Characterization of Specific N2-Adsorption Site Existing on CuZSM-5 Type Zeolite: Effect of Ion-Exchange Level on Adsorption Properties

Yasushige Kuroda* and Yuzo Yoshikawa

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530, Japan

Shuichi Emura

ISIR-Sanken, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Ryotaro Kumashiro and Mahiko Nagao

Research Laboratory for Surface Science, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530, Japan

The specific adsorption property of copper-ion-exchanged ZSM-type zeolite (CuZSM-5) for dinitrogen molecules (N_2) has been elucidated by methods such as infrared (IR) and emission (ES) spectroscopy and by the measurements of heat of adsorption and adsorption isotherms of N_2 and CO. In the IR spectra an intense band appears at 2295 cm^{-1}, which is attributed to the adsorbed N_2 species. The amount of adsorbed CO, as well as the adsorbed N_2, increases with increasing copper-ion-exchange level of the ZSM-5 sample. By use of CO as a probe molecule, it was found that on the 873 K treated CuZSM-5 sample there are at least three types of adsorption sites available for CO adsorption; these are responsible for giving the IR bands due to the adsorbed CO species at 2159, 2151, and 2135 cm^{-1}. The adsorption behavior of N_2 molecules on the samples, which have various copper-ion-exchange levels and preadsorbed CO species, has been investigated, and it was found that the 2151 cm^{-1} band in the IR spectra reflects an N_2 adsorption site. Emission spectra were also obtained at each step of N_2 adsorption; the emission band due to the exchanged copper-ion species decreases in intensity with increasing pressure of N_2. These results can be interpreted as follows. The monovalent copper ion (Cu^+) formed during the evacuation of the sample at 873 K acts as an effective site for N_2 adsorption. Moreover, the site responsible for giving the IR band at 2151 cm^{-1} and the ES band at 18500 cm^{-1} plays an important role in the N_2 adsorption. By reference to the results of X-ray absorption fine structure (XAFS) measurements reported previously, it is thought that the active site, i.e., Cu^+ species, for N_2 adsorption interacts with the lattice oxygen and with CO or N_2 molecules to produce a pseudotetrahedral four-coordination structure. The relation between the heat values and the frequency of the IR band due to the adsorbed CO species gives a linear regression, which indicates that σ-bonding is predominantly operative in the bonding of Cu^+ with CO or N_2 molecule.

Introduction

Recently, our group[1,2] and Zecchina's group[3] have found independently the specific property of copper-ion-exchanged zeolite for dinitrogen (N_2) adsorption at room temperature. This adsorption, which takes place even at room temperature, is very interesting and leads us to expect that the copper-ion-exchanged zeolite has a potential to be used effectively for various phenomena associated with dinitrogen such as separation and fixation.

Copper-ion-exchanged ZSM-5-type zeolite (CuZSM-5) has occupied the attention of a number of researchers since Iwamoto et al. recognized this material as a useful catalyst in the direct decomposition reaction of NO$_x$.[4−7] Although numerous attempts have so far been made to elucidate the active sites in highly copper-ion-exchanged ZSM-5 zeolite as well as the mechanism of such a reaction, the origin of active sites is still debatable.[8−23]

The specific property of CuZSM-5 for N_2 adsorption will also be utilized to analyze the active sites in the decomposition reaction of NO$_x$. Such a unique property of CuZSM-5 has been well established and reproducible,[1−3] but little is known about the active sites for N_2 adsorption. In zeolite systems, coexistence of different exchangeable sites makes it difficult to elucidate the structural and electronic properties of the active sites through the analysis of spectroscopic data and by quantitative examination of N_2 adsorption and exchange capacity of the sample.

These standpoints have prompted us to study the specific properties of CuZSM-5 zeolite for N_2 adsorption in more detail and also to elucidate the nature and the coordinative environment of copper-ion-exchanged in ZSM-5 zeolite. In the present study we would also like to show a potential of copper-ion-exchanged ZSM-5-type zeolite as a useful catalyst for N_2-separation and -fixation. In addition, the key to analyzing active centers for catalytic decomposition and selective reduction of NO$_x$ will be presented briefly.

* To whom correspondence should be addressed. E-mail: kuroda@cc.okayama-u.ac.jp. Telephone: +81-86-251-7844. Fax: +81-86-251-7853.
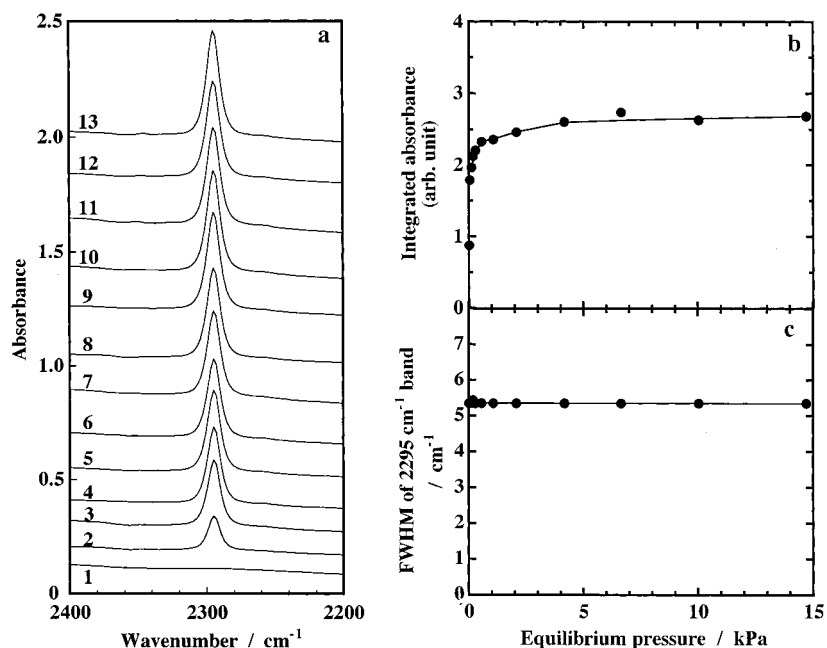
Figure 1. IR spectra of N_2 adsorbed on the CuZSM-5-141 sample at 298 K. (a) The sample was first evacuated at 873 K and then equilibrated with N_2 gas at various pressures: (1) zero pressure, (2) 5, (3) 43, (4) 105, (5) 182, (6) 282, and (7) 547 Pa and (8) 1.06, (9) 2.06, (10) 4.16, (11) 6.64, (12) 10.0, and (13) 14.7 kPa. (b) Integrated band area plotted against the equilibrium pressure. (c) Relationship between fwhm of the 2295 cm^{-1} band and the equilibrium pressure.

Experimental Section

Materials. The starting material of a sodium type of ZSM-5 zeolite (NaZSM-5) with a Si/Al ratio of 11.9 was supplied by Tosoh Co. By the conventional ion-exchanging method, approximately 5 g of this material was ion-exchanged in 500 cm^3 of a 0.3 M $CuCl_2$ solution for 1 h at 363 K. This procedure was repeated several times to obtain the copper-ion-exchanged ZSM-5 zeolite samples at varying exchange levels. The ion exchange capacity of the sample was calculated on the assumption that one copper ion is exchanged with two sodium ions. The copper-ion-exchanged ZSM-5 sample is hereafter designated as CuZSM-5-*x*, where *x* denotes the exchange level in percentage.

N_2 gas was obtained by evaporating liquid dinitrogen, and CO gas was purchased from GL Sciences Ltd. These gases were purified by the trapping method at 77 K prior to use.

IR Measurement. IR spectra were collected at a resolution of 2 cm^{-1} using a Galaxy 3020 FTIR spectrophotometer with a DTGS detector. The zeolite sample was pelleted into a self-supporting disk and placed in a cell that was made of quartz and equipped with KRS-5 windows. The sample was first activated at 873 K for 2 h in vacuo and then cooled to room temperature. The IR spectra were recorded at 300 K by transmission mode.

Measurements of Adsorption Isotherm and Heat of Adsorption. The adsorption experiments were carried out volumetrically at 298 K using an MKS Baratron pressure sensor (type 310 BH). The first adsorption measurement was performed at 298 K for the sample pretreated at 873 K under a reduced pressure of 1 mPa. After this measurement, the sample was evacuated at 298 K to remove the weakly adsorbed species, and then the second adsorption process was monitored at 298 K.

