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Adsorption Characteristics in Zeolite Nano-Pore Evaluated by use of Nitrogen Monoxide as a Probe Adsorbate

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Abstract. Adsorption isotherms of nitrogen monoxide (NO) and in situ EPR spectra of adsorbed NO on mordenite zeolites (MOR) of different cation types (HM, NaM and CaM) are measured at different temperatures to elucidate the effect of the strong adsorption promoted by the enhancement of potential field in micropore of MOR (micropore filling) as well as the electrostatic interaction in MOR on NO adsorption. The NO molecules adsorb irreversibly and fill up the micropore of MOR at 201 K, above the critical temperature of NO, regardless of the kind of cation species. The NO adsorption takes place even at 273 K. In the adsorption at 273 K, the strength of electrostatic field formed by cation sites affects the adsorptivity and the order of saturation amount of adsorption (V_s) corresponds to that of the electrostatic field strength. EPR results show that NO molecules strongly interact with cation sites in MOR and dispropanation reaction of NO take place on CaM.

Keywords: adsorption, EPR, mordenite, MOR, NO, zeolite

Introduction

Microporous zeolites are crystalline aluminosilicates with framework anions and exchangeable cations in their structure. The anion-cation pairs form strong electrostatic fields and strongly interact with adsorbate molecules (Barrer, 1966, 1978; Kiselev, 1965). The electrostatic field strength varies with cation types as well as Si/Al ratios of the zeolites and the difference in the strength affects the adsorption phenomena such as heat of immersion (Tsutsumi and Takahashi, 1970, 1972).

In the case of adsorption on micropores the pore width of which is less than ca. 1.2 nm, an interaction between solid surface and a molecule is enhanced by overlapping of the potential field of pore walls. This enhancement exhibits strong adsorption, which is called micropore filling (Stoeckli, 1974; Everett and Powl, 1976; Gregg and Sing, 1982).

Mordenite (MOR) zeolite has a unidimensional channel structure with pore opening of 0.65 × 0.67 nm (Meier, 1992). The pore dimension of MOR is small enough to cause the micropore filling in the adsorption. Furthermore, cation sites in the channel of MOR form a strong electric field that exert strong attractive force on polar adsorbates. Therefore, MOR would be an appropriate adsorbent to study the effect of the micropore filling as well as the electrostatic interaction relevant to adsorption.

Nitrogen monoxide (NO) becomes a supercritical fluid above its critical temperature (T_c) of 180 K. Above T_c, almost none of microporous adsorbents are able to sufficiently adsorb NO. However, the adsorptivity increases when transition metal oxides are highly dispersed on the microporous adsorbents (Kaneko, 1987, 1989). In this case, it is considered that a chemically active NO is adsorbed on the highly-dispersed metal oxides through chemical interaction followed by condensation in the micropores by micropore filling.

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Free NO molecules do not show EPR signals due to the degeneracy among the π orbitals, however, the interaction with strong electrostatic field of zeolites quenches the degeneracy and reveals the EPR signals (Kasai, 1976). Therefore, NO is an ideal probe for studying the electrostatic field associated with the cation sites of zeolites. A number of investigations on the EPR spectra of adsorbed NO on zeolites have been made (Lunsford, 1968; Gardner and Weinberger, 1968; Kasai, 1976; Kasai and Bishop, Jr., 1972; Kasai and Gauro, 1982; Gutsze et al., 1996). These investigations were focussed on the interaction between NO and cation sites giving the EPR signals and/or the characterization of adsorbed states of NO on the zeolites, and the EPR measurements were thus carried out at 77 K or lower temperatures.

In this study, the adsorption characteristics of NO on MOR of different cation types were studied by measurements of NO adsorption isotherms and in situ EPR spectra at various temperatures to elucidate the effect of electrostatic field strength on NO adsorptivity as well as the enhancement of adsorption by micropore of zeolite.

