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Thermochimica Acta 416 (2004) 99–104

thermochimica acta

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Calorimetric study of N_2 adsorption on copper-ion-exchanged ZSM-5 zeolite

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Received 24 October 2002; accepted 27 December 2002

Abstract

Adsorption of nitrogen molecules (N_2) at room temperature on a copper-ion-exchanged ZSM-5 zeolite [CuZSM-5(A)] prepared by using an aqueous solution of $Cu(CH_3COO)_2$ was examined by measuring the heat of adsorption, IR and emission spectra. The results obtained were compared to those for the samples prepared by using other ion-exchanging solutions such as $CuCl_2$, $Cu(NO_3)_2$ and the solution containing $[Cu(NH_3)_2]^+$ complex ions. It became clear that the N_2 adsorption property of the copper-ion-exchanged ZSM-5 zeolites varies depending on the ligands (CH_3COO^-, Cl^-, $NO_3{}^-$ and NH_3) involved in the copper-ion exchanging solutions, and among these zeolite samples, CuZSM-5(A) has the most efficient adsorption property (i.e., strong adsorption) for N_2 molecules. The emission spectra revealed that there exist at least two types of Cu^+ species on the CuZSM-5(A) sample; the Cu^+ species that gives a band at 535 nm interact strongly with N_2 molecules, while those giving a band at 475 nm are inactive for N_2 adsorption. The heat of adsorption of N_2 on the former type of Cu^+ species was found to be 80 kJ mol^{-1}, being much larger than those observed for usual metal oxides.

Keywords: N_2 adsorption; Heat of adsorption; Emission spectra; Copper-ion exchange; ZSM-5 zeolite

1. Introduction

It is well known that the copper-ion-exchanged ZSM-5 zeolite (CuZSM-5) exhibits a high activity in the decomposition of NO_x into N_2 and O_2 [1–3]. In addition, this material has an interesting and specific property for N_2 adsorption; CuZSM-5 adsorbs N_2 molecules even at room temperature though N_2 molecules are inactive and ordinarily adsorbed on the solid surface at a low temperature of 77 K [4,5]. It has been proved that the monovalent copper-ion (Cu^+) species formed by the heat treatment in vacuo acts as an active center either in NO_x decomposition or in N_2 adsorption [5–7]. Therefore, the analysis of active sites responsible for strong N_2 adsorption on CuZSM-5 will be helpful in evaluating the catalytic activity in the decomposition reaction of NO_x and in developing the materials for separation, fixation and activation of N_2 molecules.

The heat of adsorption measurement is one of the useful techniques to examine the interaction of solid surface with gaseous molecules. We have so far reported that the N_2 adsorption on the CuZSM-5 sample prepared by the ion-exchange in an aqueous solution of $CuCl_2$ gives an initial heat of adsorption of 70 kJ mol^{-1} [5]. This value is considerably larger than those for other systems; for example, 11 kJ mol^{-1} for TiO_2–N_2 system [8], 19 kJ mol^{-1} for ZnO–N_2 system [9] and 37 kJ mol^{-1} for LiZSM-5–N_2 system [10]. Moreover, on the basis of the calorimetric and spectroscopic data, we have proposed that there are at least two types of exchangeable sites for the copper ions in ZSM-5 [5,7,11]. More recently, we have succeeded in preparing the CuZSM-5 sample through the ion-exchange in an aqueous solution of $Cu(CH_3COO)_2$, and it has been found that this sample exhibits more efficient adsorption of N_2 molecules, compared to the CuZSM-5 samples examined so far [12]. However, the effect of ion-exchange method on the N_2 adsorption is still not completely elucidated.

In the present study, we intended to examine the N_2 adsorption property of a newly prepared CuZSM-5 sample by

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doi:10.1016/j.tca.2002.12.001

measuring the heat of adsorption and adsorption isotherm of N_2 and CO, and IR and emission spectra. By comparing with the results obtained for other samples prepared by using different ion-exchanging solutions, the influence of the types of ligands in the exchanging solutions (i.e., CH_3COO^-, Cl^-, NO_3^- and NH_3) on the nature of sites occupied by the copper ions was also elucidated.