Differential heats of adsorption were measured at 298 K by using an adiabatic type of adsorption calorimeter. A detailed description of the calorimetric system is given elsewhere.[24,25] The heat of adsorption and adsorption isotherm were measured

simultaneously, from which the differential heat of adsorption was obtained.

Emission Spectra. Emission spectra of the samples were measured at 300 K with a Hitachi F-2000 fluorescence emission spectrophotometer. When the exciting light (33300 cm^{-1}) was focused on the sample cell, the emission was observed at a right angle to the incident beam. After the sample was evacuated at 873 K, the sample was subjected to contact with N_2 gas at different pressures. Emission spectra were also obtained at each step of N_2 adsorption.

Results

Figure 1 shows the IR spectra for the CuZSM-5-141 sample in equilibrium with N_2 gas of different pressures, together with the variations of integrated band area and fwhm (full width at half-maximum) with N_2 pressure. A single absorption band appears at 2295 cm^{-1} by N_2 adsorption, and it increases in intensity with increasing N_2 pressure (spectra 2−13). However, this absorption band vanished by the evacuation at room temperature. Taking into consideration that the N_2 molecule has usually no dipole moment and hence gives no IR band, the appearance of such an IR band implies that a strong interaction enough to break molecular symmetry takes place between the N_2 molecule and the CuZSM-5 sample. Moreover, since such a band was not observed for the NaZSM-5 sample, this absorption band is obviously assigned to the N≡N stretching vibration in the N_2 molecule adsorbed on the copper ion species exchanged in the CuZSM-5 sample.

Figure 2 represents the heats of adsorption and adsorption isotherms of N_2 at 298 K on the NaZSM-5 and CuZSM-5 samples evacuated at 873 K. For the NaZSM-5 sample, the adsorbed amount increases linearly with increasing equilibrium pressure. This adsorption isotherm is of Henry type, indicating a weak interaction between the solid surface and the N_2 molecule. Such adsorption behavior is well reflected in the differential heats of adsorption; the heat of adsorption is a relatively constant value of 35 kJ mol^{-1} over the whole range

CuZSM-5 Type Zeolite

*J. Phys. Chem. B, Vol. 103, No. 12, 1999* **2157**
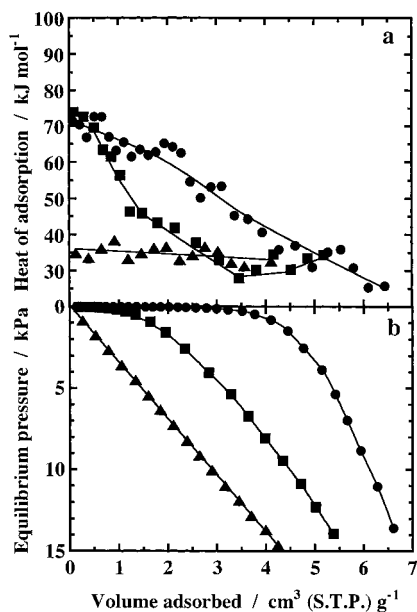
Figure 2. Differential heats of adsorption (a) and adsorption isotherms (b) of N_2 at 298 K on ZSM-5 zeolite samples pretreated at 873 K: (▲) NaZSM-5; (■) CuZSM-5-36; (●) CuZSM-5-141.

of coverage. On the other hand, for the CuZSM-5 samples, the adsorbed amount increases remarkably in the lower pressure region, indicative of a strong interaction. The initial heat value is about 75 kJ mol^{-1} for both samples of CuZSM-5-36 and CuZSM-5-141, and it decreases with increasing coverage to reach the same value of 35 kJ mol^{-1} as for the NaZSM-5 sample. The difference in the copper-ion-exchange level of the sample is clearly reflected in the adsorbed amounts and adsorption heats. The adsorbed amounts are much larger for the highly exchanged sample (CuZSM-5-141) than for the sample with lower exchange level (CuZSM-5-36), and the adsorption heats are also larger for the former sample than for the latter sample in the wide range of coverage. These results give strong support to the concept that the effective site for N_2 adsorption is a copper-ion species exchanged in the zeolite sample.

Figure 3 shows the adsorption isotherms of N_2 on the NaZSM-5 and CuZSM-5 samples with different copper-ion-exchange levels. The monolayer capacities were obtained from the adsorption heats data by assuming that the monolayer capacity corresponds to the adsorbed amounts that give the same heat value as that for the NaZSM-5−N_2 system (ca. 35 kJ mol^{-1}).[26] These values are shown in Figure 3b as a function of exchange level of the sample. It is clearly seen from this figure that the monolayer capacity increases with increasing exchange level of the sample up to 100% and gives an almost constant value of 6.0 cm^3 (STP) g^{-1} beyond this level.

Carbon monoxide (CO) is widely used as a probe molecule in the titration of the number and strength of Cu^+ sites by comparing the intensity and the shift of the IR absorption band due to the adsorbed CO molecule with those for gaseous CO molecule.[27−35] In the present study we tried to elucidate the state of exchanged copper-ion in the zeolite sample through the IR measurements. In this experiment, the sample was first evacuated at 873 K and then exposed to the CO gas of 13.3 kPa at 300 K followed by reevacuation at the same temperature. Resulting spectra and their curve-fitting for the CuZSM-5 samples are shown in Figure 4. The spectral change due to the evacuation treatment at different temperatures is also depicted in this figure for the CuZSM-5-83 sample as a typical example.
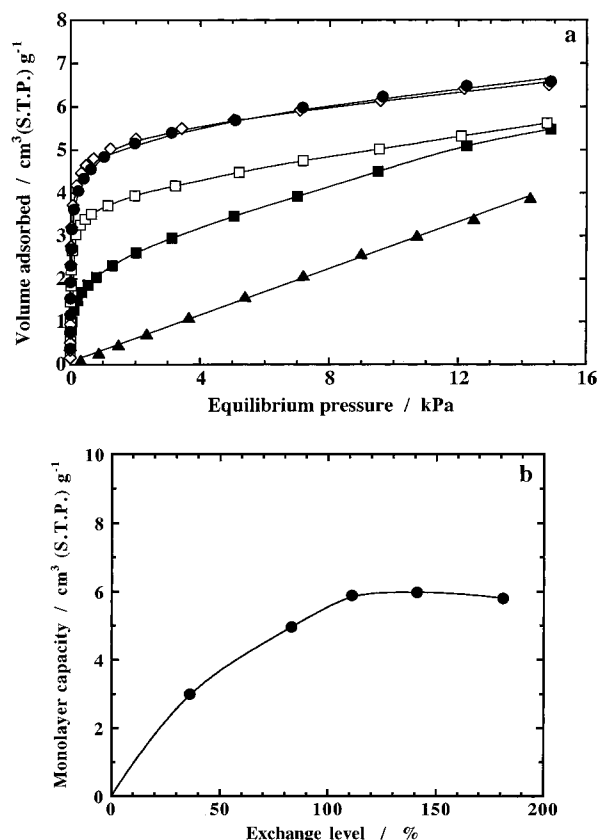

Figure 3. Adsorption isotherms of N_2 on ZSM-5 samples pretreated at 873 K (a) and monolayer capacities as a function of the ion-exchange level of the sample (b): (▲) NaZSM-5; (■) CuZSM-5-36; (□) CuZSM-5-83; (◇) CuZSM-5-111; (●) CuZSM-5-141.

A broad band, which appears to be accompanied by a tailing toward the lower wavenumber, is observed at around 2155 cm^{-1}. The absorption band still remains after evacuating the sample at 300 K. This fact indicates a formation of monovalent copper ion species, Cu^+, by reference to the data accumulated so far. It is clearly confirmed that the observed band is composed of two major components, 2159 and 2151 cm^{-1} bands, and of one minor band at 2135 cm^{-1}. At lower exchange level, the band at 2159 cm^{-1} is dominant, while a distinct band at 2151 cm^{-1} increases with exchange level of the sample. The desorption behavior of adsorbed CO molecules was examined to elucidate the state of ion-exchangeable sites; the IR spectra were taken at each desorption stage after CO adsorption (Figure 4b). The 2135 cm^{-1} band disappears by the evacuation at 373 K, the 2151 cm^{-1} band does by 473 K evacuation, and finally the 2159 cm^{-1} band vanishes by the evacuation at 673 K. These facts clearly indicate the existence of three types of ion-exchangeable sites.

