

Strong Adsorption of Dinitrogen on Copper-ion-exchanged Mordenite at Room Temperature

Yasushige Kuroda,* Shin-ichi Konno, Kazuya Morimoto and Yuzo Yoshikawa

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

An intense IR absorption band is observed at 298 K for dinitrogen adsorbed on copper-ion-exchanged mordenite-type zeolite, in which copper ions are exchanged in excess of the value expected from stoichiometry considerations.

The interaction of dinitrogen with a solid surface is of considerable interest, in particular from the viewpoint of dinitrogen fixation catalysis.¹ The IR spectra of dinitrogen adsorbed on various oxide surfaces and supported metal catalysts, such as ZnO,² Al₂O₃,³ TiO₂,⁴ Na-zeolite-A,⁵ ZrO₂,⁶ Rh/Al₂O₃,⁷ and Ni/SiO₂,⁸ show the fundamental band, which is forbidden by the IR selection rule, indicating that the dinitrogen is strongly adsorbed on the surface of these materials, decreasing its symmetry. To the best of our knowledge, there is only one report of IR studies of the absorption of dinitrogen on a metal oxide surface at room temperature,⁶ and we now report a new substance that strongly adsorbs dinitrogen and exhibits an intense IR absorption band due to dinitrogen at 298 K.

The sodium form of mordenite (TSZ-644) having an Si/Al ratio of 10 was used as starting material (NaM; TOHSO Co. Ltd.). This zeolite was ion-exchanged with aqueous Cu²⁺ or Ni²⁺ as described previously^{9,10} and the extent of exchange determined assuming that one divalent ion can be exchanged for two sodium ions; these samples are designated CuM-*X*, *X* denoting the percentage of exchange. Highly pure dinitrogen was supplied by Chugoku-Kasei Sanso Co. Ltd.

The powder samples were pressed to form self-supporting disks (usually 12 mg, 1 cm in diameter) for IR measurements. Each sample was evacuated in a vacuum of 1 mPa for 2 h at 873 K in an *in situ* cell. The IR spectra were recorded at 298 K in transmission mode.

For the measurement of adsorption isotherms, the samples were first degassed at 873 K under a vacuum of 1 mPa for 4 h,

and the adsorption isotherm of N₂ was measured at 298 K (1st adsorption). After this measurement, the sample was evacuated at 298 K for 4 h under a vacuum of 1 mPa, and the adsorption isotherm remeasured at 298 K (2nd adsorption). After this measurement, the sample was degassed at 298 K, and the adsorption isotherm remeasured at 278 K to obtain the isosteric heat of adsorption (q_{iso}).

Fig. 1 shows the IR spectra of NaM, NiM-84 and CuM-150, which had been pretreated at 873 K, before and after the adsorption of N₂ at 298 K. The equilibrium pressure for the adsorption of N₂ was adjusted to 13.1 kPa. The IR spectra of NaM and NiM-84 give absorption bands at 3640 cm⁻¹ (NaM) and 3770 and 3628 cm⁻¹ (NiM-84). The absorption at 3770 cm⁻¹ may be ascribed to the stretching vibration of free hydroxy groups in mordenite. The band at 3640 or 3628 cm⁻¹ may be assigned to the stretching vibration of hydrogen bonded OH groups. A band due to adsorbed N₂ could not be observed for NaM and NiM-84 at 298 K, even when N₂ gas was introduced on these samples.

The IR spectrum of CuM-150 shows an absorption band at 3644 cm⁻¹, assignable to hydrogen bonded OH stretch. The most striking feature of the spectrum of CuM-150 on which N₂ had been adsorbed at 298 K is the appearance of an additional sharp band at 2299 cm⁻¹. This band must be associated with the dinitrogen N≡N stretching vibration, because the band appears only if N₂ gas is present, and rapidly decreases in intensity and finally disappears on evacuation at 298 K. The observation of a strong IR absorption due to N₂ in our system is exceptional and suggests a strong interaction of adsorbed N₂