2. Experimental

A sodium-type ZSM-5 zeolite (NaZSM-5 having a Si/Al ratio of 11.9), which was kindly supplied by Tosoh Co., was used as a starting material. The CuZSM-5 samples were prepared by ion-exchanging in an aqueous solution of $Cu(CH_3COO)_2$, $CuCl_2$, or $Cu(NO_3)_2$. Approximately, 5 g of NaZSM-5 was dispersed in an aqueous solution of 0.01 M $Cu(CH_3COO)_2$ with stirring for 1 h at room temperature, and this process was repeated several times to obtain the CuZSM-5 sample. On the other hand, the ion-exchange by using an aqueous solution of 0.3 M $CuCl_2$ or $Cu(NO_3)_2$ was performed at 363 K. The CuZSM-5 samples that were ion-exchanged in an aqueous solution of $Cu(CH_3COO)_2$, $CuCl_2$, or $Cu(NO_3)_2$ are hereafter designated as CuZSM-5(A), CuZSM-5(C), or CuZSM-5(N), respectively. The ion-exchange level was determined by assuming that when two sodium ions in NaZSM-5 can be exchanged with one divalent copper ion the ion-exchange level is 100%. Therefore, if one sodium ion is exchanged with one divalent copper ion, which can be often possible in zeolite [5,11–17], ion-exchange level goes to 200% in maximum. The ion-exchange levels determined for the present samples are 143% for CuZSM-5(A), 147% for CuZSM-5(C) and 88% for CuZSM-5(N). In addition to these samples, we also prepared the CuZSM-5 sample by the direct introduction of monovalent copper ion using an aqueous solution containing $[Cu(NH_3)_2]^+$ complex ions (0.14 M), and the sample obtained is denoted as CuZSM-5(AM). The stability of zeolite framework was confirmed by X-ray diffraction patterns.

Measurements of the heat of adsorption and adsorption isotherm of N_2 or CO were carried out at 301 K using an adiabatic-type calorimeter equipped with a volumetric adsorption apparatus [18,19]. Prior to the measurement, the sample was treated at 873 K under a reduced pressure of 1 mPa for 4 h. The equilibrium pressure of gas phase was monitored with a MKS Baratron pressure sensor (type 310 BH).

IR spectra were recorded at room temperature using a Mattson 3020 FTIR spectrophotometer. The sample was pressed into a self-supporting disk and was placed in a quartz cell with KRS-5 windows that is capable of heat treatment and gas adsorption in situ. The sample was pretreated in the same manner as in the adsorption measurements.

Emission spectra were measured at room temperature by using a Hitachi F-2000 photoluminescence 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.

3. Results and discussion

The IR spectra of the CuZSM-5 samples in equilibrium with N_2 gas at 13.3 kPa are shown in Fig. 1. For all the CuZSM-5 samples, a single absorption band is observed at 2295 cm^{-1}, which can be assigned to a N≡N stretching vibration in the N_2 molecule adsorbed on the Cu^+ species that were formed during the evacuation of the ion-exchanged sample at an elevated temperature (873 K) [5]. Taking into consideration that the N_2 molecule is IR inactive because it has no dipole moment, the appearance of such an IR band indicates a strong interaction between the N_2 molecule and Cu^+ species. In addition, every band observed is symmetrical in shape, suggesting that a single type of adsorbed species is formed in every CuZSM-5 sample examined.

Fig. 2 shows the adsorption isotherms and the differential heats of adsorption of N_2 at 301 K for the NaZSM-5, CuZSM-5(A) and CuZSM-5(C) samples. For NaZSM-5, the adsorbed amount increases linearly with increasing equilibrium pressure; the isotherm is of Henry type, which indicates a weak interaction between NaZSM-5 and N_2 molecules. The heat of adsorption gives a constant value of about 35 kJ mol^{-1} in the whole range of coverage. As is different from the case of the NaZSM-5 sample, for the CuZSM-5(A) and CuZSM-5(C) samples the adsorbed