The relative band area for respective IR bands to the area of 2135 cm^{-1} band for the CuZSM-5-12 sample is plotted against the exchange level of the CuZSM-5 sample in Figure 5. The intensity of the 2135 cm^{-1} band increases almost linearly with increasing exchange level of the sample. For the 2159 cm^{-1} band it increases at the lower exchange level and saturates at about 80% exchange. As to the increase of the 2151 cm^{-1} band intensity, it is suppressed in the lower exchange level and then appears to be enhanced at the exchange level of 80%. It is interesting to note that this band intensity increases definitely even in the region of exchange level exceeding 100%. In the region of lower exchange level, the intensity of the IR band decreases in the order 2159 cm^{-1} > 2151 cm^{-1} > 2135 cm^{-1}. On the other hand, in the higher exchange level, it is different:
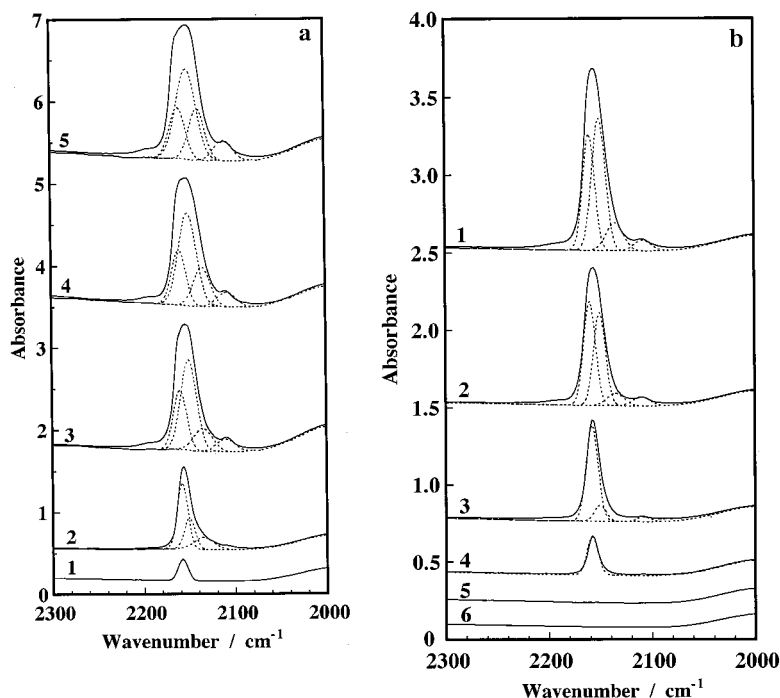
Figure 4. (a) IR spectra of CO adsorbed on the CuZSM-5-*x* samples: (1) CuZSM-5-12; (2) CuZSM-5-36; (3) CuZSM-5-83; (4) CuZSM-5-141; (5) CuZSM-5-181. The sample was first pretreated at 873 K and then contacted with CO gas followed by evacuation at 300 K. Curve-fitted spectra are also shown in the observed spectra. (b) IR spectra taken after evacuation at each temperature for the CuZSM-5-83 sample: (1) 300, (2) 373, (3) 473, (4) 523, (5) 573, and (6) 673 K.
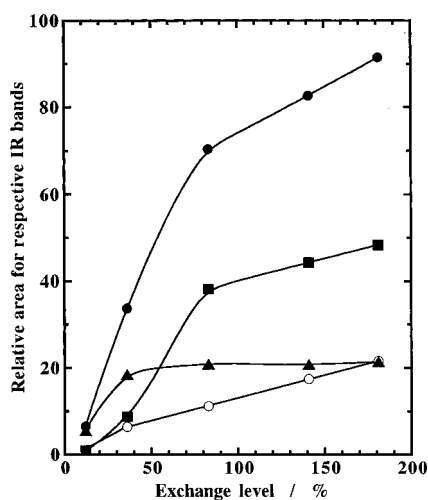
Figure 5. Variation of relative band area of component band with copper-ion-exchange level of the sample: (○) 2135 cm^{-1} band; (■) 2151 cm^{-1} band; (▲) 2159 cm^{-1} band; (●) observed band (total).

2151 cm^{-1} > 2159 cm^{-1} > 2135 cm^{-1}. It should be noted at the present stage that the variation of intensity of the 2151 cm^{-1} band with exchange level of the sample seems to be quite similar to that of monolayer capacity for N$_2$ adsorption with exchange level (Figure 3b).

Figure 6 shows the emission spectra for the CuZSM-5 samples and the variation of relative intensity (with respect to the band area) of the component spectrum obtained by a curve-fitting procedure with the exchange level of the sample. The emission bands are observed at around 20800 and 18500 cm^{-1} for all the samples examined. These dominant bands are due to an electronic transition from the 3d^{9}4s^1 to 3d^{10} orbital of copper ion, indicating a formation of Cu$^+$ species in the CuZSM-5 sample by the treatment at high temperature, 873 K, in vacuo.[36] This Cu$^+$ species obviously results from a reduction of divalent copper ion (Cu^{2+}) exchanged in ZSM-5, being coincident with

the IR data described above. By assuming a Gaussian function, the spectra were separated (curve-fitting) into three components: emission bands at 20800, 19600, and 18500 cm^{-1} (dotted line in Figure 6a). Barrie et al.[37] observed the emission bands at 23500 and 19000 cm^{-1} for the Cu/β-Al$_2$O$_3$ sample, and they ascribed these two bands to the monomeric and dimeric Cu$^+$ species, respectively. Such an assignment was valid for several years. Recently, Wichterlová et al.[18,36] have observed the emission bands at 20800 and 18500 cm^{-1} in the detailed examination of various CuZSM-5 zeolites, and they assigned the former band to the Cu$^+$ species adjacent to two Al atoms in the zeolite framework and the latter one to the same species situated in the vicinity of one Al atom in the framework. Although their explanation is logical, we will discuss the present results from a different point of view in the later part of this paper. The relative band area to the area of the 19600 cm^{-1} band for the CuZSM-5-12 sample is plotted against the ion-exchange level (Figure 6b), on the basis of the consideration that total band area corresponds to the adsorbed amount that can be estimated from the adsorption data. It is found by the curve analysis that three bands appear at 20800, 19600, and 18500 cm^{-1}; the intensity of the 19600 cm^{-1} band is almost constant irrespective of the exchange level, and that of the 20800 cm^{-1} band increases with increasing exchange level to reach a saturated value at the exchange level of about 80%. As for the 18500 cm^{-1} band it increases with exchange level up to 150%. It is obvious from the emission spectra that the CuZSM-5 sample has three different types of exchangeable sites for copper ions,[18,38] consistent with the IR data. The sites responsible for the emission bands at 20800, 19600, and 18500 cm^{-1} correspond to those giving IR bands at 2159, 2135, and 2151 cm^{-1} due to the adsorbed CO species, respectively.

