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Microwave-assisted simple ion-exchange of ZSM-5-type zeolites with copper ions and their specific adsorption properties for N_2 molecules at room temperature

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Copper ion-exchanged ZSM-5 samples, prepared using an easy method that takes advantage of microwaves, exhibit a quite peculiar adsorption feature for dinitrogen molecules, in that a large volume of chemisorbed N_2 was detected, even at room temperature, and the specificity of the adsorption properties was clarified by comparing with the properties of samples prepared by an ordinary ion-exchange method.

The catalytic decomposition of NO into N_2 and O_2 on a copper-ion-exchanged ZSM-5-type zeolite (CuZSM-5) is an attractive way to remove NOx from exhaust streams.[1–3] In addition, there has recently been an interesting independent observation by ourselves and by Zecchina's group that copper-ion-exchanged zeolites having a high Si/Al ratio, and acting as NOx-decomposition catalysts, can strongly adsorb N_2 molecules, even at room temperature.[4–7] This property will help us to understand the mechanism of the NOx-decomposition reaction by using dinitrogen as a probe molecule, because this molecule is produced in the direct decomposition of NOx. However, an analysis of the active sites for these phenomena encounters difficulties, because of the existence of some exchangeable sites in the zeolites. The properties of these materials change, depending on which sites are occupied by the copper ions, and to what extent these sites are occupied by copper ions. A clear and detailed understanding of the states of the exchanged copper ion enables us to design a CuZSM-5 sample with higher NOx decomposition and N_2 adsorption activities. The difference in NOx decomposition properties is supposed to arise from the different occupancies of the copper ions at the several sites that exist in the ZSM-5 zeolites, and these depend on the ion-exchange method used.[8–10] To clarify the state of the active site related to these phenomena, it is essential to examine the adsorption properties of samples prepared by different methods. In addition, the development of a simple preparative method is important for the use of these materials in their various catalytic applications.

In the present paper, we report on a new, simple ion-exchange method to prepare CuZSM-5 samples, and describe the prominent adsorption features of the dinitrogen molecule at room temperature on the CuZSM-5 samples prepared, by comparing the results with the adsorption properties of samples obtained by an ordinary ion-exchange method.

The ion-exchange procedure was performed as follows. Five grams of a sodium-ion-type ZSM-5 zeolite (NaZSM-5) from the Tosoh Co. having an Si/Al ratio of 11.9 was exchanged with 100 cm^3 of 0.3 M aqueous $Cu(NO_3)_2$ solution for 1.5 min utilizing microwave power. This procedure was repeated five times, using freshly prepared aqueous solution each time. Ordinary ion-exchange was carried out at 363 K using 0.3 M aqueous $CuCl_2$ solution, as described previously.[7,11] In the present case, we denote the samples by CuZSM-5(NM)-108 and CuZSM-5(C)-111, where N and C signify that nitrate and chloride counter ions were used, respectively, and where M denotes that microwaves were used as the heating method. The final numbers indicate the ion-exchange capacity in percent.

IR spectra were recorded on a Mattson 3020 FTIR spectrophotometer. X-Ray absorption spectra were recorded using beam line BL-10B at KEK in Tsukuba. Measurements of the CO and N_2 adsorption isotherms were carried out on samples that had been evacuated at 873 K under a reduced pressure of 1 mPa.

