Characterization of Active Sites on Copper Ion-Exchanged Mordenite for Dinitrogen Adsorption by Using CO as a Probe Molecule

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The peculiar feature of copper ion-exchanged mordenite in dinitrogen (N_2) adsorption has been investigated through the measurements of infrared (IR) and emission spectra (ES) and X-ray absorption fine structure (XAFS). IR spectra provided the definitive evidence for the existence of at least two kinds of adsorption sites on the 873 K-treated copper ion-exchanged mordenite; the absorption bands centered at 2160 and 2150 cm^{-1} appeared when CO molecules were adsorbed. The adsorbed species assigned to the former band was desorbed at 573 K *in vacuo* and that to the latter one at 473 K. It was found that the site responsible for the latter band acts as effective sites for N_2 adsorption. XAFS spectra also showed new bands due to the CO adsorption on copper ion at 1.48 Å, 2.52 Å, and 8.981 keV, together with bands at 1.85 Å and 8.993 keV. The former set of bands was concomitant with the appearance of an IR band at 2150 cm^{-1} due to the adsorbed CO species. The two bands (at 8.981 and 8.993 keV) observed in the XAFS spectra for the CO-adsorbed sample are explained in terms of the formation of a planar three- or four-coordinate site through the reaction of copper ions with CO molecules. CO adsorption also caused a significant shift of the emission band from 470 to 430 nm. This band reverted to the original position by evacuating the sample at 473 K, accompanying a liberation of CO. This makes possible the interpretation that the adsorption site responsible for respective bands at 2150 cm^{-1} in IR, at 430 nm in ES, and at 8.981 keV in XAFS spectra through the interaction with CO molecules is effective for N_2 adsorption at ambient temperature.

Introduction

Recently, it has been found that copper ion-exchanged zeolite has a unique activity against N_2 adsorption at room temperature.[1−3] This phenomenon is very interesting and is said to be specific for copper ion-exchanged zeolite, because it is well-known that N_2 gas is adsorbed on the solid surface only under the conditions of lower temperature[4−6] and/or higher pressure.[7] Accordingly, copper ion-exchanged zeolite could become a new candidate for N_2-separation, -fixation, and -activation catalysts.[8−11] In the preceding paper,[2] we reported that the N_2 species adsorbed on the copper ion-exchanged mordenite gives an IR band at 2299 cm^{-1} and a heat of adsorption of 60 kJ mol^{-1}. X-ray absorption near edge structure (XANES) and emission spectra for the 873 K-treated copper ion-exchanged mordenite sample gave the bands attributable to Cu^+ species.[2] Taking account of these results, we have concluded that Cu(I) formed in the evacuation process plays an important role in the N_2 adsorption. However, little is known on the structure and electronic state of effective sites for N_2 adsorption. On the other hand, it is well-known that copper ion-exchanged zeolite is a useful catalyst for NO_x decomposition reaction.[12−14] From these points of view, it is required by all means and urgently to obtain more detailed information on the state of copper ion exchanged in the zeolite in more detail.

The purpose of the present work is to get more detailed information on the structural and electronic features of the active site for N_2 adsorption of copper ion-exchanged mordenite using CO molecule as a probe,[15] and this study underlines the fact that the CO species allows drawing any distinction between N_2-adsorption sites existing in the copper ion-exchanged mordenite.

Experimental Section

Copper ion-exchanged mordenite was prepared by the conventional ion-exchanging method[2,16] from a sodium form of mordenite-type zeolite (Si/Al ratio of 10), which was furnished by Tosoh Co. Hereafter the copper ion-exchanged mordenite sample is designated CuM-*X*, where *X* denotes the percentage of exchange. Pure CO gas was supplied by GL Sciences Ltd., and the N_2 gas was prepared by evaporation of liquid N_2.

The adsorption isotherm was measured by using a conventional volumetric apparatus for the sample pretreated at 873 K *in vacuo.*

The IR spectra were measured at 4 cm^{-1} resolution on a Mattson FTIR 3020 spectrophotometer equipped with a TGS detector. The IR cell was made of quartz and equipped with KRS-5 windows, which can treat the sample from room temperature to 1000 K *in situ.* The zeolite samples were in the form of self-supporting wafers, and the spectra were recorded by transmission mode after exposing the pretreated sample to CO and N_2 gases.