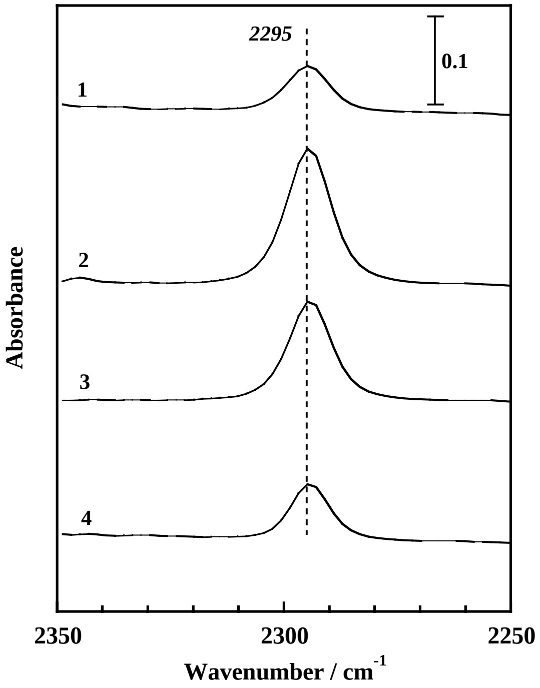

Fig. 1. IR spectra of N_2 species adsorbed on the CuZSM-5 samples: (1) CuZSM-5(C); (2) CuZSM-5(A); (3) CuZSM-5(N) and (4) CuZSM-5(AM).

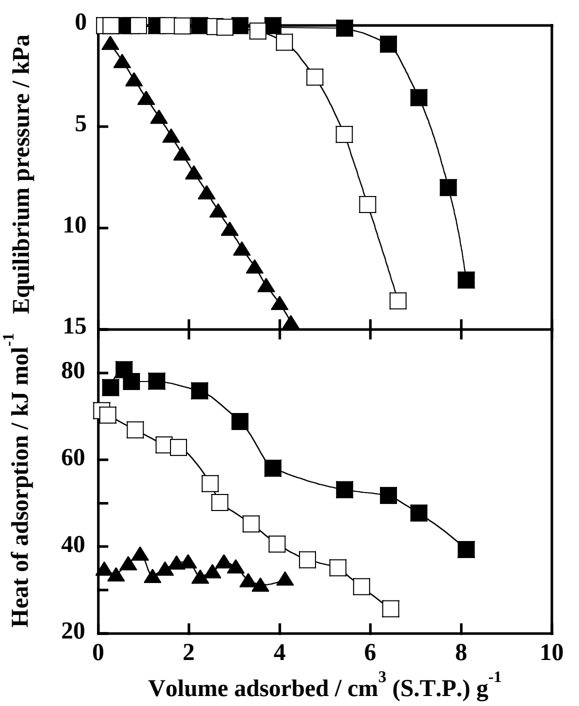

Fig. 2. Adsorption isotherms and differential heats of adsorption of N_2 at 301 K on the ZSM-5 samples: (▲) NaZSM-5; (■) CuZSM-5(A) and (□) CuZSM-5(C).

amount increases remarkably in the lower pressure region; the isotherms are of Langmuir type, indicating a strong interaction of these CuZSM-5 samples with N_2 molecules. The monolayer capacities estimated by applying the Langmuir equation to these isotherms are 7.9 and 6.5 cm^3 (STP) g^{-1} for the CuZSM-5(A) and CuZSM-5(C) samples, respectively. By taking into account of the quantity of copper ions exchanged in the ZSM-5 zeolite, we can evaluate an N_2/Cu^{n+} ratio: 0.43 for CuZSM-5(A) and 0.34 for CuZSM-5(C), which implies that the strong adsorption of N_2 molecules is more efficient on the former sample than on the latter one. On the other hand, the heats of adsorption at the initial adsorption stage are about 80 and 70 kJ mol^{-1} for the CuZSM-5(A) and CuZSM-5(C) samples, respectively, and they decrease with increasing coverage and reach the values of 40–30 kJ mol^{-1}. These higher heats of adsorption, compared with those for the NaZSM-5–N_2 system, substantiate the assignment that the active site for N_2 adsorption is a Cu^+ species formed in the ZSM-5 zeolite during the evacuation at high temperature. Moreover, it is apparent that the heats of adsorption are larger for the sample CuZSM-5(A) than for the CuZSM-5(C) sample in the whole range of coverage; in other words, the Cu^+ species in the former sample interact more strongly with N_2 molecules compared to those in the latter sample. It is interesting to note here that for the CuZSM-5(A) sample, two plateaus (approximately 80 and 50 kJ mol^{-1}) can be clearly observed in the differential heat of adsorption curve. The appearance of such a plateau in the heat of adsorption curve suggests that the energetically homogeneous adsorption sites exist on the CuZSM-5(A) sample. In contrast with this, on the CuZSM-5(C) sample there exist adsorption sites having different interaction energies with N_2 molecules.

