

An Estimation of the Peak Splitting of IR Bands Observed for $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ Mixture Adsorption on H-mordenite at Low Temperature

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Abstract

$^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ mixture adsorption on H-mordenite at 135K was studied by *in situ* Fourier transform infrared spectroscopy (*in situ* FT-IR), to examine the adsorption structure of dinitrogen species on the zeolite. Six bands were observed at 2352, 2336, 2312, 2297, 2272 and 2257 cm^{-1} in N-N stretching mode region. The first two bands were assigned to N-N stretching of $^{14}\text{N}_2$ species adsorbed on Lewis acid site (LAS) and Brønsted acid site (BAS) of H-mordenite, respectively, and the middle two bands were to those of $^{14}\text{N}^{15}\text{N}$ species, and the last two were to those of $^{15}\text{N}_2$ species, on LAS and BAS, respectively. Neither splitting nor obvious band broadening of $^{14}\text{N}^{15}\text{N}$ species' bands were observed. In order to examine whether this result really indicates that dinitrogen species are attached to the zeolite in side-on fashion, an estimation of peak splitting was carried for $^{14}\text{N}^{15}\text{N}$ species adsorbed on LAS using simple coupled oscillation model. This result indicates that the peak splitting is probably less than 1.8 cm^{-1} . It is, therefore, difficult to observe any separation or obvious band broadening of this species limited by its band's width (from 4 to 8 cm^{-1} in FWHM) and the spectrometer resolution (2 cm^{-1}) employed in this work. The result also implies that N-N bond is strengthened by adsorption to LAS of H-mordenite, indicating that N_2 species on LAS is adsorbed mainly through σ bonding, which indirectly suggests the end-on type adsorption of this species.

1. Introduction

Zeolite is an aluminosilicate with microporous structures connected in one to three dimensional way. It is widely used in industries, our daily life and other many field as sorbents, catalysts, detergent builders and so on, because of its unique properties arising from molecular size pore structures and ion exchangeable properties. It is well known that the acidities of zeolites play an important role in its applica-

tions to catalyst, and its acidic properties have been extensively studied using various techniques (RABO, 1989–90; KARGE 1991), such as calorimetry (AUROUX *et al.*, 1979), titration with indicators (TANABE, 1970; FORNI, 1974), temperature-programmed desorption (TPD) (KARGE, DONDUR and WEITKAMP, 1991), X-ray photoelectron spectroscopy (XPS) (BORADE *et al.*, 1990), infrared spectroscopy (IR) (WARD, 1976), solid-state NMR (THOMAS and KLINOWSKI 1985; PFEIFER, 1989; KLINOWSKI, 1991), quantum chemical calculations (SAUER, 1990), and so forth. It is well recognized that zeolitic hydroxyl groups are responsible for the Brønsted acidities of zeolites, mainly from IR studies (WARD, 1976). But its dynamical properties are not well understood so far.

We have begun detailed FT-IR study of the interaction of zeolitic hydroxyl groups and small molecules in order to understand the dynamical properties of zeolitic hydroxyl groups. Investigating the nitrogen adsorption on H-mordenite at low temperatures, we have observed two IR bands at 2352 cm^{-1} and 2335 cm^{-1} in N–N stretching mode region, and assigned them to dinitrogen species adsorbed on Lewis acid sites (LAS) and Brønsted acid sites (BAS) respectively, considering their interaction with zeolitic hydroxyl groups and the effect of steam treatment of the zeolite (WAKABAYASHI *et al.*, 1992).

On the course of the study, we have carried $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ mixture adsorption experiment to examine whether the dinitrogen species are attached to the zeolite substrate in end-on or side-on fashion, and observed three IR bands for LAS species and BAS species respectively (WAKABAYASHI *et al.*, 1992). This method is called “the isotope scrambling technique” (NAKAMOTO, 1978), first applied by ANDREWS (1969) to determine the structure of the ion-pair complex Li^+O_2^- in an Ar matrix at 15 K. The oxygen isotopic mixture of $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ was reacted with Li vapor in an Ar matrix, and three absorption bands of O–O stretching mode were observed in the IR spectrum. He concluded that dioxygen species are coordinated in side-on fashion because four absorption bands are expected for the end-on type coordination. This method was also applied successively to the nitrogen-metal systems in inert gas matrices (NAKAMOTO, 1978). OZIN and VOET (1973) observed three bands for $\text{Co}-^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ system in an Ar matrix at 10 K and concluded the side-on type coordination of dinitrogen species to Co atom. On the other hand, the same group (HUBER *et al.*, 1973) found four distinct peaks for the system of Ni– N_2 isotopic mixture indicating that N_2 species are coordinated in end-on fashion to a Ni atom. The splitting of the Ni– $^{14}\text{N}^{15}\text{N}/\text{Ni}-^{15}\text{N}^{14}\text{N}$ central components was 3.8 cm^{-1} .