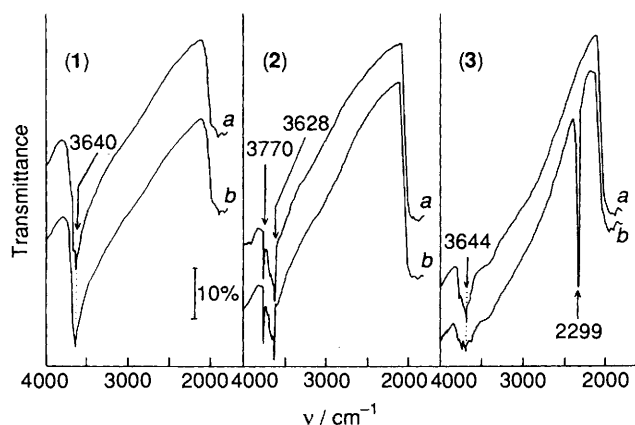


Fig. 1 IR spectra of NaM, NiM-84 and CuM-150, evacuated at 873 K: (a) before and (b) after the adsorption of N_2 at 298 K; (1) NaM; (2) NiM-84; and (3) CuM-150

with the exchanged copper ions; the N_2 is tentatively assumed to be end-on adsorbed, on the basis of the discussion of Wang and Yates.⁷ The wavenumber of this band is lower than the value (2331 cm^{-1}) for the free molecule.¹¹ Sakata *et al.*⁶ observed a stretching vibration due to N_2 adsorbed on ZrO_2 at 300 K, at slightly higher wavenumber than the gas-phase value, and with low absorbance, suggesting that the strength of the $N\equiv N$ bond is not changed substantially by the adsorption.

In our case, the observed shift to lower energy and the large absorbance value are particularly interesting, and are considered to arise *via* a synergistic effect of electron donation from the N_2 3σ to the metal $d\sigma$ orbital and 'back-donation' from the metal $d\pi$ to the N_2 2π orbital. It is possible to evaluate the bonding mechanism of N_2 in zeolites from measurement of the frequency of the other dipole mode ($M-N_2$). However, this information could not be obtained in the present study, because this mode may be beyond the IR range accessible to us or may be superposed upon the frequency of zeolite lattice mode.

Fig. 2(a) shows the adsorption isotherm of N_2 at 298 K on NaM treated at 873 K. This isotherm is well described by a Freundlich-type equation, and the amount of N_2 adsorbed in the first adsorption is the same as that in the second one. It thus follows that chemisorption or strong adsorption of N_2 does not occur on the surface of NaM, even if the sample had been treated at 873 K. The same applies to N_2 adsorption on NiM-84 as shown in Fig. 2(b), but the amount of N_2 adsorbed on NiM-84 is larger than that on NaM at all stages in the pressure range. Furthermore, the shape of the isotherm for N_2 adsorption on NiM-84 is different from that on NaM, being described by the Langmuir equation. This shows that there are stronger adsorption sites on NiM-84 for N_2 compared with NaM.

The adsorption isotherm of N_2 on CuM-150 at 298 K is shown in Fig. 2(c); it is of the same type as that on NiM-84. However, the adsorbed amount increases rapidly at low coverage compared with that of NiM-84 at the same pressure and the total adsorbed amount of N_2 is larger than that for NiM-84. Fig. 3(c) shows another specific feature: the monolayer capacity of the first adsorption isotherm is larger than that of the second one. This difference corresponds to the amount of adsorbed N_2 remaining on mordenite after evacuation at 298 K. This finding indicates that strong adsorption of N_2 occurs in the first adsorption on CuM-150, unlike the cases of NaM and NiM-84. This interpretation was confirmed by the following experiment: the gas evolved on heating at 400 K was analysed by mass spectrometry and found to be N_2 .