The sample CuZSM-5(A) would be an advantageous material for investigating the state of active sites, and therefore, we tried to analyze the active sites for N_2 adsorption on this sample in more detail. We may direct our special attention to the plateau observed in the initial adsorption stage. The adsorption sites in the region where the heat of adsorption is 70 kJ mol^{-1} or above and the adsorbed amount attains to ca. 3.0 cm^3 (STP) g^{-1} are substantially active sites for N_2 adsorption. Particularly, the adsorption sites giving an adsorbed amount up to 2.0 cm^3 (STP) g^{-1}, which corresponds to a difference in the adsorbed amounts between CuZSM-5(A) and CuZSM-5(C), act more effectively and strongly in the N_2 adsorption.

The results for the CuZSM-5(N) and CuZSM-5(AM) samples are shown in Fig. 3. The heat of adsorption curve for the CuZSM-5(AM) sample is similar to that for the CuZSM-5(A) sample, which indicates that the sample prepared by the direct introduction of monovalent copper ions interacts strongly with N_2 molecules. The heat curve for the CuZSM-5(N) sample rather resembles that for the CuZSM-5(C) sample. It can be said from these results that for the copper-ion-exchanged CuZSM-5 samples the N_2 adsorption property, especially, with regard to a strong adsorption, varies depending on the ion-exchange method, namely, the ligand involved in the copper-ion-exchanging solution.

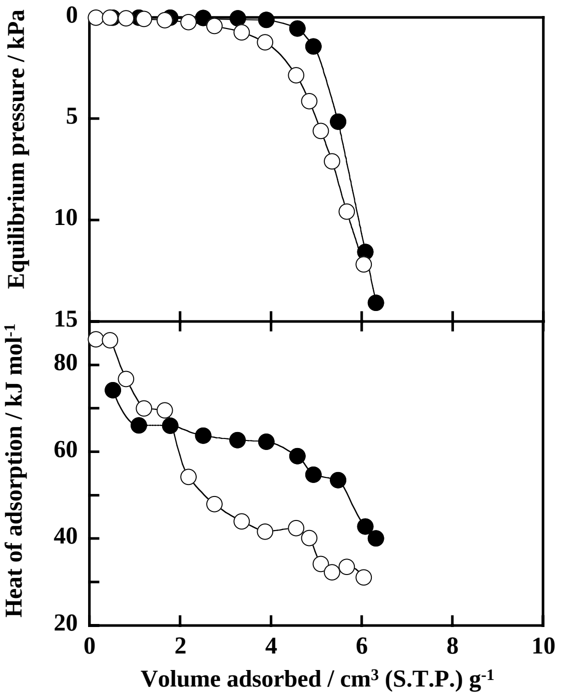

Fig. 3. Adsorption isotherms and differential heats of adsorption of N_2 at 301 K on the CuZSM-5 samples: (●) CuZSM-5(N) and (○) CuZSM-5(AM).

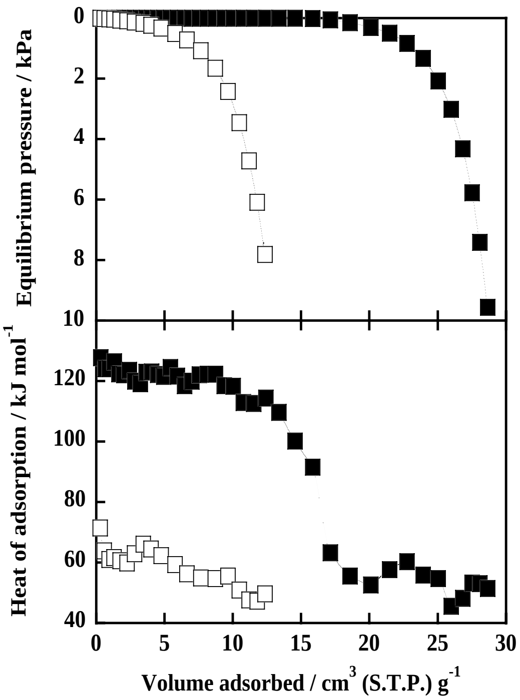

Fig. 4. Adsorption isotherms and differential heats of adsorption of CO at 301 K on the CuZSM-5(A) sample: (■) first adsorption and (□) second adsorption.