After the treatment of the original NaZSM-5 sample in an aqueous solution of $Cu(NO_3)_2$ utilizing microwave power, an ion-exchange capacity of 100% or more was easily attained. Langmuir-type N_2 adsorption isotherms were obtained at 298 K for both samples, and showed that these systems were able to strongly adsorb a considerable volume of N_2. The above phenomena are related to the existence of monovalent copper ions which selectively exchanged at a certain site. After the first adsorption measurement, the samples were re-evacuated at 298 K, and the second isotherms were measured. The volumes recorded for the second adsorption were substantially lower than those recorded for the first adsorption. The difference between these two isotherms indicates that the adsorbed N_2 species survives on the surface after evacuation at 298 K, indicating the existence of irreversibly adsorbed N_2 on the CuZSM-5 samples (chemisorption). Another specific feature observed in these isotherms was that a large difference exists in the case of the CuZSM-5(NM)-108–N_2 system. The first and second CO adsorption isotherms of both of these samples were also measured at 298 K. From the difference between the volumes of the first and second CO adsorption isotherms of the respective samples, we evaluated the chemisorbed volumes, which correspond to the number of monovalent copper ions on the respective CuZSM-5 samples.[12,13] Both N_2- and CO-adsorption data allowed us to estimate the effective monovalent copper ion concentration for N_2 adsorption, and this was especially so for the strong adsorption of N_2, which was not desorbed from the surface even after evacuation at 298 K. The values of the $Cu^{I}_{(N)}/Cu^{I}$ ratio were calculated for the respective samples, and these results are shown in Table 1. These results distinctly show that the sample prepared using microwaves shows excellent chemisorption for N_2 around 300 K.

Fig. 1 shows the IR spectra of both the CuZSM-5(NM)-108 and CuZSM-5(C)-111 samples which were evacuated at 873 K, followed by N_2-adsorption at 300 K under a pressure of *ca.* 60 Torr, and then successively re-evacuated at 300 and 373 K. The main feature is the appearance of a strong band at 2295 cm^{-1} after the adsorption of N_2, indicating the existence of a strong interaction between the monovalent copper ion and an N_2 molecule. The interesting and most pronounced feature is the appearance of a band at 2295 cm^{-1} on the CuZSM-5(NM)-108 sample, even after evacuation at 300 K, indicating the presence of a chemisorbed (or strongly adsorbed) N_2 species, which is consistent with the adsorption data. This band ultimately diminished after evacuation at 373 K, indicating that strong

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Table 1 Data obtained from adsorption isotherms and from the amounts of copper ion exchanged

	N_2/cm^3 g^{-1}			CO/cm^3 g^{-1}				
	V_{m1}	V_{m2}	V_{chem}	V_{m1}	V_{m2}	V_{chem}	Cu^I/Cu	Cu$^I_{(N)}$/Cu^I
CuZSM-5(NM)-108	7.40	5.74	1.66	15.76	9.84	5.92	0.41	0.28
CuZSM-5(C)-111	6.40	5.80	0.60	20.30	11.70	8.60	0.62	0.07

V_{m1}: monolayer capacity obtained from the first adsorption isotherm. V_{m2}: monolayer capacity obtained from the second adsorption isotherm. V_{chem}: chemisorbed amount ($= V_{m1} - V_{m2}$). Cu^I: amounts of the monovalent copper ion. Cu: total amounts of copper ion. Cu$^I_{(N)}$: amounts of active sites for the chemisorption of N_2.

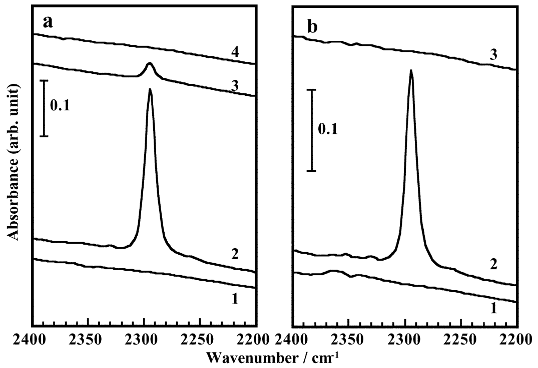

Fig. 1 IR spectra of (a) CuZSM-5(NM)-108 and (b) CuZSM-5(C)-111 at 300 K. (1) evacuated at 873 K; (2) N_2 adsorption at 300 K under a pressure of *ca.* 60 Torr; successively re-evacuated at (3) 300; (4) 373 K.

adsorption takes place on the CuZSM-5(NM)-108 sample. It is worth noting that the band for the chemisorbed species was scarcely observable for the CuZSM-5(C)-111 sample.