Experimental

Samples

Na-type MOR (Toso Corp., Japan) with Si/Al ratio of 4.9 was used as original zeolite, and denoted NaM-10. Ca^{2+}-exchanged (CaM-10) and H-type (HM-10) MOR were prepared by ion exchange of the Na-type MOR with calcium nitrate and ammonium nitrate solution, respectively. The crystal structure of HM-10 and CaM-10 was found intact after the ion-exchange treatments by powder X-ray diffraction measurements. Chemical composition and pore characteristics of each zeolite were determined by inductive-coupled plasma (ICP) analysis and nitrogen adsorption at 77 K, respectively.

NO Adsorption

NO with 99.99% purity was used after further purification by several freeze-thaw cycles. The adsorption and desorption isotherms of NO were measured gravimetirically at 273 and 201 K. At the final stage of each desorption measurement, the sample was evacuated at high vacuum ($>$10 mPa) for 24 h at the desorption temperature, and the residual amount was regarded as the irreversible amount of adsorption.

EPR spectra before and after NO adsorption were measured in situ at 77 K or 120–201 K by using an X-band spectrometer (JEOL JES-FE1XG). The equilibrium pressure was set at 16.5 kPa through the experiments. The g values of EPR signals were corrected by a signal position of 1,1-diphenyl-2-picryl-hydrazyl (DPPH) solution at $g = 2.0036$. The spin concentration was determined by comparing the peak area of an integrated signal of the first derivative spectrum with that of a signal of $CuSO_4 \cdot 5H_2O$ at each adsorption temperature. IR spectral change of CaM-10 with NO adsorption was measured in situ at 298 K by using a self-supporting wafer of the zeolite.

Samples were heated at 773 K and 1 mPa for 10 h before each experiment.

Results and Discussion

Samples

Chemical composition and pore characteristics by nitrogen adsorption of each zeolite used in this study are presented in Table 1. The pore volumes of NaM-10 and CaM-10 are almost identical (0.17 mL/g), while HM-10 is 0.20 mL/g. The ionic radii of Na^+ and Ca^{2+} are 0.116 and 0.114 nm, respectively, and these ions occupy considerable space in micropores of mordenites. However, in the case of HM-10, the space occupied by either protons or hydroxyl group is negligible. Therefore, nitrogen was able to diffuse more easily and to be adsorbed more densely in HM-10 cavities than in NaM-10 or CaM-10, resulting in the increased adsorption capacity.

NO Adsorption

Figure 1 shows the adsorption and desorption isotherms of NO on each MOR at 201 K. A noticeable hysteresis was observed and most of adsorbed NO remained after evacuation under high vacuum. Each adsorption isotherm was of Type Ib in the IUPAC classification (Rouquerol et al., 1999). The adsorbed amount increased up to a pressure of ca. 50 kPa, then leveled off at a constant value under further pressure increase. The saturation capacity (V_s) of each MOR calculated by Langmuir plot was 20.1–24.9 molecules/(unit cell) as shown in Table 2. The V_s of each MOR was higher than the number of cation sites shown in Table 1. The order of V_s was HM-10 $>$ NaM-10 $\approx$ CaM-10. The V_s

Table 1. Characteristics of mordenite samples used in this study.

Sample name	Composition	Si/Al ratio	Surface area[a] (m^2 g^{-1})	Pore volume[b] (mL g^{-1})	Pore volume[b] (molecules (unit cell)$^{-1}$)	Cation sites (unit cell)$^{-1}$)
NaM-10	$Na_{8.2}Al_{8.2}Si_{39.8}O_{96}$	4.9	329	0.17	23.0	8.2
HM-10	$H_{8.1}Al_{8.1}Si_{39.9}O_{96}$	4.9	383	0.20	25.5	8.1
CaM-10	$Ca_{3.0}Na_{2.1}Al_{8.1}Si_{39.9}O_{96}$	4.9	320	0.17	22.9	3.0(Ca^{2+}), 2.1(Na^+)

[a] Apparent value determined by the BET method.

[b] Determined by applying DR-plot on nitrogen isotherm.

Table 2. NO adsorption capacity on M-10 samples.