The state of Cu^+ species might be affected by the ligands through the heat treatment after copper-ion-exchanging, though the details of which remained unknown at present.

It is generally accepted that the CO molecule is useful as a probe molecule to get information on the state and the number of Cu^+ species in the CuZSM-5 sample since it can be adsorbed selectively on the Cu^+ species [20–22]. Fig. 4 shows the first and second adsorption isotherms and the differential heats of adsorption of CO at 301 K for the CuZSM-5(A) sample. The first adsorption isotherm was obtained for the sample evacuated at 873 K and the second one was for the sample re-evacuated at 301 K after the first adsorption run. As in the case of N_2 adsorption, these isotherms are of Langmuir type. Similar features were observed for other CuZSM-5 samples. The monolayer capacities were estimated to be 28.6 and 13.1 cm^3 (STP) g^{-1} for the first and second adsorption, respectively. The difference in the adsorbed amounts between the first adsorption and second adsorption is assumed to be a chemisorbed amount or the number of chemisorption sites. According to the same manner as done in the previous work [5], the value of CO/Cu^+ ratio can be evaluated from the amounts of chemisorbed CO and the number of exchanged copper ions: 0.57 for the CuZSM-5(A) sample. The values for other CuZSM-5 samples are summarized in Table 1.

In the first adsorption, the heat of adsorption is approximately 120 kJ mol^{-1} in the initial adsorption region (i.e., chemisorption region), and it decreases stepwise to about 110 kJ mol^{-1} and then decreases drastically to 55 kJ mol^{-1} with increasing coverage. The heat of adsorption curve for the second adsorption is similar to that for the latter half of the first adsorption, where the relatively lower heat values are observed. This fact indicates an occurrence of reversible adsorption (i.e., physisorption) in the second adsorption process. The appearance of two plateaus (120 and 110 kJ mol^{-1}) provides the evidence for the existence of at least two types of Cu^+ species that interact strongly with CO molecules. These plateaus correspond, respectively, to the adsorption regions of up to 8 cm^3 (STP) g^{-1} and from 8 to 13 cm^3 (STP) g^{-1}. The latter adsorption region, where the amount of adsorption is 5 cm^3 (STP) g^{-1}, can be correlated with a region where the strong N_2 adsorption takes place (Fig. 2). These results are consistent with our previous findings that the Cu^+ species, which interact strongly with CO molecules to give a heat of adsorption of 100 kJ mol^{-1}, act as active sites in the N_2 adsorption [5,11].

Table 1
Comparison of the values of CO/Cu^+ ratio

CuZSM-5(C)	0.51
CuZSM-5(A)	0.57
CuZSM-5(N)	0.46
CuZSM-5(AM)	1.00[a]

[a] This value is reference one because the sample was prepared by using monovalent copper ions.

The emission spectra of the CuZSM-5 samples evacuated at 873 K are shown in Fig. 5. The all spectra observed are due to the Cu^+ species. Moreover, these spectra can be separated into three components, that is, the bands centered at about 475, 500 and 535 nm, respectively, suggesting that the

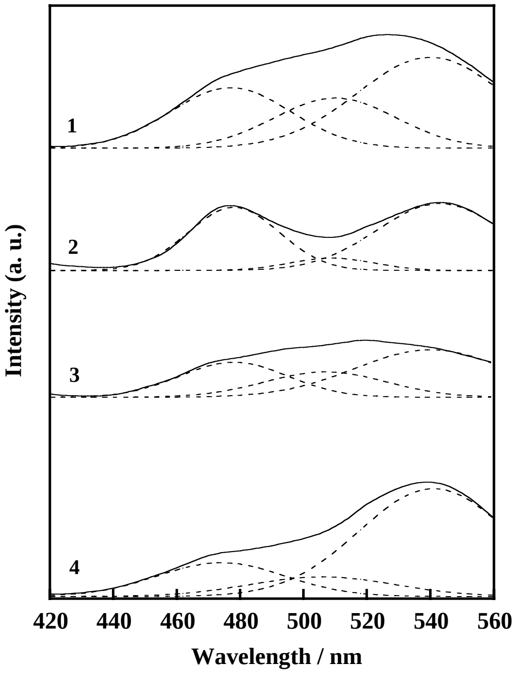

Fig. 5. Emission spectra of the CuZSM-5 samples: (1) CuZSM-5(C); (2) CuZSM-5(A); (3) CuZSM-5(N) and (4) CuZSM-5(AM).

