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Electric Fields on FSM-16 Surface

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Abstract. The surface of mesoporous silicate, FSM-16, was investigated by infrared spectroscopy (IR) using methane and carbon monoxide as molecular probe. The appearance of ν_1-peak of adsorbed CH_4 indicated the presence of electric field (1.4×10^5 esu) which is attributed to a weakly polarized free silanol site (site-1). The site was located at the void of oxygen framework in FSM-16 pore wall. In addition, the presence of site-2 without any electric field was found by IR spectra of adsorbed CO. The latter site was assigned to a interacted silanol groups and/or a Si—O—Si site.

Introduction

Ordered mesoporous silicates with high surface area were successively synthesized (Yanagisawa et al., 1990; Kresge et al., 1992; Inagaki et al., 1993), and they were expected to be unique adsorbents or catalyst carriers. Although their structures were investigated using various technique such as TEM, XRD (Yanagisawa et al., 1990; Kresge et al., 1992), N_2 adsorption (Yanagisawa et al., 1990; Kresge et al., 1992; Branton et al., 1994, 1996), and ^{28}Si MAS-NMR (Yanagisawa et al., 1990; Kresge et al., 1992), fundamental questions concerning the surface of pore wall, such as numbers and property of surface sites, are still remaining to be clarified. In this study, the surface of FSM-16 was characterized by IR spectroscopy using methane and carbon monoxide as molecular probes.

Experimental

FSM-16 sample was prepared from kanemite and $[C_{16}H_{33}N^+(CH_3)_3]$ as source materials based on the procedure described by Inagaki et al. (1993). The pore diameter and the specific surface area of the sample were evaluated to be ca. 2.5 nm and 1060 m^2/g, respectively, using N_2 adsorption. IR spectra were obtained by a transmission method at various level of amounts of adsorption using Bio-rad FTS 165 spectrometer equipped with MCT detector under resolution of 2 cm^{-1}. To avoid the destruction of pore structure, FSM-16 sample was pelletized to a wafer (ca. 10 μm thickness) under pressure of 230 MPa before removal of the template material by calcination at 600°C in air stream. The calcined sample was evacuated in IR cell at 350°C for 12 h before IR measurement.

Results and Discussion

An example of IR spectra of adsorbed CH_4 is shown in Fig. 1. The main peak around 3000 cm^{-1} is assigned to the IR allows ν_3-band, and the sharp peak around 2900 cm^{-1} is assigned to the ν_1-band which is inherently IR inactive in gas phase. The ν_1-band always appears in IR spectra of methane adsorbed on zeolites, and it has been assigned to an induced band by the electric field of cation (Yamazaki et al., 1988). Therefore, the appearance of ν_1-band shows the presence of some electric field on FSM-16 surface. In the case of the siliceous materials, a similar peak has been already reported for silica glass (Sheppard and Yates, 1956) and silica (Chen et al., 1995b), but not for silicalite (Yamazaki et al., 1988). Since it is well known that many silanol sites are existing on the surface of highly ordered mesoporous silicates (Yanagisawa et al., 1990; Chen et al., 1995a), some kind of silanols seem to be the source of this electric field.

The magnitude of ν_1-peak shift from the position of gaseous CH_4 (2914 cm^{-1} in Raman spectra (Hertzberg, 1945)) reflects the strength of electric field on the adsorption site. Applying the theoretical model introduced by Buckingham (1960), a correlation between

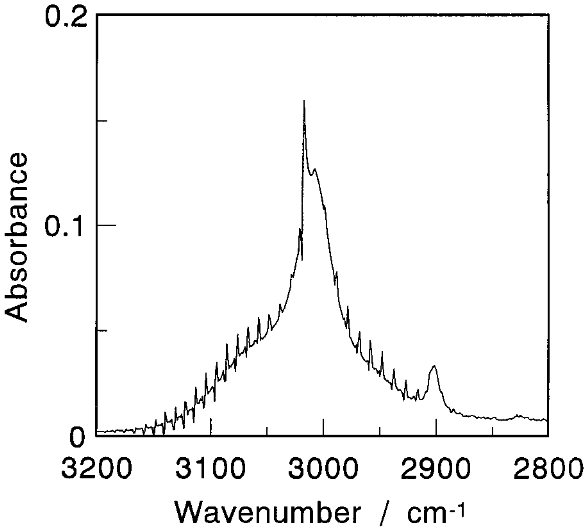

Figure 1. IR spectra of CH_4 adsorbed on FSM-16 at 198 K and 5.3 kPa.