Sample	Saturated adsorption amount (V_s)[a] at 201 K (molecules (unit cell)$^{-1}$)	273 K (molecules (unit cell)$^{-1}$)	201 K (mL g^{-1})	273 K (mL g^{-1})	Irreversible adsorption amount at 201 K (molecules (unit cell)$^{-1}$)	273 K (molecules (unit cell)$^{-1}$)
NaM-10	20.1	11.8	0.16	0.09	19.5	6.4
HM-10	24.9	7.0	0.20	0.06	22.0	3.5
CaM-10	18.8	14.2	0.15	1.13	19.6	11.3

[a] Determined by Langmuir plots for 201 K data. Because of discrepancy from Langmuir plot for 273 K data, the adsorption amount at 80 kPa was used for apparent value.

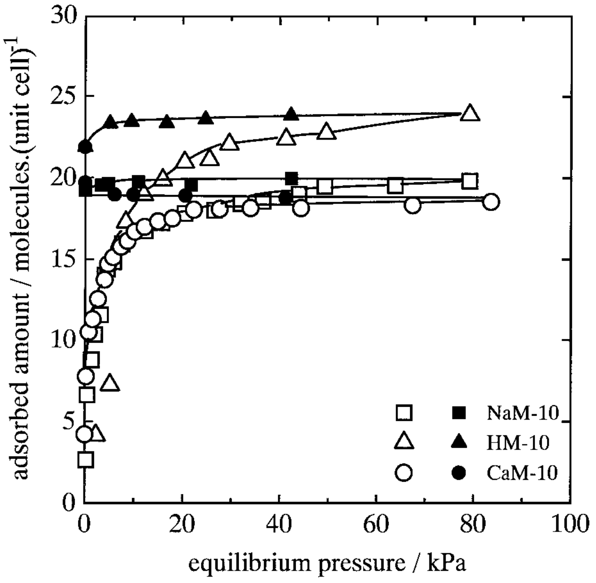

Figure 1. Adsorption isotherms of NO on M-10 at 201 K. Open and closed symbols denote adsorption and desorption, respectively.

values in milliliters per unit weight are also shown in Table 2, which were calculated under the assumption that the density of adsorbed NO was equal to that of liquid phase at 180 K. The V_s values corresponded to 90–100% of the micropore volumes estimated by nitrogen adsorption. This suggests that NO molecules fill up mordenite cavities at 201 K regardless of the kind of cation species.

The overlapping of potential field from pore walls enhances adsorption of molecules in micropores (Everett and Powl, 1976; Gregg and Sing, 1982). The enhancement of dispersion interaction between an NO molecule and pore walls was estimated with an assumption that NO is a spherical molecule with mean radius of 0.33 nm and the mordenite micropore is cylindrical with diameter of 0.68 nm (Stoeckli, 1974; Everett and Powl, 1976). The potential depth of the interaction at the center of the main channel of MOR was estimated 1.4–1.6 times deeper than the energy minimum on flat surface. Furthermore, the cation sites in micropores of zeolites exhibit strong electrostatic field, which causes strong adsorption of polar molecules (Tsutsumi and Takahashi, 1970, 1972). Whereas, the mean kinetic energy of NO at 201 K is only 1.1 times higher than that at T_c. Consequently, the strong adsorption of NO and the noticeable hysteresis at 201 K would be caused by combination of the enhancement of dispersion potential and the electrostatic interaction in micropores of MOR.

Figure 2 shows the adsorption isotherms of NO at 273 K. The adsorbed amounts increased more gradually with increase in equilibrium pressure than those at 201 K. The V_s decreased to 7–14 molecules/(unit cell), as shown in Table 2, and the cavities of MOR could