This isotope scrambling technique were applied to the dinitrogen-metal surface adsorption systems which are important from the point of view of catalysis. WANG and YATES, Jr. (1984) applied this technique to the $\text{N}_2\text{-Rh}/\text{Al}_2\text{O}_3$ system, and were unable to distinguish the bonding mode of chemisorbed N_2 species on Rh metal surface due to the high bandwidth exhibited by adsorbed N_2 . Chemisorption systems have disadvantage in application of this technique because bandwidth of adsorbed species is rather broad (typically more than 10 cm^{-1}) due to inhomogeneous broadening

and/or lifetime broadening compared with very homogeneous metal-ligand compounds in inert gas matrices.

The dinitrogen species observed in our system, however, have rather narrow bandwidth ranging from 4 to 8 cm^{-1} , so that any separation or unambiguous broadening of $^{14}\text{N}^{15}\text{N}$ species' peak would be observed, if these species were adsorbed in end-on fashion on zeolite acid sites and had enough peak splitting. But as mentioned above, no separation and no unambiguous broadening was observed. So we have carried simple coupled oscillation calculation to estimate the peak splitting of $^{14}\text{N}^{15}\text{N}$ species adsorbed on Lewis acid sites of H-mordenite. In this note, we show the IR spectrum observed for $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ mixture adsorption on H-mordenite at first, and a calculated result which indicates that the peak splitting may be too small to be observed in our IR measurement conditions.

2. Experimental

H-mordenite, JRC-Z-HM20, was supplied by Catalysis Society of Japan (CSJ). Its total $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is 19.9, and its other properties were reported by CSJ (1988). The zeolite sample was pressed with pressure of 49.0MPa for a period of 10 min into a self-supported disk (typical density is ca. 10 mg/cm^3). The sample disk was placed in a quartz *in situ* IR cell (temperature range: 100–1000 K) attached to the conventional Pyrex closed circulation system, in which both sample treatment and IR measurement are possible. At the first sample treatment, the sample disk was heated gradually up to 773 K under evacuation, and maintained the same temperature for several hours. Then, temperature was raised to 873 K in order to remove contaminants completely. Treatment above 873 K is necessary to produce enough amount of Lewis acid site in H-mordenite (WAKABAYASHI *et al.*, 1992). After cooling to room temperature, O_2 of ca. 12kPa was admitted into the IR cell, and the sample was gradually heated up to 773 K, and then maintained the same temperature for several hours, followed by the evacuation at the same temperature for 1 hour. Except for the first treatment, only O_2 treatment followed by evacuation at 773 K was carried before each adsorption measurements.

FT-IR measurements were performed using Jasco FT/IR-7000 equipped with liquid nitrogen cooled MCT detector, under the conditions of 2 cm^{-1} in resolution and 128 in scan times typically. Pretreated sample was cooled to low temperature with liquid nitrogen passed through the stainless pipe that was coiled around the IR cell. An FT-IR spectrum of clean sample was measured at low temperature, and used as a background. Adsorption gas was introduced into the cell at low temperature, and FT-IR spectra were measured after adsorption equilibrium state was achieved.

High purity nitrogen gas was supplied by Takachiho Co., Ltd., Japan, and used after a purification passing slowly through the liquid nitrogen cooled trap to remove residual water and other impurities. $^{15}\text{N}_2$ (99.5 atom % in ^{15}N) was supplied by Shoko Co., Ltd., Japan, and used without further purification. The nitrogen isotopic mixture

$^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ was prepared by the method described by ANDREWS (1969); near-equimolar amount of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ was discharged in a Pyrex gas reservoir for 8 minutes using Tesla coil, leading to the nearly 1 : 2 : 1 molar ratio mixture.