the strength of electric field (E) and the magnitude of peak shift ($\Delta\nu_1$) of the ν_1-band of adsorbed methane is given by Yamazaki et al. (1996)

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

and the value of E is calculated to be 1.4×10^5 esu. The resultant value was much smaller than that in NaZSM-5 (2.4×10^5 esu) or HZSM-5 (2.0×10^5 esu) estimated in the similar manner, but it almost coincided with that on a silica gel (CARiACT-Q-3; Fuji Silysia Chemical Ltd.). Therefore, it is suggested that the adsorption site for methane on the FSM-16 surface is neither a residual Na^+ cation nor a protonic site, but looking from the weakness of electric field and considering from the IR spectra in O—H stretching vibration region, it may be free silanol. Beebe et al. pointed out the presence of a weakly charged OH site on SiO_2 surface, and they also assigned it to free silanol group (Beebe et al., 1984). This site will hereafter be called site-1 in this paper.

The intensity of ν_1-band (S_1) is also correlated to the strength of electric field (E) on the adsorption site as follows (Yamazaki et al., 1996):

$$S_1 = \pi \cdot N_A \cdot n_1/2.303 \cdot 3c^2 \cdot (\partial\alpha/\partial Q_1)^2 \cdot E^2, \quad (2)$$

where N_A, n_1, c, and $(\partial\alpha/\partial Q_1)$ are Avogadro's number, amount of adsorption on site-1, the velocity of light, and the first derivative of polarizability α with normal coordinate (Q_1) of ν_1-vibration, respectively. Combining Eqs. (1) and (2), and adopting $\partial\alpha/\partial Q_1$ the value of gaseous methane ($2.27 \times 10^{-16}\mathrm{cm}^2\cdot\mathrm{g}^{-1/2}\cdot\mathrm{N}^{1/2}$ (Cohen de Lara et al., 1985)), one can estimate the amount of adsorption (n_1) on site-1. The results at 198 K are plotted in Fig. 2. It can be seen that the amount n_1 increased almost linearly with the increase in pressure within the range of present measurement, occupying only a small part (ca. 10%) of the total amount of adsorption measured separately by a volumetric technique. Namely, a large part of methane molecule is adsorbed on sites other than site-1. This observation seems quite reasonable since the additional interaction energy by the electric field mentioned above ($\alpha \cdot E^2 \cdot N_A/2 = 1.6$ kJ/mol (Bezus et al., 1978)) is rather small compared to the heat of adsorption (ca. 15 kJ/mol) obtained on the basis of Clapeyron-Clausius equation, and the total amount of sites on FSM-16 (9.9 mmol/g) estimated from cross-sectional area of methane (0.178 nm^2 (McClellan and Harnsberger, 1967)) and the BET surface area of the adsorbent is quite large.

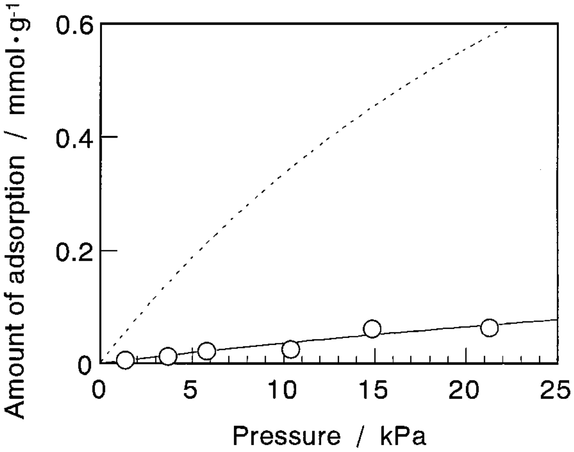

Figure 2. Adsorption isotherms of methane at 198 K; ----: total, ○: amount adsorbed on the free silanol site.