The copper X-ray absorption edge (XANES: X-ray absorption near edge structure) of samples measured after various treatments are shown in Fig. 2. A weaker pre-edge peak assigned to the dipole-forbidden 1s–3d transition for the CuZSM-5(NM)-108 sample is explained in terms of a slight existence of divalent copper species. The sharp and intense transitions observed at 8.983 and 8.995 keV in the spectra are from the 1s–4p electronic-allowed bands characteristic of the monovalent copper species.[14] The intensity of the 8.983 keV band was stronger for the CuZSM-5(C)-111 sample compared to that of the CuZSM-5(NM)-108 sample. This fact indicates that the degree of reduction of CuZSM-5(C)-111 is higher than that of the CuZSM-5(NM)-108 sample after evacuation at 873 K, and corresponds well with the data evaluated from the irreversible CO adsorption volumes. When N_2 is adsorbed on the CuZSM-5(NM)-108 sample, the intensity of the lower energy component band at 8.983 keV, decreases in its intensity markedly, indicating the existence of a strong interaction between Cu^+ and N_2. Another striking feature was also seen in the spectrum of the CuZSM-5(NM)-108 sample; the band intensity of the 1s–4p transition weakened even after re-evacuation at 300 K, and only recovered after heat treatment at 373 K. As for the CuZSM-5(C)-111 sample, the 8.983 keV band became slightly less intense with the introduction of N_2 gas at 300 K, and this band almost recovered its original intensity after evacuation at 300 K. The results of the spectral features of both samples are quite different. The decrease in intensity of the original split 8.983 keV band for the CuZSM-5(C)-111 sample was far less than that for the CuZSM-5(NM)-108 sample when N_2 was adsorbed, although the intensity of the 8.983 keV band of the former sample was stronger than that of the latter sample. These data clearly indicate the existence of a strong adsorption site for N_2 molecules on the CuZSM-5(NM)-108 samples. Moreover, the observation of the splitting of the 1s–4p band into two components points to the presence of copper ions surrounded by lattice oxygen atoms in linear (two) or planar (three) coordination states.[8,14,15] Hence, the following mechanism is suggested to account for the anomalous behaviour observed for the CuZSM-5(NM)-108 sample. Dinitrogen is adsorbed onto a three-coordination site, resulting in the formation of a distorted tetrahedral arrangement, and consequently, the intensity of the dominant 8.983 keV band decreases.

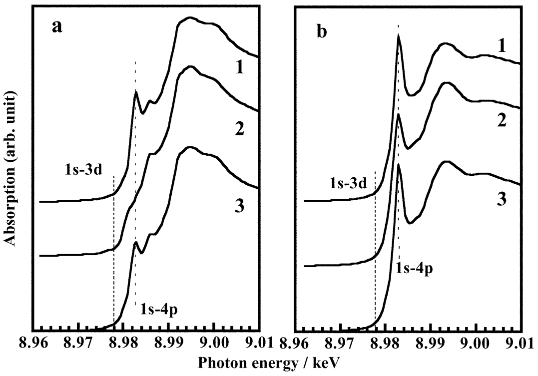

Fig. 2 XANES spectra of (a) CuZSM-5(NM)-108 and (b) CuZSM-5(C)-111 at 300 K. (1) evacuated at 873 K; (2) N_2 adsorption at 300 K under a pressure of *ca.* 60 Torr; successively re-evacuated at (3) 300 K.

A new ion-exchange method utilizing microwaves was developed for preparing the CuZSM-5 sample. This method provides for an easy ion-exchange operation of the copper ions into the zeolite. One remarkable property is highlighted for the samples thus-prepared: there was clear evidence for the chemisorption of dinitrogen molecules, even at room temperature. This work will pave the way for the potential use of this material as a new, and effective, N_2-separation and -fixation catalyst, as well as providing a guide for the development of more efficient catalysts for NOx-decomposition.

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