The emission spectra of the samples were measured at around 300 K with a Hitachi F-2000 fluorescence emission spectrophotometer. The exciting light (300 nm) was focused on the sample cell, and the emission was observed at a right angle to the incident beam. Every measurement was carried out *in situ* and at room temperature after evacuating the sample at 873 K and treating it with CO gas of various pressures.

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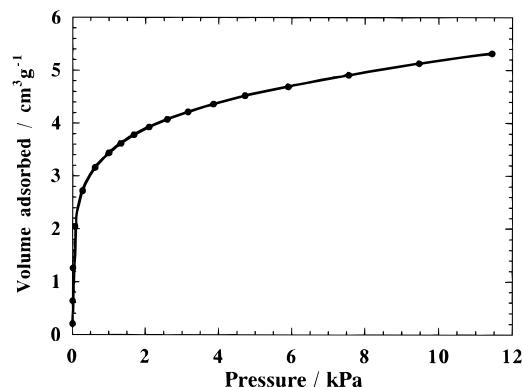*J. Phys. Chem. B, Vol. 101, No. 8, 1997* **1313**

Figure 1. Adsorption isotherm at 298 K of dinitrogen on copper ion-exchanged mordenite pretreated at 873 K.

The spectra of extended X-ray absorption fine structure (EXAFS) and of X-ray absorption near edge structure (XANES) were obtained under a ring-operating condition of 2.5 GeV and using beam line BL-10B in the Photon Factory at the National Laboratory of High Energy Physics (KEK) in Tsukuba. The photon energy was calibrated by a characteristic pre-edge peak in the spectrum for copper foil as 8.9788 keV. All the measurements were carried out *in situ*.

Results and Discussion

Figure 1 shows the adsorption isotherm of N₂ on CuM-150 evacuated at 873 K. This isotherm is of Langmuir type, suggesting the presence of strong interaction between the CuM-150 sample and the N₂ molecule. The adsorbed amount corresponding to the formation of the monolayer is *ca.* 0.29 for the N₂/Cu ratio.

Since the characteristic carbonyl frequency shifts depending on the copper oxidation state and its coordination environment,[17] the CO molecule was used here as a selective probe molecule in order to obtain more detailed information on the state and chemical properties of the copper center. The IR spectra in the 2000−2400 cm⁻¹ region for CuM-150 samples pretreated under various conditions are shown in Figure 2. There are no peaks in this region for the sample evacuated at 873 K (spectrum a). At the first stage of CO adsorption (at an equilibrium pressure of nearly zero), a new band is observed at 2160 cm⁻¹, which is obviously due to the CO species adsorbed on Cu(I) (spectrum b). The fact that this specific band is single and rather sharp strongly suggests that only one type of copper ion site in zeolite is responsible for CO adsorption at an initial stage. After evacuation of the sample at 300 K, the band scarcely changes in intensity, and hence the adsorbed CO species is the chemisorbed one. Further addition of CO gas (*P* = 26.6 Pa) causes an increase in the band intensity, predominantly in the lower wavenumber region (spectrum c). The fact that the difference spectrum obtained by subtracting spectrum b from c gave a new band at 2153 cm⁻¹ indicates the presence of other adsorption sites for CO molecules. As the CO pressure is increased to 240 Pa, two new bands related to CO molecules interacting with copper species appear at 2112 and 2177 cm⁻¹ (spectrum d), and this spectral pattern is little affected by further CO addition (spectrum e). The former band can be attributed to the Cu(0)−CO species[18,19] and the latter one, which is present at a relatively high CO pressure, either to the CO species adsorbed weakly on the Lewis acid site of the zeolite[20,21] or to the symmetric stretching vibration between the two coupled CO oscillators.[22,23] The correct assignment of the latter band is still unsettled, although it may not be the main subject in this study.