Assuming that the CH_4 molecule is adequately accessible to OH site, the partial charge (Z) of site-1 can be calculated from the E value as $Z = E/(e/d^2)$, where e and d are the elementary electric charge and the distance between $H^{\delta+}$ and CH_4 molecule, respectively. Since the value of d is speculated to be 0.25–0.31 nm from the uncertainty of the radius of $H^{\delta+}$, the resultant value of Z are 0.2 and 0.3. These value of Z are reasonably coincide with that estimated from MO calculation for silica cluster, 0.31–0.37 (Zhidomirov and Kazansky, 1986; Ugliengo et al., 1990).

The integrated molar extinction coefficient of ν_3-band of adsorbed methane was calculated to be

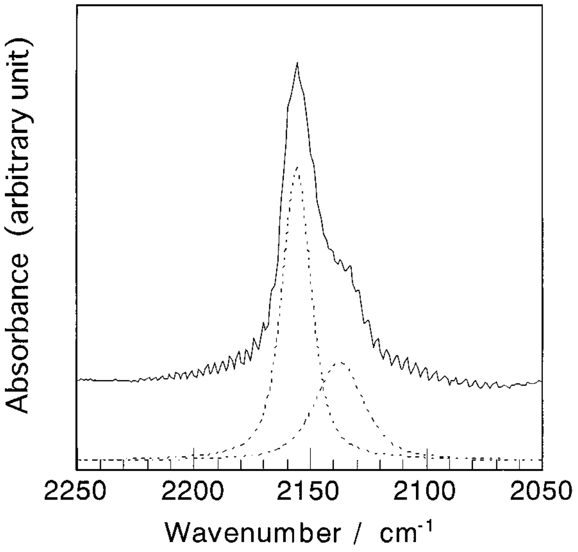

Figure 3. IR spectra of CO adsorbed on FSM-16 at 198 K and 1.2 kPa.

$1 \times 10^6\,\mathrm{cm \cdot mol^{-1}}$ from the ν_3-peak area and the amount of adsorption. The value was smaller than that of gaseous methane $2.9 \times 10^6\,\mathrm{cm \cdot mol^{-1}}$ (Thorndike et al., 1947). This reduction may also be the result of electric field on the FSM-16 surface.

An example of IR spectra of adsorbed CO on FSM-16 at 203 K is shown in Fig. 3. The observed band can be deconvoluted into two peaks as shown by dotted lines in the same figure (peak-1 at 2156 $\mathrm{cm^{-1}}$ and peak-2 at 2136 $\mathrm{cm^{-1}}$). According to previous studies on zeolite adsorbents (Katoh et al., 1994), a peak located at the wave number higher than that of gaseous CO (2143 $\mathrm{cm^{-1}}$) was assigned to the species adsorbed on the cation site through its carbon atom, and the blue shift was interpreted as a result of the interaction with the electric field in the vicinity of the cation. The magnitude of the peak-1 shift was less than those on Na-zeolites, but almost the same to that on silicagel (Beebe et al., 1984). In addition, this peak position was independent of CO pressure. Looking from the peak symmetry, and comparing with the observation with methane probe described above, a free silanol site seems to be the source of the field, and little of residual Na cation may be incorporated in the adsorbent prepared through Na-kanemite, although this peak position was close to that of CO adsorbed NaCl crystal surface (Noda and Ewing, 1990).