Table 2
Comparison of the relative proportion (%) of each component band in the emission spectra

	CuZSM-5(C)	CuZSM-5(A)	CuZSM-5(N)	CuZSM-5(AM)
475 nm	27	38	27	18
500 nm	23	7	22	12
535 nm	50	55	51	70

Cu^+ species are in the different states. Here, the bands at 475 and 535 nm can be assigned to the emission of Cu^+ species existing on the two types of exchangeable sites in the ZSM-5 zeolite. It is reasonable to consider that these two types of Cu^+ species chemisorb CO molecules to give the heats of adsorption of about 120 and 110 kJ mol^{-1}. On the other hand, the band at 500 nm can be ascribed to the Cu^+ species deposited on the surface of silicious part of ZSM-5 [5]. We can compare the relative proportion of each component band by assuming a total amount of unity, and the results are given in Table 2. Although the amounts of Cu^+ species formed, which were estimated from the CO-adsorption experiment, are almost equal in all the CuZSM-5 samples (Table 1), the states of Cu^+ species are different depending on the ligands involved in the copper-ion-exchanging solutions. The effective sites (i.e., Cu^+ species) for N_2 adsorption were examined by the intensity change of emission spectra for the CuZSM-5(A) sample; the sample was first evacuated at 873 K, and then exposed to an N_2 gas of 5.5 kPa, followed by re-evacuation at room temperature (Fig. 6). The distinct band observed at 535 nm was reduced drastically in intensity when the sample was exposed to N_2 gas, and this band could be recovered by the succeeding re-evacuation at room temperature. No change was observed for the band at 475 nm by such treatments. These facts clearly indicate that the Cu^+ species giving the 535 nm band interact with N_2 molecules, while the Cu^+ species responsible for 475 nm band are inactive for N_2 adsorption.

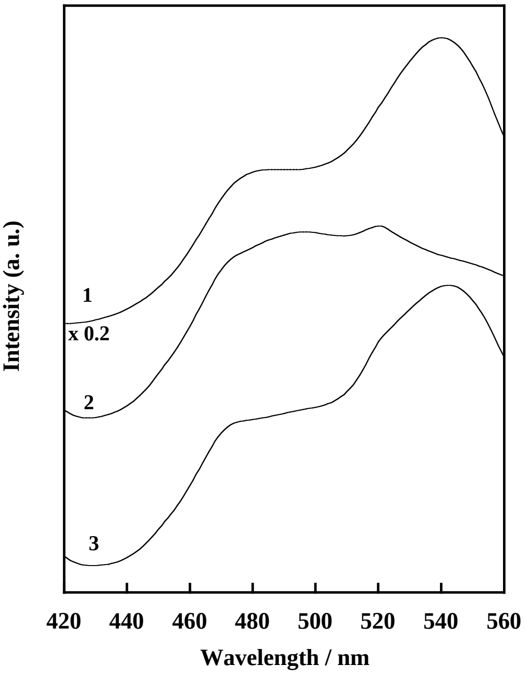

Fig. 6. Emission spectra of the CuZSM-5(A) sample under various conditions: (1) evacuated at 873 K; (2) followed by exposure to N_2 gas at 5.5 kPa; (3) re-evacuated at room temperature.

4. Conclusions

By the calorimetric and spectroscopic examination for the copper-ion-exchanged ZSM-5 zeolite (CuZSM-5)–N_2 or CO system, some new information on the adsorption property of CuZSM-5 was obtained. The N_2 adsorption property was found to vary depending on the ligands (e.g., CH_3COO^-, Cl^-, $NO_3{}^-$ and NH_3) involved in the copper-ion exchanging solutions. The CuZSM-5 sample prepared by using an aqueous solution of $Cu(CH_3COO)_2$ has the most efficient adsorption property for N_2 molecules. Furthermore, it was revealed that the Cu^+ species giving a band at 535 nm in the emission spectrum interact strongly with N_2 molecules, while the Cu^+ species responsible for the 475 nm band are inactive in the N_2 adsorption.

Acknowledgements

This work was supported partly by the Sasakawa Scientific Research Grant from the Japan Science Society. Atsushi Itadani gratefully acknowledges the generosity of this organization.

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