Zecchina et al.[24] reported that the CO stretching frequency (ν₍CO₎) for alkali metal ions exchanged in zeolites depends linearly
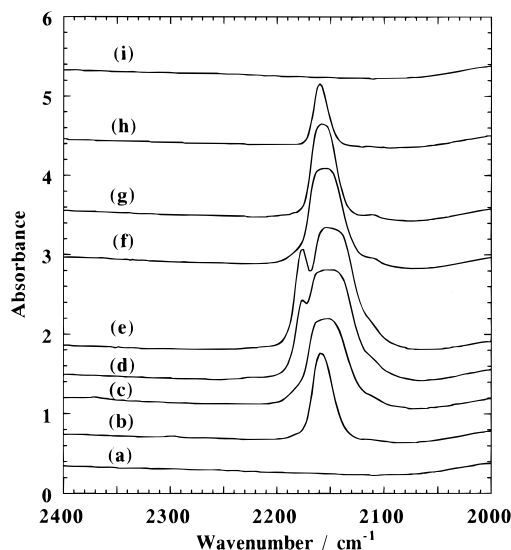

Figure 2. Infrared spectra for CuM-150 that was pretreated in the following manner: (a) evacuated at 873 K; (b) equilibrated with CO gas at 300 K under nearly zero pressure after procedure a; (c) successively equilibrated with CO under a pressure of 26.6 Pa; (d) 240 Pa; (e) 6.20 kPa; followed by reevacuation at (f) 300 K; (g) 373 K; (h) 473 K; and (i) 573 K. Spectra b-i are shifted to the direction of the ordinate with respect to spectrum a, for clarity.

upon the term $1/(R_X + R_{CO})^2$, where R_X and R_{CO} are the radii of metal ions and CO molecule (taken as 0.21 nm), respectively, and they regarded this finding as definitive evidence for a significant contribution of the electrostatic force between the metal ion and the CO molecule. However, such a relationship is not satisfied for the present system containing Cu(I) species even by using the value reported by Shannon,[25] which suggests a contribution of covalent-bond nature between the Cu ion and CO molecule. Therefore, the nature of this bond is considered in terms of the σ and π bonding models; the formation of bonding between CO and copper ion exchanged in mordenite consists of a donation of the CO 5σ-electron pair to the hybrid d−s orbitals of the copper ions (σ-bonding) or an electron transfer from the occupied d orbitals to the corresponding symmetry of the CO 2π antibonding orbitals, namely, a back-donation.[26] The actual system appears to be due to the combination of these opposite effects on the band shift in IR spectra. When CO molecules are adsorbed on the highly charged ions, they are held mainly by the formation of σ-bonding, which leads to a stabilization of the bond between C and O, i.e., 5σ orbital being of weak antibonding character.[27,28] In such a case, the CO stretching frequency may shift to the higher frequency relative to that for the free gas molecule (2143 cm⁻¹). On the other hand, π-bonding, which increases the electron density on the antibonding orbitals of CO, brings about a low-frequency shift of ν₍CO₎ relative to that for the free gas molecule. The stretching vibration frequencies for the CO species on the copper ion in zeolite will depend upon the electronic state of the adsorption site. Therefore, the appearance of two absorption bands (at 2160 and 2150 cm⁻¹) indicates the presence of at least two kinds of adsorption sites for CO molecules differing in the extent of σ-donation and π-back-donation. The spectrum for the sample that was evacuated at 300 K after equilibration with CO gas of 6.20 kPa (spectrum f in Figure 2) gave a spectral pattern similar to that for the sample treated with CO gas of 26.6 Pa. The intensity of this broad band at around 2155 cm⁻¹ decreases with increasing pretreatment temperature of the sample. Evacuation at 373 K brings about a decrease in the absorption intensity in the lower energy side. By the evacuation at 473 K the relative intensity of the
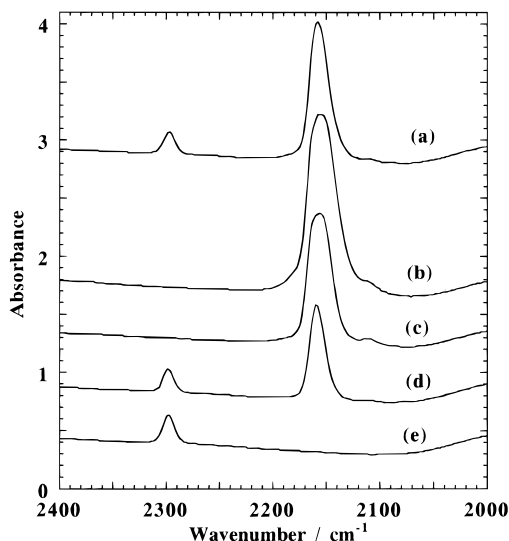
Figure 3. Infrared spectra for the CuM-150 sample, which was treated under various conditions, measured in the presence of N_2 of 13.3 kPa and at 300 K. The sample was first pretreated at 873 K and then (a) reevacuated at 300 K after CO adsorption (equilibrated at a pressure of nearly zero); (b) reevacuated at 300 K after CO adsorption (equilibrium pressure of 26.6 Pa); followed by reevacuation at (c) 373 K; (d) 473 K; and (e) 573 K. Spectra a−d are shifted to the direction of the ordinate with respect to spectrum e, for clarity.
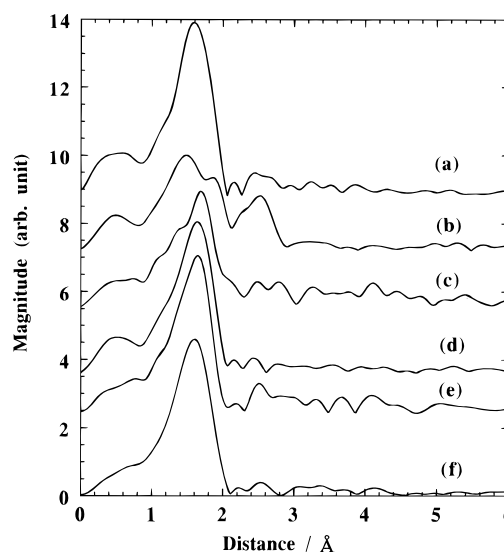

