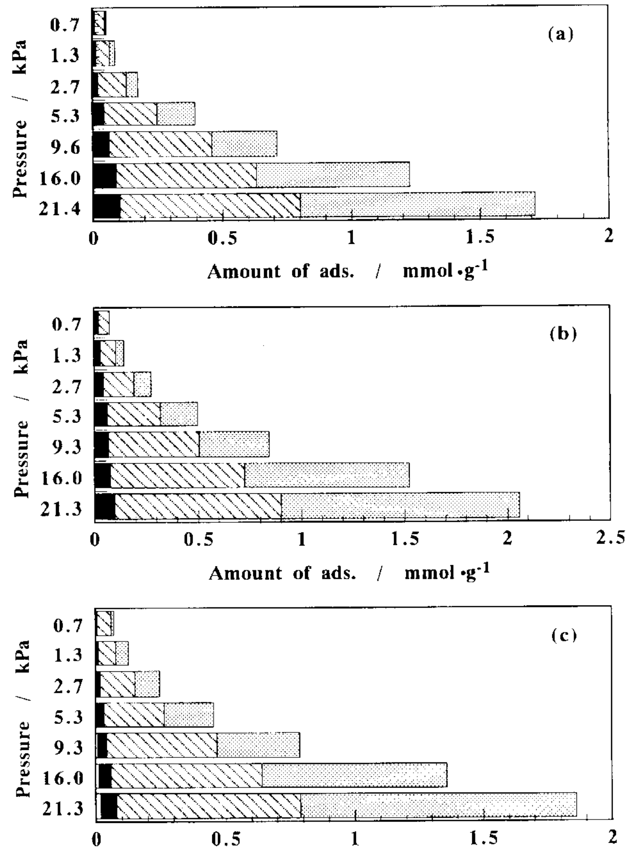

Fig. 9. Amount of adsorption on each adsorption sites (░: pore wall, ▧: silanol, ■: Na ion, and □: Ga polycation sites); (a) Al–MCM-41, (b) Fe–MCM-41, and (c) Ga–MCM-41.

Si/Al,[15] but the values of MCM-41 (Si/Al = 20) are not large compared with those of high silica zeolites such as ZSM-5 (Si/Al = 11.65). Therefore, it was suggested that Na^+ cations may be encaged in pore wall or their electronic state may be different from that of zeolites. It was known that the acid strength of proton type metalosilicates depends on the element incorporated,[16] and it has been already reported in the cases of MCM-41 that there is a difference of acid strength between Ga–MCM-41 and Al–MCM-41.[3] However the natures of cations in Met–MCM-41 samples in this work were similar with respect to electric field.

On the other hand, the shoulder around 2882 cm^{-1} for Ga–MCM-41 should be induced by a strong electric field (7.23×10^9 V m^{-1}) which is larger than that of Na-zeolites. Such a strong field is responsible for a poly cation on MCM-41 surface. Namely, unentering Ga^{3+} ions during synthesis or cations extricated during calcination are deposited in ion-exchange site on Met–MCM-41 surface, and then they can act as a source of electric field. In addition, the broad width of shoulder suggests that the signals of several gallium cation species as Ga^{3+}, $Ga(OH)^{2+}$ are convoluted. In fact, a broad band of acidic OH vibration around 3600 cm^{-1} appeared in Ga–MCM-41, but not for the other MCM-41 samples. Therefore it is reasonable that a few hydrolyzed species ($Ga(OH)^{2+}+H^+$) can act as adsorption sites.

5 Distribution of Methane Adsorption on the Sites. The amounts of adsorption on each site (silanol and Na^+ sites) are plotted in Fig. 9 as a function of equilibrium pressure of methane. The amounts of adsorption on the pore wall site were estimated by subtracting amounts on the cationic sites from the total amounts which were estimated from ν_3-peak areas. The relative amounts of adsorption on Na^+ sites were very small, and the adsorption site seems to be almost covered at 22 kPa. On the other hand, the adsorption on the silanol site was dominant at the condition, and it was confirmed that the surface properties on Met–MCM-41 at the low pressure region were subjected to properties of the silanol. However, the amount adsorbed on pore wall site increased linearly with the increase in pressure, which was classified as a Henry-type isotherm. Therefore non-electrostatic sites (pore wall site) should be dominant at high pressure or high temperature regions.

The amounts of the sites were calculated from the adsorption capacities estimated by applying Langmuir equation to the adsorption isotherms for each site. They are listed in Table 3 together with amounts of cations calculated theoretically from the metal contents. However, the amount of the pore wall site could not be estimated using the isotherms because of the shape of the isotherm (Henry-type). The amount of Na^+ sites in Al–MCM-41 was larger than the amounts of other Met–MCM-41 samples. It suggests that the amount of substituting metal introduced in Al–MCM-41 skeleton is larger than those of Ga– and Fe–MCM-41 samples. However, even for the Al–MCM-41 sample, the amount of methane accessible Na^+ sites was smaller than that calculated from metal content. They suggests that most of Na cations are probably encaged in pore walls, and then the oxygen pore wall prevents the Na cation from adsorbing methane molecules. The

Table 3. Amounts of Some Adsorption Sites

Sample	Silanol site	Na^+ site
	mmol g^{-1}	mmol g^{-1}
Si–MCM-41	1.7	
Al–MCM-41	2.3	0.22 (0.79)[a)]
Ga–MCM-41	1.8	0.09 (0.77)
Fe–MCM-41	3.0	0.10 (0.78)

a) Theoretical amount of Na^+ site.

amounts of silanol sites in Met–MCM-41 were larger than that of Si–MCM-41. In the cases of zeolites, enhancement of the silanol sites means the increase of defects in the crystal. Thus, the trivalent metals introduced into MCM-41 may increase defect sites.

Conclusion

In this work, we studied about the cation sites in Met–MCM-41 by IR spectroscopy. The amounts of the sites and the strength of electric fields generated by them are estimated. The results obtained in this study can be summarized as follows:

Si–MCM-41 has two types of adsorption sites. One of the sites is a pore wall site without an electric field and the other is a silanol site of which the electric field is 4.23×10^9 V m^{-1}. The amount of silanol sites which a methane molecule is capable of accessing is estimated to be about 1.7 mmol g^{-1}. For the Met–MCM-41 samples, the Na^+ sites formed in pores exert a strong electric field (5.7—6.0×10^9 V m^{-1}) on admolecules. Methane molecules on Met–MCM-41 surfaces were distributed over at least three different sites depending on total coverage. In the case of Ga–MCM-41, the other strong field was also present, and it was responsible for external polycations such as Ga^{3+} or $Ga(OH)^{2+}$.

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