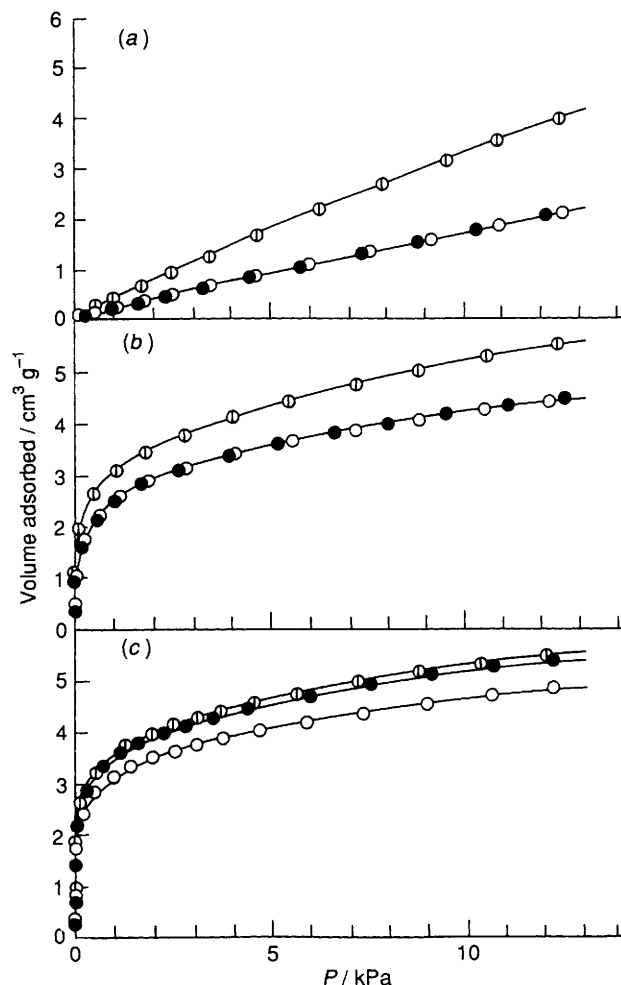


Fig. 2 Adsorption isotherms of N_2 on various mordenites treated at 873 K: (a) NaM, (b) NiM-84 and (c) CuM-150; ●, first adsorption at 298 K; ○ and ◻, second adsorptions at 298 and 278 K, respectively

This fact allows us to conclude that irreversible or strong adsorption sites for N_2 are present on CuM-150. The aforementioned species detected by IR spectroscopy (Fig. 1) does not correspond to the strongly adsorbed species, because the signal at 2299 cm^{-1} disappeared on evacuation at 298 K. The strongly adsorbed species which is not eliminated by evacuation at 298 K is not observed by IR spectroscopy under our experimental conditions, possibly owing to the lower concentration of strongly adsorbed species or the overlap of the IR band of this species with that of the bulk zeolite lattice mode. Only when CuM-150 is used as adsorbent does the absorption band of adsorbed N_2 appear at 2299 cm^{-1} , showing that even physisorption is strong in this case. The q_{iso} values for CuM-150, NiM-84 and NaM, determined by applying the Clausius-Clapeyron equation to the second adsorption isotherms, for a surface coverage of 0.25, were approximately 50, 40 and 27 kJ mol^{-1} , respectively. Copper ions in mordenite with N_2 show a stronger tendency than the other ions to adsorb N_2 , indicating the formation of a specific bond, such as a coordination bond, with the copper ions, consistent with the IR findings. It has been proved previously that a number of dimeric species exist in highly copper ion-exchanged mordenite.^{9,10} Taking this fact into consideration, we suggest that the adsorption site may be a bridged copper ion-exchanged species (dimer species), though the exact state of the ion-exchanged copper treated at high temperatures is not well known. Further investigation is needed to construct a model of the active site for strong adsorption of N_2 .

This work was supported by the Foundation of Okayama Science and Technology, and Iketani Science and Technology Foundations.

Received, 9th July 1992; Com. 2/03646K

References

- 1 (a) M. Grunze; (b) R. Raval, M. A. Harrison and D. A. King, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, ed. D. A. King and D. P. Woodruff, Elsevier, Amsterdam, (a) vol. 4, 1982; (b) vol 3 (part A), 1990.
 - 2 C. C. Chang and R. J. Kokes, *J. Phys. Chem.*, 1973, **77**, 2640.
 - 3 S. A. Zubkov, V. Yu. Borovkov, S. G. Gagarin and V. B. Kazansky, *Chem. Phys. Lett.*, 1984, **107**, 337.
 - 4 Y. Sakata, N. Kinoshita, K. Domen and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2765.
 - 5 E. Cohen de Lala and Y. Delaval, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 790.
 - 6 Y. Sakata, H. Abe, J. Kondo, K. Maruya, K. Domen and T. Onishi, *Chem. Lett.*, 1989, 711.
 - 7 H. P. Wang and J. T. Yates, Jr., *J. Phys. Chem.*, 1984, **88**, 852.
 - 8 R. Van Hardeveld and A. Van Montfoort, *Surf. Sci.*, 1966, **4**, 396.
 - 9 Y. Kuroda, A. Kotani, A. Uemura, Y. Yoshikawa and T. Morimoto, *J. Chem. Soc., Chem. Commun.*, 1989, 1631.
 - 10 Y. Kuroda, A. Kotani, H. Maeda, H. Moriwaki, M. Nagao and T. Morimoto, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1583.
 - 11 W. F. Murphy, W. Holzer and H. J. Bernstein, *Appl. Spectrosc.*, 1969, **23**, 211.
-