As described above, we can separate the two types of dominant sites effective for CO adsorption by utilizing the heat-treatment temperature in vacuo, from which the state of effective sites for N$_2$ adsorption can be elucidated. Figure 7 shows the

CuZSM-5 Type Zeolite

J. Phys. Chem. B, Vol. 103, No. 12, 1999 **2159**
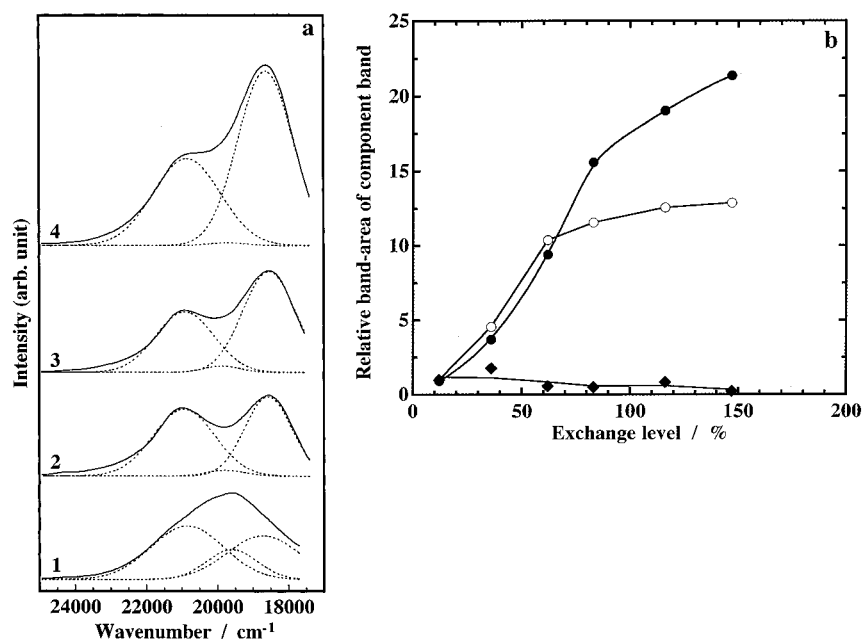
Figure 6. Emission spectra of CuZSM-5-*x* samples (a) and variation of the relative band area of component band with copper-ion-exchange level of the sample (b). The component bands was obtained by a curve-fitting analysis, which is shown by the dotted line in the respective emission spectra: (1) CuZSM-5-12; (2) CuZSM-5-83; (3) CuZSM-5-116; (4) CuZSM-5-147. Component emission bands are at 20800 cm^{-1} (○), 19600 cm^{-1} (◆), and 18500 cm^{-1} (●).
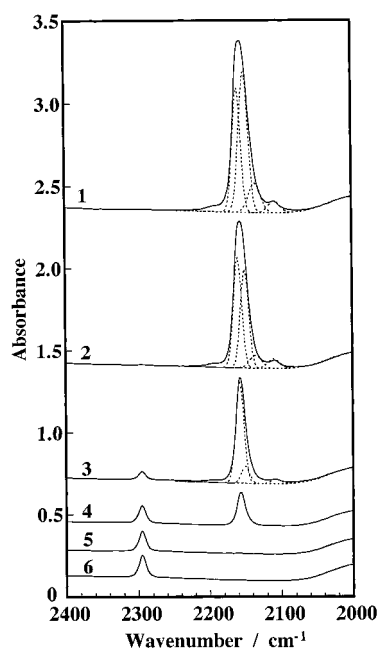

Figure 7. IR spectra of CuZSM-5-83 sample taken after CO and N$_2$ adsorption. The sample was first evacuated at 873 K and then exposed to CO gas at room temperature. After this procedure the sample was reevacuated at each temperature and was subjected to contact with N$_2$ gas of 13.3 kPa. The spectral number corresponds to the reevacuation temperature: (1) 300, (2) 373, (3) 473, (4) 523, (5) 573, and (6) 673 K.

IR spectra for the CuZSM-5-83 sample that was reevacuated at respective temperatures after CO adsorption and then subjected to contact with N$_2$ gas. The sample reevacuated at 300 K after CO adsorption (without contact with N$_2$) gives a broad band centered at 2155 cm^{-1}, ascribed to the adsorbed CO species (spectrum 1). Introduction of N$_2$ gas of 13.3 kPa onto this sample gives no band attributable to the adsorbed N$_2$ species. In such a case three types of active sites are occupied by CO molecules. The absorption band due to the adsorbed N$_2$ species is hardly discernible when the sample was evacuated at 373 K after CO

adsorption, by which procedure the sites responsible for the IR band at 2135 cm^{-1} has been cleaned. This fact implies that the effective sites for N$_2$ adsorption cannot be restored by the evacuation procedure at 373 K. By the treatment at increasing temperature, e.g., at 473 or 523 K, the sample gives a distinct band at 2295 cm^{-1} that is obviously ascribed to the adsorbed N$_2$ species, accompanying a decrease in the band intensity at 2151 cm^{-1}. Further evacuation at 573 or 673 K causes a disappearance of the CO band, accompanying a slight increase in intensity of the 2295 cm^{-1} band. From these observations it can be reasonably concluded that the site responsible for the 2151 cm^{-1} band due to the adsorbed CO species is the effective site for the N$_2$ adsorption.

To obtain more information regarding the specific site for N$_2$ adsorption, the correspondence of the emission band to the N$_2$ adsorption was examined and the results are represented in Figure 8. The emission spectrum observed for the CuZSM-5-141 sample evacuated at 873 K changes in its feature with an increase in N$_2$ pressure, and the bands centered at 20800 and 18500 cm^{-1} are reduced in intensity; this is accompanied by a slight shift of the latter band to 18200 cm^{-1}. These bands ultimately vanish by contacting the sample with N$_2$ gas of 13.1 kPa (spectrum 13). Such spectral changes also indicate that the Cu$^+$ species acts as an active site for N$_2$ adsorption, consistent with the conclusion derived from the IR measurements using CO. The assignment of the band at 18200 cm^{-1} is not well understood at present. However, the shift of this band owing to the interaction with N$_2$ molecules may be explained in terms of the movement of copper ions due to the N$_2$ addition. Similar explanation has been given for the system of copper-ion-exchanged Y type zeolite by Strome and Klier[39] and also for the CuZSM-5−CO system by us.[40] When the sample is reevacuated at 300 K, the spectrum recovers its original pattern (spectrum 1) except that the band intensity is lowered and the 18500 cm^{-1} band shifts to 18200 cm^{-1} (spectrum 14). Further increase in evacuation temperature is needed to restore the original band intensity; the emission bands at 20800 and 18500 cm^{-1} completely recover their original intensities upon evacu-
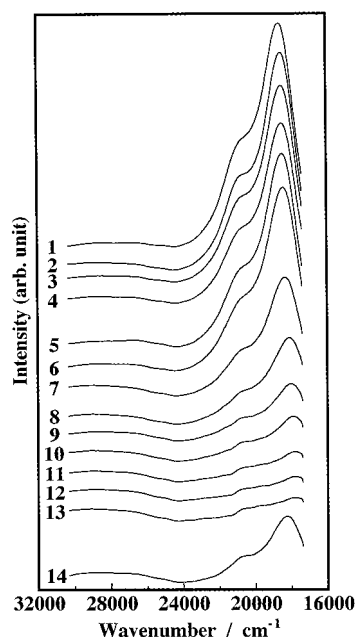
Figure 8. Effect of adsorbed N_2 species on emission spectra of CuZSM-5-141. Spectral number corresponds to the following conditions: (1) evacuated at 873 K; contacted with N_2 gas at increasing pressure but nearly zero (2−7) and at (8) 13.3, (9) 26.6, and (10) 93.1 Pa and at (11) 1.18, (12) 3.95, (13) 13.1 kPa; (14) subsequently reevacuated at 300 K.

ation at 573 K. These facts also prove a significant role of Cu^+ species as an adsorption site for the N_2 molecule.

Figure 9 shows the adsorption isotherms of CO at 298 K for the CuZSM-5 samples evacuated at 873 K and the variation of the chemisorbed amount with the exchange level of the sample. In the first adsorption process, the adsorbed amount increases along the ordinate, keeping the equilibrium pressure zero, and then it increases gradually with increasing pressure to give a value corresponding to the monolayer capacity. The second adsorption isotherm parallels the first one, which implies that in the second adsorption process only a weak adsorption occurs. The monolayer capacities for CO adsorption were estimated by applying the Langmuir equation to these adsorption isotherms, from which the difference between the values for the first and second adsorption isotherms was obtained. This difference corresponds to the strongly adsorbed amount, in other words, irreversibly adsorbed amount, and hence may be regarded as chemisorbed amount on the CuZSM-5 sample. The chemisorbed amount of CO thus obtained is plotted against the exchange level of the sample (Figure 9b). There is a good correspondence between the variations of the chemisorbed amount of CO and of the total IR band area due to the adsorbed CO species (Figure 5).