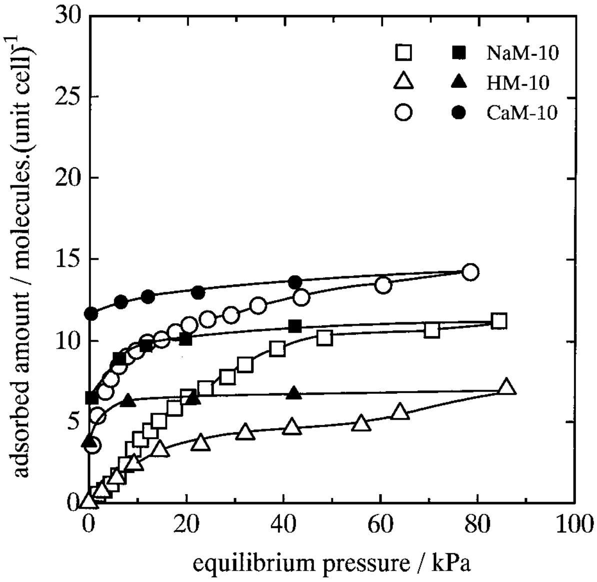

Figure 2. Adsorption isotherms of NO on M-10 at 273 K. Open and closed symbols denote adsorption and desorption, respectively.

not be filled up anymore by NO at 273 K. The mean kinetic energy of NO at 273 K is 1.5 times higher than at T_C. This vigorous motion of NO molecule would decrease the frequency of adsorption in the micropore. However, a clear hysteresis was still observed in desorption branch of each isotherm even at this temperature. These results suggest that the interaction between NO and M-10 is still strong enough to adsorb NO in the MOR cavity.

It is known that an electrostatic field in zeolite cavity depends on the number of an electric charge and an ionic radius of cation species (Tsutsumi and Takahashi, 1970, 1972). In the case of FAU with Si/Al ratio of 5.0, the field strength of CaY, NaY and HY are 1.5×10^{-10}, 3.3×10^{-11} and 4.3×10^{-11} C/m^2, respectively. Protons on cation sites easily form hydroxyl groups at low temperatures by reacting with lattice oxygen (Uytterhoeven et al., 1965), therefore, the proton sites do not particularly contribute to the formation of a strong electrostatic field. In the present study, the order of V_s became CaM-10 > NaM-10 > HM-10. Since the order of the field strength of CaM-10 and NaM-10 could be considered to correspond qualitatively to that of CaY and NaY, it is reasonable that the adsorptivity on CaM-10 was higher than that on NaM-10. In the case of HM-10, most of proton sites were of hydroxyl form, so that the adsorptivity was the lowest among those three samples. These results suggest that the electrostatic interaction plays a more important role in the adsorption at the higher temperature, 273 K. Beside the proton sites, presence of the adsorption sites that strongly interact with NO is suggested by EPR measurements. However, the site would be small in number and would not affect the change in V_s, which will be discussed below.

EPR Spectral Changes with NO Adsorption

No EPR signal was observed in each MOR after heating at 773 K in vacuo. However, EPR signals were observed after NO adsorption at 120 K on each MOR as shown in Fig. 3. Each spectrum in Fig. 3 is similar to that already reported on several types of zeolites including MOR (Lunsford, 1968; Gardner and Weinberger, 1968; Kasai and Bishop, Jr., 1972; Kasai, 1976; Kasai and Gauro, 1982; Gutsze et al., 1996). Possible assignments of g values observed in the present study are shown