Figure 4. EXAFS spectra for the CuM-150 sample that was pretreated in the following manner: (a) evacuated at 873 K; (b) equilibrated with CO gas under a pressure of 13.3 kPa at 300 K after procedure a; successively reevacuated at (c) 300 K; (d) 373 K; (e) 473 K; and (f) 573 K. Spectra a-e are shifted to the direction of the ordinate with respect to spectrum f, for clarity.

2150 cm^{-1} band becomes far less than that of the 2160 cm^{-1} band. Finally, the 2160 cm^{-1} band disappears by the evacuation at 573 K. From these observations, the two kinds of adsorbed species remaining on the sample after evacuation at 300 K are better described as chemisorbed species, and the species that gives the band at 2150 cm^{-1} is easily desorbed by the heat treatment at 473 K.

The IR spectra for the samples on which N_2 gas was introduced were also recorded immediately after each stage of adsorption and desorption of CO, and they are shown in Figure 3. The CuM-150 sample that was treated with CO (equilibrated at the pressure of nearly zero) and subsequently evacuated at 300 K gives two absorption bands by contact with N_2 gas (after measurement of spectrum b in Figure 2): a new band at 2299 cm^{-1}, which is attributable to adsorbed N_2 species on Cu$^+$ in CuM-150, and a band at 2160 cm^{-1} due to the adsorbed CO species. These facts indicate the presence of a strong interaction between this CO-treated surface and the N_2 molecule. The adsorption of N_2 on the sample, which was reevacuated at 300 K after treating with CO gas at the pressure of 26.6 Pa, gives no absorption bands attributable to the adsorbed N_2 species. In other words, the adsorbed N_2 species was not detected on the sample treated with CO of higher pressure, on which both IR bands of 2160 and 2150 cm^{-1} were observed. The absorption band at 2299 cm^{-1} due to the adsorbed N_2 species is hardly discernible when the sample is evacuated at 373 K after the adsorption of CO of 26.6 Pa. This fact reveals that the effective sites for N_2 adsorption are not restored yet by the evacuation procedure at 373 K (spectrum c). The treatment of the sample at 473 K gives a significant increase in intensity of the band at 2299 cm^{-1}, concomitant with a decrease in the band intensity at around 2150 cm^{-1}, and further evacuation at 573 K causes a disappearance of the CO band and a slight increase in intensity of the band at 2299 cm^{-1}, compared with that for the 473 K-treated sample. From these facts it can be concluded that the site that gives the band at 2150 cm^{-1} due to the adsorbed CO species is the effective one for N_2 adsorption.