Disussion

Strong Adsorption of N_2. As seen in Figure 1b, the peak intensity (strictly, integrated band area) exhibits a significant increase in the lower N_2-pressure region and it reaches a saturated value at around 15 kPa. The appearance of an IR band due to the adsorbed N_2 species clearly indicates the existence of strong sites for N_2 adsorption on the CuZSM-5 zeolite. Other important features can be also seen in Figure 1; the absorption band appears at a fixed wavenumber, 2295 cm^{-1}, and its fwhm is constant, ca. 5 cm^{-1}, both of which are irrespective of the N_2 pressure (Figure 1c). Therefore, in the copper-ion-exchanged zeolite at least one type of site available to N_2 adsorption exists.
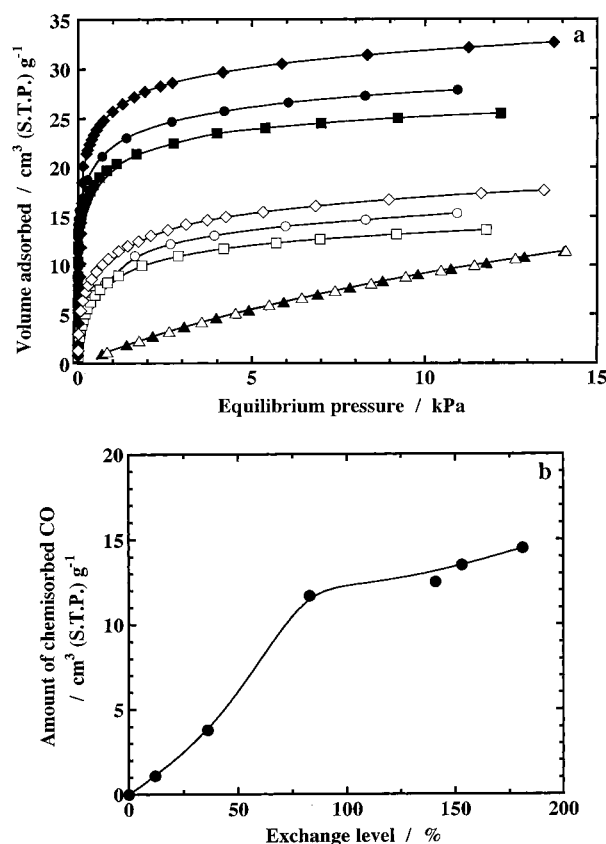
Figure 9. Adsorption isotherms of CO on NaZSM-5 and CuZSM-5-*x* (a) and related chemisorbed amounts as a function of ion-exchange level of the sample (b): (▲, △) NaZSM-5; (■, □) CuZSM-5-83; (●, ○) CuZSM-5-141; (◆, ◇) CuZSM-5-181. Filled and open marks represent the first and second adsorption, respectively.

Another interesting feature obtained from the adsorption heat curves is a linear decrease of adsorption heat with coverage, which suggests either that the surfaces of these samples are energetically heterogeneous against N_2 molecules or that the repulsive interaction takes place between the adsorbed N_2 molecules. The fact that the IR band due to the adsorbed N_2 molecules appears at a fixed wavenumber (2295 cm^{-1}) and fwhm (ca. 5 cm^{-1}) irrespective of the coverage may favor the latter interpretation. Here, if we assume a Langmuir type of adsorption and a repulsive force being worked between the adsorbate species, the adsorbed amount or the number of sites occupied by the adsorbed species (N_A) can be expressed by the following equation:

$$N_A = (N_S K'P)/(1 + K'P)$$

where N_S is the total number of adsorption sites, P is the equilibrium pressure, and K' is a constant. Assuming that the repulsion energy is proportional to the coverage ($\theta = N_A/N_S$), K' is given by the expression

$$K' = K \exp(-u\theta/(RT))$$

where u means the repulsive potential energy of adsorbed molecules exerted by the circumstances when N_A equals N_S ($\theta = 1$), and K is also constant and represented as $\exp(q_{initial}/(RT))$, where $q_{initial}$ is the initial differential heat of adsorption. If such a situation is satisfied, it is apparent that the differential heat of

CuZSM-5 Type Zeolite

J. Phys. Chem. B, Vol. 103, No. 12, 1999 **2161**

adsorption, q_{diff}, decreases linearly until the coverage of unity is established:

$$q_{diff} = q_{initial} - u\theta$$

One explanation for this phenomenon may be that the repulsive interaction between the adsorbed dinitrogen molecules is operative in the present system.

States of Copper Ion Exchanged in ZSM-5 Samples and of N_2 Adsorption Site. In our recent studies, we have already provided the evidence for the existence of a tetragonal hydroxyl-bridged species, e.g., dimer, of copper ions in the excessively ion-exchanged mordenite sample on the basis of the XAFS data.[41,42] Hamada et al.[43] and Sachtler's group[17,19] have also described the presence of dinuclear species in the excessively copper-ion-exchanged ZSM-5 sample. The reduction of cupric ion exchanged as binuclear species, $[Cu_2(H_2O)_4(OH)_2]^{2+}$, is expected to occur with an evolution of O_2 gas via the mechanism reported for mordenite system,[41,42] though the improvement may be recommended in detailed respects.

As for the state of exchangeable sites, recently, Lamberti et al.[35] have reported, on the basis of EXAFS data, that there exist two types of ion exchange sites on the ZSM-5 zeolite; one is two-coordination and the other is three-coordination with respect to the lattice oxygen. By reference to their data, we tentatively assigned the bands at 2159 and 2151 cm^{-1} to the CO species strongly adsorbed on the copper-ion species that were bound to two and three lattice oxygen atoms, respectively, depending on the difference in the extent of charge compensation of copper ion owing to the variation of the number of coordinated oxygen atoms. Such interpretation is in agreement with the explanation given by Brand et al.[44] The interaction of CO molecules with the cations of a transition metal may imply an electron donation from the 5σ orbital of CO to the empty 4s and 4p orbitals of the metal in synergy with a back-donation from the metal to the empty antibonding $2\pi^*$ orbital of CO.[45] The nature of bonding between the copper ion and the CO molecule will be given later, in comparison with the one in the gas phase. The IR band at 2135 cm^{-1}, which can be easily eliminated by the evacuation at lower temperature, e.g., 373 K, probably arises from the CO molecule adsorbed on the Cu^+ species deposited on the siliceous part of ZSM-5 sample, since CO on Cu^+/SiO_2 exhibits a band at a similar wavenumber.[46] However, such an assignment is not well established at present and will be confirmed by further investigation.

ES data (Figure 8) also provide the information on the state of exchangeable sites; the curve-fitting analysis of the emission spectra was performed by assuming a Gaussian function. The variation of the band intensity (integrated band area) for the respective bands at 20800 and 18500 cm^{-1} with the number of dosing of N_2 gas is represented in Figure 10, where the ratio of the band intensity, A_{18500}/A_{20800}, is also depicted. The emission band at 18500 cm^{-1} is reduced in intensity in the initial range of N_2 adsorption. The preferential interaction of the site responsible for the 18500 cm^{-1} band in ES with the N_2 molecules seems to be reflected in the variation of the band intensity of the 2151 cm^{-1} band in the IR with N_2 adsorption. As mentioned above, both band areas of the 2151 cm^{-1} band in IR (Figure 5) and of the 18500 cm^{-1} band in ES (Figure 6b) increase with increasing ion-exchange level of the sample. On the basis of these considerations, we tentatively regarded the site responsible for the 18500 cm^{-1} band as an effective site for N_2 adsorption.

Here, we can calculate the ratio of CO/Cu^+ (expressed in the number of species) from the data of both the chemisorbed
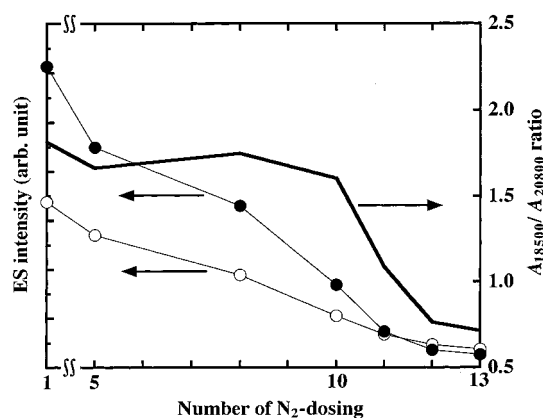
Figure 10. Variation of integrated band intensity of respective emission bands with the number of N_2 dosing. Symbols represent respectively 20800 cm^{-1} band (○) and 18500 cm^{-1} band (●), and solid line indicates the ratio of band intensity (A_{18500}/A_{20800}). The number of N_2-dosing on the abscissa corresponds to the spectral number in Figure 8.