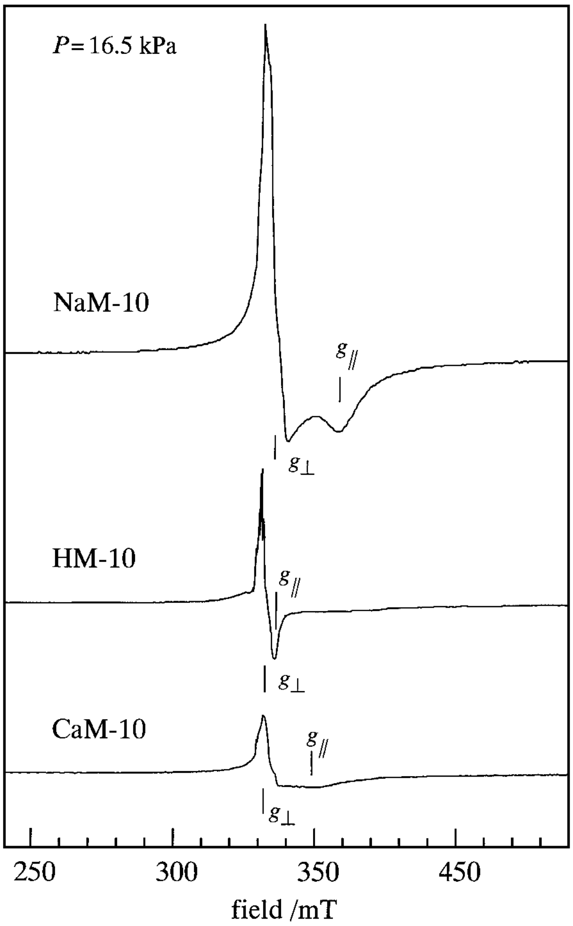

Figure 3. EPR spectra of adsorbed NO on M-10 at 120 K.

Table 3. EPR signals of adsorbed NO on MOR at 120 K.

Sample	g_{xx}		g_{yy} ($g_{\perp}$)		g_{zz} ($g_{//}$)	Δg_{zz}[a]
NaM-10	2.007		1.989		1.878	0.124
HM-10	2.001	2.010	1.999	1.995	1.980	0.022
CaM-10	2.001	2.005	1.998	1.992	1.897	0.105

[a] $\Delta g_{zz} = g_e - g_{zz}$, where g_e is the g value of free electron, 2.002316.

in Table 3 (Lunsford, 1968; Gardner and Weinberger, 1968; Kasai and Bishop, Jr., 1972; Kasai, 1976; Kasai and Gauro, 1982; Gutsze et al., 1996).

According to the definition of the g tensor of adsorbed NO upon cation sites, the difference between g_{zz} and g_e, $\Delta g_{zz} = g_{zz} - g_e$, becomes smaller when the interaction with cation sites increases (Kasai, 1976). In the present study the order of Δg_{zz} was NaM-10 $>$ CaM-10 $>$ HM-10. The difference between NaM-10 and CaM-10 can be explained by the difference in their electrostatic field. In the case of HM-10, the smallest Δg_{zz} value suggests the strongest interaction between NO molecules and adsorption sites, although the results of NO adsorption isotherms show that the proton sites are of hydroxyl form and do not particularly interact with NO molecules. It is considered that NO adsorption sites in H-type zeolites would be trigonal aluminum at the oxygen deficient sites of the framework (Lunsford, 1968), interstitial aluminum (hydro)oxy cations (Kasai, 1976) and "true" Lewis-acid sites, such as $(Al_xO_y)^{n+}$ (Gutsze et al., 1996) rather than protons or hydroxyl groups. Regardless of the types of these proposed sites, the interaction between these sites and NO molecules is strong enough to give the small Δg_{zz} value in HM-10. However, the number of sites bringing about such strong interaction would be too small to show a detectable effect on the adsorption isotherms at 273 and 201 K. The number of the strong interactive sites will be mentioned later in connection with the EPR spin concentration.

Figure 4 shows EPR spectra of adsorbed NO on NaM-10 at different temperatures. The equilibrium pressure was set to 16.5 kPa through the temperature range of experiments. No clear EPR signal of adsorbed NO was observed above 238 K, although a considerable amount of NO of ca. 9 molecules/(unit cell) which coincided with the number of Na^+ sites was adsorbed in the zeolite. The EPR signals were detected below 193 K and increased in its intensity with decreasing the temperature. The intensity of the EPR signals or the spin concentration correlates with the number of the interactive sites. The adsorbed NO molecules would not be able to strongly interact with cation sites to degenerate the π^* orbitals of NO above 238 K by vigorous kinetic motion of NO.