Figure 4 shows the EXAFS spectra for CuM-150 pretreated under various conditions. The first band observed at 1.59 Å

(no phase-shift correction) for sample (a) is attributed to a backscattering from the first nearest O atoms, and the resulting averaged coordination number and the Debye−Waller factor (σ^2) are estimated to be *ca.* 2.5 ($\Delta N = \pm 0.1$) and 0.008/Å^2, respectively, through the least-squares method by using Cu$_2$O as a reference substance. The analysis concerning the first nearest shell for sample (a) is performed by selecting the data in the region of 0.99−2.05 Å. These results obtained are almost the same as those reported in the preceding paper.[2] Loss of the second band observed in the region from 2.6 to 3.5 Å, which exists in the original sample evacuated at 300 K,[16] by evacuation at 873 K suggests that copper ion exchanged in the hydroxy-bridged form in mordenite collapses its form at higher temperatures to move from the original position to a more stable site and finally comes into the isolated state. The spectrum taken after exposure to CO gas shows new bands at 1.48, 1.85, and 2.52 Å. Taking account of the bond length of the CO molecule (1.13 Å),[26] these bands can be assigned to the backscatterings from C, O (lattice oxygen), and O atoms in the CO molecule, respectively. These data are well consistent with those for CuZSM-5 obtained by Yamashita et al.[29] The increase in bond length of Cu−O (lattice oxygen) from 1.59 to 1.85 Å reflects the movement of copper ion from the original position to the center of the zeolite pore. This effect may be referred to as a CO adsorption-assisted phenomenon. Evacuation at 300 K causes a decrease in intensities of the bands attributed to CO molecules, and the difference in band appearance from the 873 K-treated sample is hardly discernible except that the shoulder is observed at 1.42 Å and the band due to Cu−O (lattice oxygen) is observed at 1.69 Å. As the evacuation temperature increases, the intensity of the band at 1.42 Å due to the adsorbed CO molecule decreases, accompanying a change of the Cu−O (lattice oxygen) bond length from 1.69 to 1.60 Å; copper ion reverts to the original position.

Figure 5 shows the effect of the adsorbed CO molecules on the XANES spectra for copper ion in CuM-150. The spectrum for the 873 K-evacuated sample exhibits a distinct splitting of the 4p orbital. Both the strong band at 8.983 keV and the broad band at around 8.993 keV are ascribed to the 1s−4p transition, on the basis of the data collected by Solomon et al.[30] on the model complexes. The sharp and strong band at 8.983 keV is

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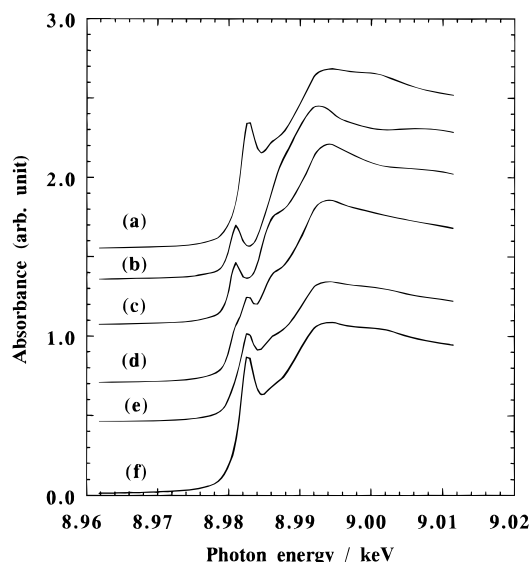*J. Phys. Chem. B, Vol. 101, No. 8, 1997* **1315**

Figure 5. XANES spectra for the CuM-150 sample that was pretreated in the following manner: (a) evacuated at 873 K; (b) equilibrated with CO under a pressure of 13.3 kPa at 300 K after procedure a; successively reevacuated at (c) 300 K; (d) 373 K; (e) 473 K; and (f) 573 K. Spectra a−e are shifted to the direction of the ordinate with respect to spectrum f, for clarity.