TABLE 1: Ratios Estimated from Various Data for Copper-Ion-Exchanged ZSM-5 Samples
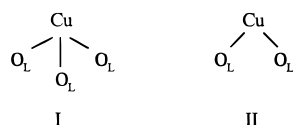
	CuZSM-5-83	CuZSM-5-141	CuZSM-5-181
CO/Cu^+	0.92	0.68	0.63
N_2/Cu^+	0.46	0.33	0.26
ratio of effective sites for N_2 molecule to Cu^{+a}	0.50	0.36	0.32

[a] These values were estimated from both IR and isotherm data of CO adsorption, corresponding to the value $(A_{2151}/A_{total})(CO/Cu^+)$. The detailed procedure was described in text.

amount of CO and the copper-ion content obtained by the titration method. Table 1 shows the value of CO/Cu^+ ratio, together with the N_2/Cu^+ value. The ratio of CO/Cu^+ is ca. 0.7 for every CuZSM-5 sample. Taking account of the presence of divalent copper ions that scarcely act as adsorption sites for the CO molecules, we may go on to the conclusion that the CO molecule interacts with the Cu^+ species in a ratio of 1:1. In the case of N_2 adsorption, the ratio of N_2/Cu^+ is found to be smaller than 0.5. This fact indicates that part of the sites effective for the CO adsorption acts as useful sites for the N_2 adsorption. No correspondence seems to be found between these two ratios, CO/Cu^+ and N_2/Cu^+. However, it admits of no argument that the site that is responsible for the 2151 cm^{-1} band due to the adsorbed CO species is an effective one for N_2 adsorption. An alternative estimation of the number of N_2 adsorption sites was tried; multiplying the ratio of the band area (A_{2151}) of the component 2151 cm^{-1} band to the total band area (A_{total}) for the band (at around 2155 cm^{-1}) experimentally obtained by the value of CO/Cu^+, we tried to estimate the number of effective sites for N_2 adsorption. As can be seen from Table 1, these values appear to be in agreement with the value of N_2/Cu^+.

In the EXAFS spectra for the CuZSM-5 sample evacuated at 873 K, the band observed at 1.59 Å (no phase-shift correction) can be attributed to a backscattering from the first nearest-neighboring oxygen atoms and the resulting averaged coordination number can be estimated to be ca. 2.5 ($\Delta N = \pm 0.1$), consistent with the value obtained by Lamberti et al.[35] This result, combining with the IR data, was interpreted in terms of an existence of two types of exchangeable sites for copper ions, that is, two- and three-coordinated copper ion sites with respect to the lattice oxygen atom.[40] Moreover, it was also obvious that the adsorption of CO molecules brings about a remarkable decrease in intensity of the band at 8.983 keV in the XANES spectra as well as an appearance of a new and weak band at

8.981 keV. A slight decrease in intensity of the 8.981 keV band and an increase in the 8.983 keV band intensity in the XANES spectra were caused by the evacuation of the sample, on which the CO molecules were adsorbed, at 300 K. These tendencies were kept until the evacuation temperature reached 473 K and finally the same spectral pattern as that for the original 873 K treated sample was obtained by the evacuation at 573 K. The band at 8.981 keV can be ascribed to the 1s−3d transition to the energy level caused by the interaction of monovalent copper ion species with CO molecules; the change of energy from 8.983 to 8.981 keV is due to the change in coordination number and the elongation of bond length between the copper ion and the lattice oxygen (O_L), resulting from the CO-induced migration of copper ion. Taking account of the coordination number obtained from the EXAFS data, the decrease in intensity of the band at 8.983 keV can be well explained by assuming a tetrahedral arrangement formed through the interaction with the three-coordinated copper ion and the CO molecule. To explain the results of these IR, ES, and XAFS experiments, the following models are proposed for the ion-exchanged sites in the CuZSM-5 zeolite.

$$
\begin{array}{cc}
\mathrm{Cu} & \mathrm{Cu} \\
O_L\diagup\big|\diagdown O_L & O_L\diagup\diagdown O_L \\
O_L & \\
\mathbf{I} & \mathbf{II}
\end{array}
$$

In addition, we can deduce that the species **I** and **II** are responsible for the IR bands at 2151 and 2159 cm^{-1} due to the adsorbed CO molecules, respectively. Since the N_2 molecules adsorbed on these sites are expected to have the same configuration as in the case of CO adsorption, the effective site for N_2 adsorption may be such a site that accepts N_2 molecule to form a pseudotetrahedral structure. This site is responsible for the IR band at 2151 cm^{-1} when the CO molecule is adsorbed. Therefore, it is reasonably concluded that one of the two types of adsorption sites in the CuZSM-5 zeolite, i.e., a three-coordination environment, is occupied selectively by an N_2 molecule, while both types of sites are occupied by a CO molecule.

Nature of Bonding between Cu$^+$ and CO or N$_2$. The nature and property of adsorption sites can be derived from a change in the frequencies of the fundamental stretching vibration (ν) of a simple gas molecule when adsorbed. Additional information on the nature of bonding between the metal ion on the surface and the adsorbed species would also be obtained by analyzing the relationship between the value of ν for the adsorbed species and the differential heat of adsorption, q_{diff}. These approaches will be useful in the more detailed identification of the different types of adsorption sites because the value of ν (strictly, the shift of ν) reflects a bond strength of the adsorbed species, e.g., the strength of C−O bonding in the adsorbed CO molecule, and the value of q_{diff} reflects a strength of the interaction between the adsorption site and the adsorbed species, e.g., the strength of Cu$^+$−C bonding in the adsorption of CO onto the Cu$^+$ species on the surface. Figure 11 shows the heats of adsorption and adsorption isotherms of N_2 obtained at 298 K for the samples of CuZSM-5-141, CuM-149 (copper-ion-exchanged mordenite), and CuY-146 (copper-ion-exchanged Y type zeolite). Infrared spectra of adsorbed N_2 species on these samples are shown in Figure 12. Furthermore, the relationship between $q_{initial}$ for the copper-ion-exchanged zeolites−N_2 system and ν_{N2} in the initial adsorption range is represented in Figure 13 for the systems of copper-ion-exchanged zeolites (CuZSM-5, CuM, and CuY)−N_2, together with the previous results for the systems of CuZSM-
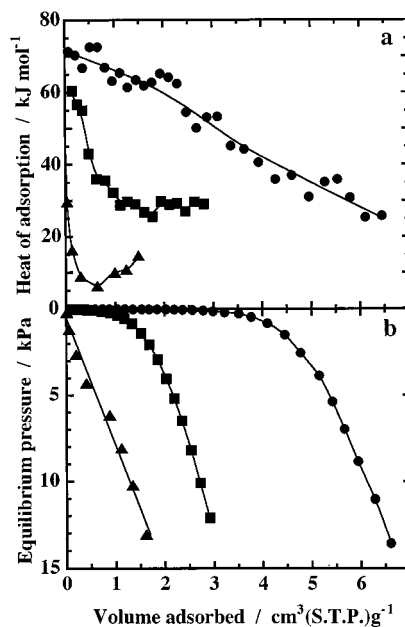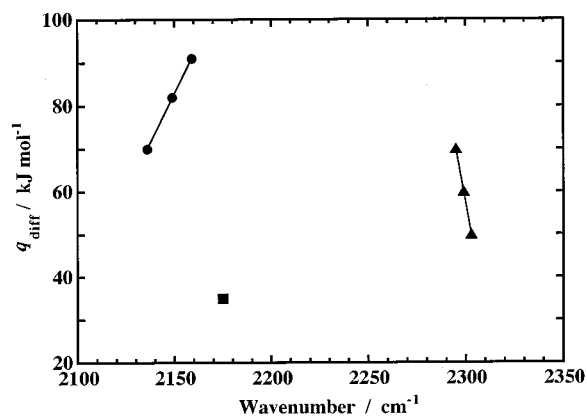

Figure 11. Differential heats of adsorption (a) and adsorption isotherms (b) of N_2 on copper-ion-exchanged zeolites at 298 K: (●) CuZSM-5-141; (■) CuM-149; (▲) CuY-146.
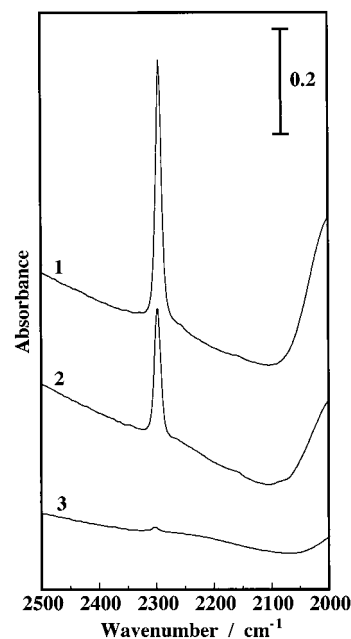
Figure 12. IR spectra of N_2 species adsorbed on copper-ion-exchanged zeolites at 300 K: (1) CuZSM-5-141; (2) CuM-149; (3) CuY-146.