The correlation between the IR peak shift of adsorbed CO and the field strength have been often discussed in literature. For example, Lambert et al. explained the shift of CO peak on NaCl surface as a vibrational Stark effect, and led to

$$(d\nu/dE) = 19 \times 10^{-5}\,\mathrm{cm^{-1} \cdot esu^{-1}} \tag{3}$$

for an end-on orientation, i.e., for the case of a positive electric field directed from C to O (Lambert et al., 1995). Pacchioni et al. also discussed the peak shift of end-on adsorbed CO on MgO surface using ab initio MO calculation, and tabulated the correlation between the peak shift and the electric field strength (Pacchioni et al., 1992). Both estimations are nearly coincide in the range of relatively weak field. Using the correlation of Pacchioni et al., the strength of electric field on FSM-16 adsorption sites was estimated to be 0.7×10^5 esu assuming an end-on orientation in the adsorbed state (Fig. 4(a)). This value was smaller than that obtained using CH_4 probe (Table 1).

Table 1. Electric field on adsorption sites detected by different probes.

	Electric filed (10^5 esu)	
	From CH_4	From CO
Site-1	1.41	0.70
Site-2	—	~0

The surface wall other than the cation could also contribute to IR peak shift to same extent. However, as Pacchioni et al. showed for case of an end-on adsorbed CO on MgO crystal surface, the wall effect may contribute to some high wave number shift (Pacchioni et al., 1992). Therefore, such underestimation of the electric field by CO probe may not ascribed to a wall effect, but this discordance may be caused by the assumption of end-on orientation of CO molecules on the adsorption site. The interaction energy (U_μ) between the dipole moment of CO and the electric field (1.4×10^5 esu) was calculated to be only 0.9 kJ/mol even if the electric field was directed from C to O.

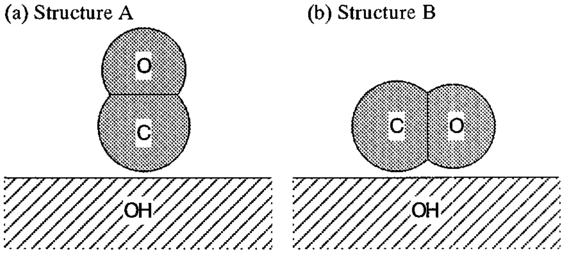

Figure 4. Adsorption models of CO on FSM-16 surface; (a) electric field dominant, (b) dispersion force dominant.

Namely, the field of silanol site is so weak that solely end-on structure cannot be kept in competition with a random or a lying-down structure (Fig. 4(b)) created by the dispersion force on a relatively flat surface of FSM-16 adsorbent. The IR peak position of adsorbed CO depends on the orientation angle between the molecular axis of CO and the electric field (Katoh et al., 1994), and the field strength would have been underestimated in the case of random orientation. Therefore, it was suggested that the $H^{\delta+}$ site of a silanol was entrapped into the oxygen framework of pore wall of FSM-16, and the most favorable structure of adsorbed CO may be intermediate between structures A and B in Fig. 4.

Peak-2, locating on the nearer position to that of gaseous CO, was assigned to physisorbed species on silicalite type surface (Si─O─Si site) without an electrostatic interaction (Katoh et al., 1994). Taking the large number of silanol sites observed by IR spectra into account, interacted silanols themselves may also act as such an adsorption site, in addition. In the latter case, such silanols may exert little electric field on admolecules because H^{+} charge are distributed to the surface.

The intensities of peak-1 and peak-2 increased with the increase in pressure within the range of present measurement (up to 22 kPa). If we assume the integrated molar extinction coefficient of adsorbed CO is same to that of gaseous one, the amounts of CO adsorbed on site-1 and site-2 at 198 K and 22 kPa were estimated to be 0.18 and 0.10 mmol/g, respectively. Since sum of these amounts was nearly equal to the total amount of adsorption (0.28 mmol/g) obtained by a volumetric measurement, it was suggested that the assumption on the molar extinction coefficient of ad-species was reasonable in this system. The larger ratio of peak-1 to peak-2 than that of methane adsorption suggests that the silanol site on the FSM-16 surface is a little hydrophilic.

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