Figure 6. Emission spectra for the CuM-150 sample that was pretreated in the following manner: (a) evacuated at 873 K; (b) equilibrated with CO under a pressure of 13.3 kPa at 300 K after procedure a; successively reevacuated at (c) 300 K; (d) 373 K; (e) 473 K; and (f) 573 K. Spectra b−f are shifted to the direction of the ordinate with respect to spectrum a, for clarity.

characteristic of Cu(I) species, and the lack of 1s−3d transition (8.978 keV) also supports this interpretation.[31] With reference to the coordination structure around the copper ion, the solid Cu_2O sample has a linear configuration around the copper ion, which raises the $4p_z$ orbital energy owing to a repulsive interaction with the ligands. Therefore, the $1s-4p_{x,y}$ transition shifts to the lower energy side more than the $1s-4p_z$ transition does. Alternatively, in the case of the copper ion experiencing a tetrahedral ligand field, all the 4p orbitals experience the same repulsive interactions and are raised in energy, which results in the fact that there are no low-energy peaks (8.983 keV) and no splittings of the 4p level in the spectrum for the tetrahedral complex.[31] On the basis of these considerations, the sharp and intense band observed at 8.983 keV for the 873 K-treated CuM-150 sample is assigned to the $1s-4p_{x,y}$ transition and that at 8.993 keV to the $1s-4p_z$ transition. The appearance of both bands for the 873 K-treated CuM-150 sample indicates that the copper ion takes a configuration of linear or planar geometry but not a tetrahedral one. It should not be ignored that the band at 8.983 keV attributable to the $1s-4p_{x,y}$ transition is sharp and intense, compared with that for the Cu_2O sample, which has a linear configuration. Moen et al.[32] indicated that the intense nature of this band is ascribed to the lack of interaction between molecular ions. In the present case, it can be interpreted that the $Cu-(O)_n$ species exists in an isolated state in the mordenite pore. The same conclusion is derived from the EXAFS results, as described above. Figure 5 also shows the effect of the added CO molecules on the XANES spectra. It is obvious that the adsorbed CO species brings about a remarkable decrease in intensity of the band at 8.983 keV as well as an appearance of the new band at 8.981 keV. These facts may be due to a change in the ligand field around the copper ion: CO-induced migration of the copper ion from the original position. The behavior of the 8.983 keV band may reveal that the copper ion takes a tetrahedral arrangement through the interaction with CO molecules. This possibility, however, is ruled out by the existence of the band at 8.981 keV. It is reasonable to consider that the band at 8.981 keV is due to a transition to the 4p orbital in which its energy of 8.983 keV is lowered through the interaction with CO molecules. Taking account of the coordination number
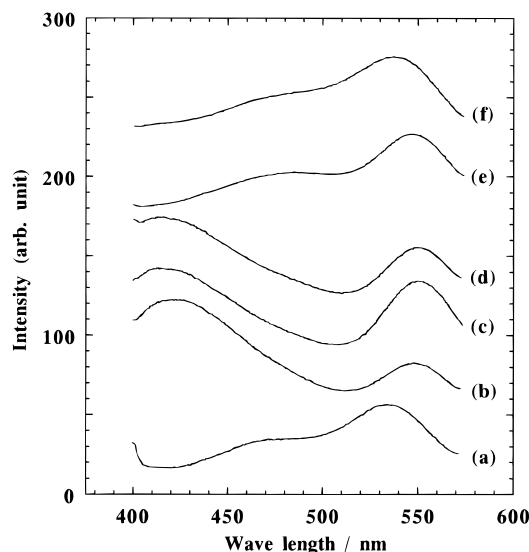
obtained from EXAFS data, the new band at 8.981 keV can be explained by assuming a trigonal or planar arrangement formed through the interaction between a two- or three-coordinated copper ion and the CO molecule. The slight decrease in intensity of the 8.981 keV band and the intensity increase in the 8.983 keV band are caused by evacuation of the sample at 300 K on which CO molecules were adsorbed. These tendencies are kept until the evacuation temperature reaches 473 K, and finally the same pattern as that for the original 873 K-treated sample is obtained by evacuation at 573 K. The band at 8.981 keV may be ascribed to the transition to the energy level caused by the interaction of Cu(I) species with the CO molecule; the change of energy from 8.983 to 8.981 keV is due to the change in coordination number and the elongation of the bond length between the copper ion and the lattice oxygen resulting from the CO-induced migration of the copper ion. Taking account of the fact that the sample that was treated with CO at 300 K and succeedingly evacuated at 473 K provides effective sites for N_2 adsorption, such a site that shows primarily the band at 8.983 keV and the consequent band at 8.981 keV through the interaction with CO gas acts as an active site for N_2 adsorption. Therefore, the N_2 species adsorbed on this site is expected to have the same configuration as in the case of CO adsorption. The effective N_2-adsorption site is such a site that accepts N_2 molecules in the planar four-coordinated or three-coordinated trigonal form but not in the tetrahedral one. This site is responsible for the band at 2150 cm^{-1} when the CO molecule is adsorbed on it.