5-141−CO and NaZSM-5−CO.[47] It is seen from this figure that as for the system of CuZSM-5−CO, an excellent linear relationship, but with an opposite slope, is established for the copper-ion-exchanged zeolites−N_2 system. In our previous study,[47] we concluded that the bonding between the Cu$^+$ species and CO molecule is σ-binding in nature. As contrasted with this, in the present copper-ion-exchanged zeolites−N_2 system the circumstance seems to be different. Here, it should be noted that ν_{CO} is shifted to the higher frequency in the CuZSM-5−CO system compared with a fundamental vibration of gaseous CO molecule and that in the copper-ion-exchanged zeolites−N_2 system ν_{N2} is shifted to the lower frequency compared with that of gaseous N_2 molecule. This arises from the difference in the nature of bonding of adsorbed molecules; the highest occupied orbital of N≡N is the 5σ orbital having a bonding

Figure 13. Relationship between the differential heat of adsorption (q_{diff}) and the wavenumber of stretching vibration ($\nu_{N\equiv N}$ or $\nu_{C\equiv O}$) in the adsorbed species for various systems: (▲) copper-ion-exchanged zeolites (CuZSM-5-141, CuM-149, and CuY-146)-N_2; (●) CuZSM-5-141−CO; (■) NaZSM-5−CO.

nature, whereas that of C≡O is also a 5σ orbital but it has a slightly antibonding nature.[48] First, the discussion will be confined to the CO system. As a result of the electron transfer from the 5σ orbital of CO to the metal ion, the C≡O bond is strengthened compared with that in an isolated molecule. Therefore, the vibrational frequencies of CO forming such a bonding should be higher than that of gaseous CO, indicating a strengthened C≡O bonding. On the other hand, the increase in electron density of the metal ion through the 5σ donation may cause a π back-donation from the d_π orbital of the metal ion to the π-antibonding orbital of CO, resulting in a decrease of bond strength of C≡O. Moreover, the extent of shift of the vibrational frequencies should be proportional to the change in the C≡O bond order, as reported by several groups.[34,45,49] From the linear relationship between the extent of shift of ν_{CO} and the values of q_{diff} corresponding to the M−C bond order observed for the CuZSM-5−CO system, we concluded that the σ-bonding nature is operative in this system.[47] For the system of copper-ion-exchanged zeolites−N_2, the σ-donation from N≡N to the Cu ion weakens the N≡N bond, giving an absorption band at a frequency lower than 2331 cm^{-1} for the free N_2 molecule because of the bonding nature of the 5σ orbital of this molecule. The contribution of π-bonding results in a further decrease in the bonding nature of N_2, that is, additional decrease in the frequency compared with the case that only the σ-bonding is operative. In both cases of N_2 and CO adsorption, the increase of σ-donating character of the molecules induces an increase in the adsorption energy, resulting in an increase of the frequency of C−O stretching vibration or in a decrease of N≡N stretching vibration. Furthermore, the contribution of π back-donation leads to a release of additional energy. If both σ-donation and π back-donation operated, the shifts of ν_{N2} to the lower frequency would be larger compared with the case of σ-donation alone, whereas ν_{CO} would shift to the higher frequency by σ-donation and to the lower one by π back-donation. For the N_2 molecule the shape of the lowest unoccupied molecular orbital (2π*) is symmetrical and its energy level is higher by ca. 3.9 eV than its zero energy level. On the other hand, for the CO molecule the shape of the orbital of the LUMO level is asymmetrical and displaces its lobe toward the C atom, its energy level being higher than the zero energy level by 3.5 eV.[50] Therefore, it is more difficult for the N_2 molecule to accept an electron from the coordinated metal ion (back-donation) than for the CO molecule. Even in the CuZSM-5−CO system, where the acceptance of an electron from the

π-bonding is easy, the π contribution is excluded. Moreover, the system in which the π-bonding is operative gives a band at much lower frequency than the gas molecule in the system such as copper metal−CO does. From these considerations it should be concluded that the σ-bonding plays an important role even in the bonding between the copper ion in zeolite and N_2 molecule, and hence, the contribution of π-bonding is excluded. It is important to keep in mind that the π character should be given to the N≡N bond through the back-donation from a metal ion to accomplish the breaking of the bonding between the nitrogen atoms in N_2 molecule. Although the adsorption energy is much larger compared with the data obtained so far,[51−55] it would be difficult to break the N≡N bonding at this stage as understood from the above discussion. However, the specific adsorption of N_2 molecules in the present system can be utilized to analyze the active sites for various reactions such as NO$_x$ decomposition.

Active Sites in NO$_x$ Decomposition Reaction. Finally, we will briefly describe the relation between the active sites for N_2 adsorption and those in NO$_x$ decomposition reaction. Our experimental results using CO and N_2 as probe molecules give the types and quantities of each adsorption site, indicating the variation of the types and amount of exchangeable sites with ion exchange capacity as shown in Figures 5 and 6b. Such data are expected to provide significant information on the active sites regarding the NO$_x$ decompositon reaction. Iwamoto et al.[5] reported that the NO decomposition activity has an S-shaped dependence on the ion-exchange level; the activity is retarded in the lower exchange levels and gradually increases with increasing exchange level. Taking their data into consideration, our present data lead to two possibilities concerning the reaction sites. (1) ZSM-5 zeolite has two or more types of cation-exchangeable sites; one is most readily exchanged with a copper ion and is inactive for the decomposition of NO, and the other sites are active for that reaction, though these are exchanged efficiently above the ion exchange level of 80%. (2) The decomposition of NO proceeds only under cooperation of two adjacent active sites that cannot be formed at low ion-exchange level. However, additional information is limited at the present stage to answer which possibility is reasonable.

Conclusion

In this study, we have investigated the adsorption properties of CuZSM-5 for N_2 and CO molecules by IR and emission spectroscopies. Both data of adsorption and IR indicate the strong interaction between N_2 molecules and copper ions exchanged in ZSM-5: the initial heat value is about 75 kJ mol^{-1} and the intense band appears at 2295 cm^{-1} due to the adsorbed N_2 species. IR data give information on the state of the copper ion as active sites for N_2 adsorption. There are at least three types of adsorption sites, giving the IR bands due to the adsorbed CO species at 2159, 2151, and 2135 cm^{-1}. In ES, three bands appear at 20800, 19600, and 18500 cm^{-1} due to the monovalent copper-ion species, and these bands decrease in intensity with increasing pressure of N_2. Combining IR and ES data, we have assigned that the sites responsible for the ES bands at 20800, 19600, and 18500 cm^{-1} correspond to those giving IR bands at 2159, 2135, and 2151 cm^{-1} due to the adsorbed CO species, respectively. On the basis of these considerations, we tentatively regarded the site responsible for the 2151 cm^{-1} and 18500 cm^{-1} bands as an effective site for N_2 adsorption. By reference to the results of XAFS measurements, it is thought that the active site, i.e., Cu$^+$ species, for N_2 adsorption, interacts with the three lattice oxygen atoms and with CO or N_2 molecules

to form a pseudotetrahedral four-coordination structure. It is also clarified that the bonding between Cu^+ and N_2 or CO molecule is predominantly of a σ-type nature. From these viewpoints one could say that the adsorption activity for N_2 molecules is closely dependent on the reducibility of Cu^{2+} located in the zeolite framework and that the N_2 adsorption occurs predominantly on one type of the exchangeable sites. This new finding, namely, the specific properties for N_2 adsorption, will give this kind of zeolite a potential to be utilized for the separation and fixation of N_2 as well as for the analysis of the active sites in NO_x decomposition reaction.