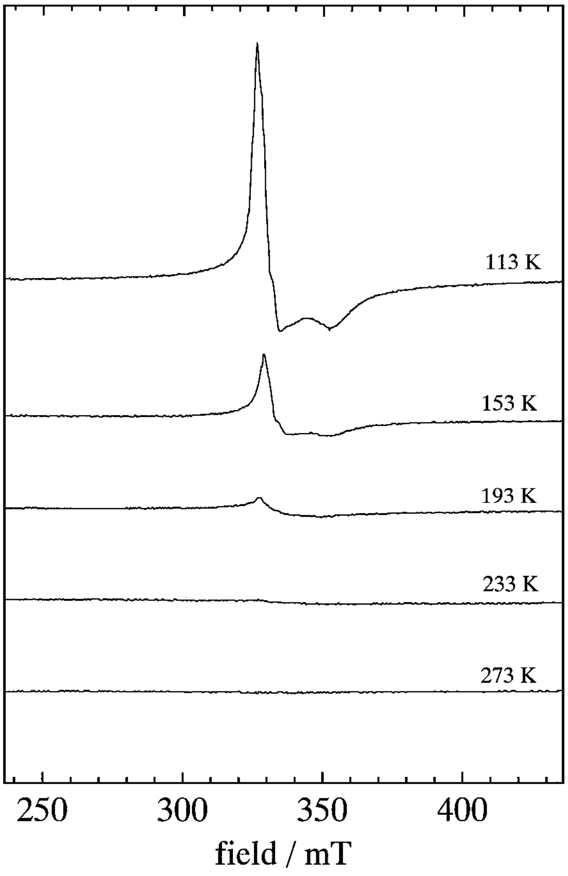

Figure 4. EPR spectra of adsorbed NO on NaM-10 at different temperatures.

The variation of the spin amount with adsorption temperature is shown in Fig. 5. The EPR spectrum and the adsorption amount on each sample were simultaneously measured in situ at 120–269 K. In Fig. 5, relative comparison of the spin concentrations among different kinds of zeolites is of interest, since absolute values include so many errors arising from experimental difficulty.

The spin concentrations of NaM-10 and HM-10 tended to increase with decreasing temperature below 230 K and reached to 3.4×10^{-1} and 1.1×10^{-1} spins/(unit cell) at 120 K, respectively. These results also suggest that the strength of the interaction between NO molecules and the cation sites increases at lower adsorption temperature. The spin concentration in HM-10 was smaller than NaM-10 due to less number of the interactive sites in HM-10. In the case of

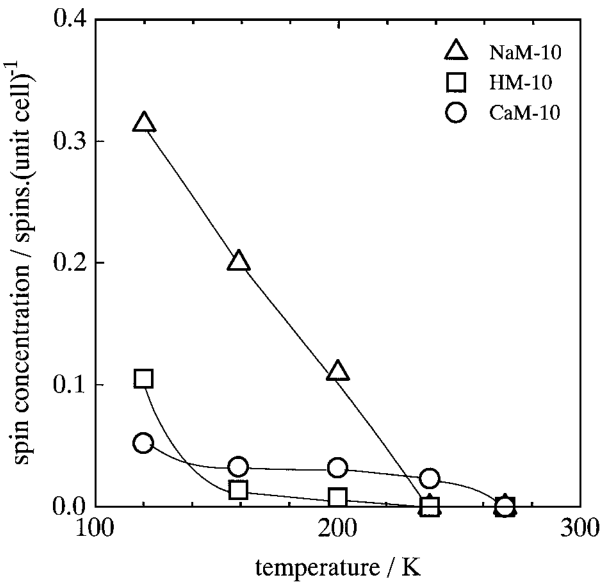

Figure 5. The variation of EPR spin concentration on M-10 with adsorption temperature.

CaM-10, the spin concentration was nearly constant, 2.3×10^{-2}–5.2×10^{-2} spins/(unit cell), below 230 K, which was much smaller than NaM-10, although Ca^{2+} ions being considered to form the strongest electrostatic field.