The emission spectrum for the 873 K-evacuated sample exhibits bands at 470 and 530 nm, as shown in Figure 6. Both bands are ascribed to the transition from the $3d^9 4s^1$ level to the $3d^{10}$ level for the Cu$^+$ ion, indicating the formation of Cu$^+$ species in mordenite through the treatment of the sample at higher temperatures *in vacuo*.[33,34] This spectral pattern changes drastically when CO molecules are adsorbed on the sample; a new band appears at 430 nm, accompanied by a decrease in intensity of the luminescence at around 470 nm and by a shift of the band at 530 nm to 550 nm. Similar results were also reported for the copper ion-exchanged ZSM-5-type zeolite system.[29] The assignment of the bands at 430 and 550 nm is not well understood at present. However, the shift of these

bands due to the interaction with CO molecules can be explained in terms of the movement of copper ions caused by CO addition, as described by Strome and Klier[35] for the copper ion-exchanged Y-type zeolite system. This interpretation is not in conflict with the present EXAFS data indicating an increase in bond length (Cu−O) caused by CO adsorption, as is seen in Figure 4. The emission spectrum for the sample treated at 300 or 373 K after CO adsorption is not so different from that for the sample in equilibrium with CO gas of 13.3 kPa. The spectral pattern for the sample treated at 473 K *in vacuo* differs markedly from that for the sample treated under the conditions just described, and it is similar to that for the original one (873 K-treated sample) except that the higher wavelength band is slightly shifted from 530 to 540 nm; the 473 K-treated sample restores the original emission band at 470 nm. The band centered at 540 nm does not revert to the original position until the sample is evacuated at 573 K. Although CO molecules remain on the 473 K-treated sample and the adsorbed CO molecules give the IR band at 2160 cm^{-1}, these adsorbed CO molecules are not capable of affecting the specific adsorption of N_2 and the 473 K-treated sample gives a strong IR band attributable to the adsorbed N_2 molecule. Taking these facts into consideration, the site giving an emission band at 430 nm through the interaction with CO molecules, as well as the 2150 cm^{-1} band in IR and the 8.981 keV band in XANES spectra, can be an important one in N_2 adsorption. It can be tentatively said that this site has a planar three- or four-coordinated geometrical structure around the copper ions rather than a tetrahedral one through the interaction with CO or N_2 molecules.

Two types of pores exist in mordenite-type zeolite; the large straight channel running along the *c*-axis connects with the small one elongated in the *b*-axis.[36] In these channels, the presence of some ion-exchangeable sites has been revealed for calcium ion-exchanged mordenite by Mortier.[37] Taking account of the van der Waals radius of the CO molecule and the coordination environment of Cu(I) species formed by evacuation at 873 K, pores of much smaller channel size make the access of the CO molecule virtually impossible. In such a case, the active sites for CO adsorption might correspond to sites IV and VI in the large pore, as suggested by Geobaldo et al. for N_2 adsorption.[38] However, this assignment is not certain at the present stage. Anyhow, further investigation is needed to clarify the detailed state and the role of copper ion in zeolite for N_2 adsorption.

Conclusion

By the use of CO as a probe molecule, an investigation was undertaken to clarify the effective sites for N_2 adsorption on copper ion-exchanged mordenite. It has become apparent that there are at least two kinds of adsorption sites on copper ion-exchanged mordenite for CO molecules that are responsible for giving the IR bands at 2160 and 2150 cm^{-1}. It was also found that the adsorbed species giving the latter IR band acts as an active site for N_2 adsorption at room temperature. XANES, EXAFS, and emission spectra also support these new findings, in addition to providing information about the electronic and structural properties of this active site. The present results suggest that elaborate experiments using the CO molecule have the potential to elucidate the active and useful sites for N_2 adsorption as well as for NO_x decomposition reactions.

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