References and Notes

(1) Kuroda, Y.; Konno, S.; Morimoto, K.; Yoshikawa, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 18.

(2) Kuroda, Y.; Yoshikawa, Y.; Konno, S.; Hamano, H.; Maeda, H.; Kumashiro, R.; Nagao, M. *J. Phys. Chem.* **1995**, *99*, 10621.

(3) Spoto, G.; Bordiga, S.; Ricchiardi, G.; Scarano, D.; Zecchina, A.; Geobaldo, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3285.

(4) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.; Kagawa, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1272.

(5) Iwamoto, M.; Yahiro, H.; Mizuno, N.; Zhang, W.-X.; Mine, Y.; Furukawa, H.; Kagawa, S. *J. Phys. Chem.* **1992**, *96*, 9360.

(6) Vayon, J.; Hall, W. K. *J. Phys. Chem.* **1993**, *97*, 1204.

(7) Nishi, Y.; Suzuki, T.; Kaneko, K. *J. Phys. Chem. B* **1997**, *101*, 1938.

(8) Schelef, M. *Catal. Lett.* **1992**, *15*, 305.

(9) Liu, D.-J.; Robata, H. J. *Catal. Lett.* **1993**, *21*, 291.

(10) Kucherov, A. V.; Gerlock, J. L.; Jen, H.-W.; Schelef, M. *J. Phys. Chem.* **1994**, *98*, 4892.

(11) Liu, D.-J.; Robata, H. *J. Appl. Catal. B* **1994**, *4*, 155.

(12) Shpiro, E. S.; Grunert, W.; Joyner, R. W.; Baeva, G. N. *Catal. Lett.* **1994**, *24*, 159.

(13) Grünert, W.; Hayes, N. W.; Joyner, R. W.; Shpiro, E. S.; Siddiqui, M. R. H.; Baeva, G. N. *J. Phys. Chem.* **1994**, *98*, 10832.

(14) Larssen, S. C.; Aylor, A.; Bell, A. T.; Reimer, J. A. *J. Phys. Chem.* **1994**, *98*, 11533.

(15) Wichterlová, B.; Dedecek, J.; Vondrová, A. *J. Phys. Chem.* **1995**, *99*, 1065.

(16) Schelef, M. *Chem. Rev.* **1995**, *95*, 209.

(17) Lei, G. D.; Adelman, B. J.; Sárkány, J.; Sachtler, W. M. H. *Appl. Catal. B* **1995**, *5*, 245.

(18) Dedecek, J.; Sobalik, Z.; Tvaruzkova, T.; Kaucky, D.; Wichterlová, B. *J. Phys. Chem.* **1995**, *99*, 16327.

(19) Beutel, T.; Sárkány, J.; Lei, G.-D.; Yan, J. Y.; Sachtler, W. M. H. *J. Phys. Chem.* **1996**, *100*, 845.

(20) Schneider, W. F.; Hass, K. C.; Ramprasad, R.; Adams, J. B. *J. Phys. Chem.* **1996**, *100*, 6032.

(21) Hass, K. C.; Schneider, W. F. *J. Phys. Chem.* **1996**, *100*, 9292.

(22) Trout, B. L.; Chakraborty, A. K.; Bell, A. T. *J. Phys. Chem.* **1996**, *100*, 17582.

(23) Jacomo, M. L.; Fierro, G.; Dragone, R.; Feng, X.; d'Itri, J.; Hall, W. K. *J. Phys. Chem. B* **1997**, *101*, 1979.

(24) Matsuda, T.; Ueno, N.; Nagao, M. *Netsusokutei* **1992**, *19*, 57.

(25) Matsuda, T.; Taguchi, H.; Nagao, M. *J. Thermal Anal.* **1992**, *38*, 1835.

(26) In general the monolayer capacity is obtained by applying the Langmuir equation to the adsorption isotherm. In the case of the CuZSM-5-36$-N_2$ system, however, the isotherm measured does not obey this equation. To avoid this disadvantage, we use the method described.

(27) Borgard, G. D.; Molvik, S.; Balaraman, P.; Root, T. W.; Dumesic, J. A. *Langmuir* **1995**, *11*, 2065.

(28) Howard, J.; Nicol, J. M. *Zeolites* **1988**, *8*, 142.

(29) Sárkány, J.; Sachtler, W. M. H. *Zeolites* **1994**, *14*, 7.

(30) Spoto, G.; Zecchina, A.; Bordiga, S.; Ricchiardi, G.; Martara, G.; Leofanti, G.; Petrini, G. *Appl. Catal. B* **1994**, *3*, 151.

(31) Miessner, H.; Landmesser, H.; Jaeger, N.; Richter, K. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2035.

(32) Yamashita, H.; Matsuoka, M.; Tsuji, K.; Shioya, Y.; Anpo, M.; Che, M. *J. Phys. Chem.* **1996**, *100*, 397.

(33) Jang, H.-J.; Hall, W. K.; d'Itri, J. L. *J. Phys. Chem.* **1996**, *100*, 9416.

(34) Iwamoto, M.; Hoshino, Y. *Inorg. Chem.* **1996**, *35*, 6918.

(35) Lamberti, C.; Bordiga, S.; Savalaggio, M.; Spoto, G.; Zecchina, A.; Geobaldo, F.; Vlaic, G.; Bellatreccia, M. *J. Phys. Chem. B* **1997**, *101*, 344.

(36) Dedecek, J.; Wichterlová, B. *J. Phys. Chem. B* **1997**, *101*, 10233.

(37) Barrie, J. D.; Dunn, B.; Hollingsworth, G.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 3958.

(38) Anpo, M.; Matsuoka, M.; Shioya, Y.; Yamashita, H.; Giamello, E.; Morterra, C.; Che, M.; Patterson, H. H.; Webber, S.; Oullette, S.; Fox, M. A. *J. Phys. Chem.* **1994**, *98*, 5744.

(39) Strome, D. H.; Klier, K. *J. Phys. Chem.* **1980**, *84*, 981.

(40) Kumashiro, R.; Kuroda, Y.; Nagao, M. *J. Phys. Chem. B* **1999**, *103*, 89.

(41) Kuroda, Y.; Maeda, H.; Moriwaki, H.; Bamba, N.; Morimoto, T. *Physica B* **1989**, *158*, 185.

(42) Kuroda, Y.; Kotani, A.; Maeda, H.; Moriwaki, H.; Morimoto, T.; Nagao, M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1583.

(43) Hamada, H.; Matsubayashi, N.; Shimada, H.; Kintaichi, Y.; Ito, T.; Nishijima, A. *Catal. Lett.* **1990**, *5*, 189.

(44) Brand, H. V.; Redonodo, A.; Hay, P. J. *J. Phys. Chem. B* **1997**, *101*, 7691.

(45) Willer, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402.

(46) Scarano, D.; Bordiga, S.; Lamberti, C.; Spoto, G.; Ricchiardi, G.; Zecchina, A.; Areán, C. O. *Surf. Sci.* **1998**, *411*, 272.

(47) Kuroda, Y.; Yoshikawa, Y.; Kumashiro, R.; Nagao, M. *J. Phys. Chem. B* **1997**, *101*, 6497.

(48) Horn, K. *Surf. Sci.* **1982**, *118*, 465.

(49) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.

(50) Jorgennsen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973.

(51) Chang, C. C.; Kokes, R. J. *J. Phys. Chem.* **1973**, *77*, 2640.

(52) Sakata, Y.; Kinoshita, N.; Domen, K.; Onishi, T. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2765.

(53) Hardeveld, R. V.; Montfoort, A. V. *Surf. Sci.* **1966**, *4*, 396.

(54) Wang, H. P.; Yates, J. T., Jr. *J. Phys. Chem.* **1984**, *88*, 852.

(55) Stradella, L. *React. Kinet. Catal. Lett.* **1985**, *28*, 307.