The strong electrostatic field formed by Ca^{2+} ions causes disproponation reactions of NO giving N_2O, N_2O_3 and NO_2 (Addison and Barrer, 1955; Chao and Lunsford, 1971a, b). The disproponation reaction would also take place on CaM-10. Figure 6 shows in situ IR spectral change with NO adsorption on CaM-10 at 298 K. Besides absorption bands assigned to gaseous NO centered at 1876 cm^{-1}, a new band assigned to N_2O species was observed at 2250 cm^{-1} by NO loading. The bands assigned to adsorbed NO_2 were not detected in the presence of gaseous NO, but were clearly observed at 2180 and 2000 cm^{-1} after evacuation of gas phase. The bands assigned to N_2O_3 were not detected. This is probably because N_2O_3 is an intermediate of the disproportion reaction. Among these three products, only NO_2 is EPR active and gives signals at the similar positions as NO. The EPR signals of CaM-10 would be due to NO_2 as well as NO. Since NO_2 has higher T_c of 431.4 K than NO, a considerable amount of NO_2 would remain on CaM-10 even at 238 K and would give the EPR signals. It is known that the NO_2 molecules further react with the lattice oxygen giving nitrato ions. It is plausible that such chemical reaction would take place on CaM-10, and thus, the spin concentration of CaM-10 became smaller.

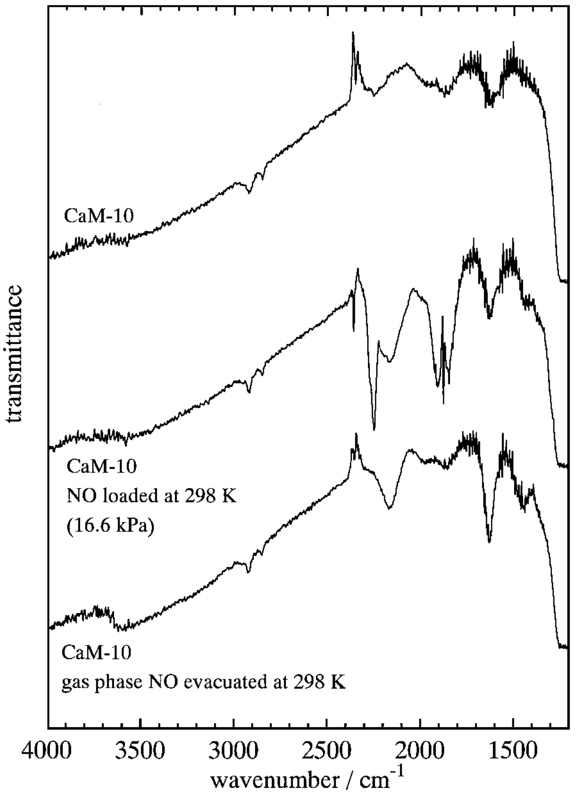

Figure 6. IR spectral change of CaM-10 with NO adsorption at 298 K.

Conclusion

The NO adsorption takes place even at 201 and 273 K, the temperatures above the T_c of NO (180 K), by the micropore filling mechanism as well as through the electrostatic interaction with the cation sites of MOR. A hysteresis appears in the desorption branch of the isotherm and irreversible adsorption is observed at each adsorption temperature. Since the mean kinetic energy of NO which is related to the motion of the molecule at 201 K is only 1.1 times higher than at T_c, NO is strongly adsorbed until filling up the micropore of MOR regardless of the types of cations. The NO adsorptivity decreases at 273 K and varies in the order of CaM-10 > NaM-10 > HM-10, which correlates to the strength of the electrostatic field formed by cations. When the kinetic energy of NO increases, the motion of NO becomes vigorous and therefore the interaction between

NO and the electrostatic field plays more important role in NO adsorption. The lowest adsorptivity in HM-10 reflects that hydroxyl sites do not show significant effect on the NO adsorption. The change in the EPR spin concentration with adsorption temperature suggests that NO molecules adsorbed in the micropores of MOR strongly interact with the cation sites of NaM-10 and HM-10 below 200 K. Since the disproponation reactions of NO take place on CaM-10, the EPR spin concentration of CaM-10 is smaller than NaM-10 signals. Therefore, NO molecule is considered a useful probe molecule to study potential enhancement and molecular interactions in microporous materials.

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