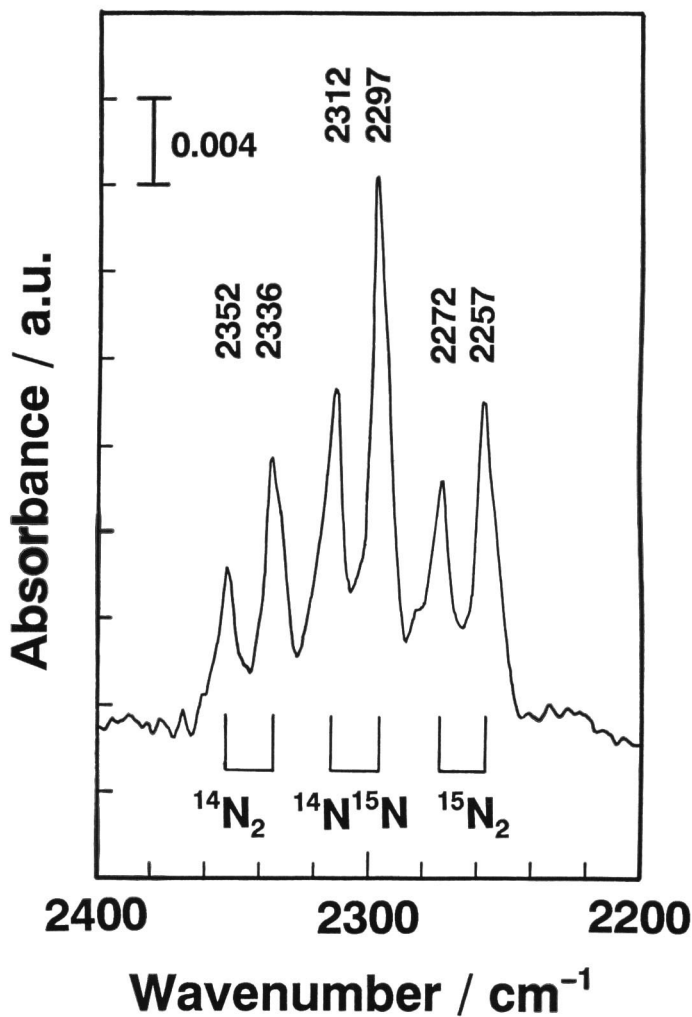


Figure 1. FT-IR spectrum of adsorbed N₂ species on H-mordenite observed for $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ mixture adsorption at 135 K. Total pressure is 0.8 kPa with molar ratio of nearly 1 : 2 : 1.

3. Result

Figure 1 shows the FT-IR spectrum of adsorbed species observed for the adsorption of isotopic mixture $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ on H-mordenite at 135 K. This spectrum was obtained by subtracting the background spectrum from as-measured spectrum, and compensating for atmospheric CO_2 bands. The bands at 2352 cm^{-1} and 2336 cm^{-1} are assigned to the N-N stretching of $^{14}\text{N}_2$ species adsorbed on Lewis acid sites and Brønsted acid sites of H-mordenite respectively, in accordance with the results of $^{14}\text{N}_2$ adsorption (WAKABAYASHI *et al.*, 1992). In the same way, the bands at 2312 cm^{-1} and 2297 cm^{-1} are attributed to those of $^{14}\text{N}^{15}\text{N}$ species, and 2272 cm^{-1} and 2257 cm^{-1} are to those of $^{15}\text{N}_2$ species, adsorbed on LAS and BAS, respectively.

Table 1. IR Bands Observed for the Adsorption of $^{14}\text{N}_2/^{14}\text{N}^{15}\text{N}/^{15}\text{N}_2$ Mixture on H-Mordenite

Isotopes	Gas Phase ^a (Raman)	Adsorbed Species				Calculated Values
		Lewis Acid Sites		Brønsted Acid Sites		
		ν/cm^{-1}	FWHM/ cm^{-1}	ν/cm^{-1}	FWHM/ cm^{-1}	
$^{14}\text{N}_2$	2330	2352	5.4	2336	7.6	
$^{14}\text{N}^{15}\text{N}$	2291	2312	6.2	2297	6.6	
$\nu(^{14}\text{N}_2)/\nu(^{14}\text{N}^{15}\text{N})$	1.017	1.017		1.017		1.017
$^{15}\text{N}_2$	2252	2272	5.6	2257	7.6	
$\nu(^{14}\text{N}_2)/\nu(^{15}\text{N}_2)$	1.035	1.035		1.035		1.035

a. J. Bendtsen, *J. Raman Spectrosc.*, **2**, 133 (1974)

Properties of these bands are tabulated in Table 1, comparing with the gas phase data obtained by Raman spectroscopy (BENDTSEN, 1974; BRODERSEN, 1979). These bands exhibited the exact isotope shift as those expected from the theoretical calculations, as shown in Table 1. Neither splitting nor obvious broadening of $^{14}\text{N}^{15}\text{N}$ species' bands were observed for both LAS and BAS species. Only slight broadening (0.6 to 0.8 cm^{-1}) was observed for LAS species, as shown in Table 1. On the other hand, bandwidth of $^{14}\text{N}^{15}\text{N}$ species was narrower (1.0 cm^{-1}) than that of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ species for BAS species, which may be caused by the existence of two kind of BAS species which apart very slightly each other.

4. Discussion

To estimate the peak splitting of $^{14}\text{N}^{15}\text{N}$ species adsorbed on H-mordenite, we have used a simple coupled oscillation system consisted of material particles with mass of m_1 (particle M_1) and m_2 (particle M_2), and substrate (S) with infinite mass as a model for the adsorption system, as shown in Figure 2. Notations k_1 and k_2 represent force constants between S and M_1 , M_1 and M_2 , respectively.

Normal modes' frequencies ω of this system are expressed as follows:

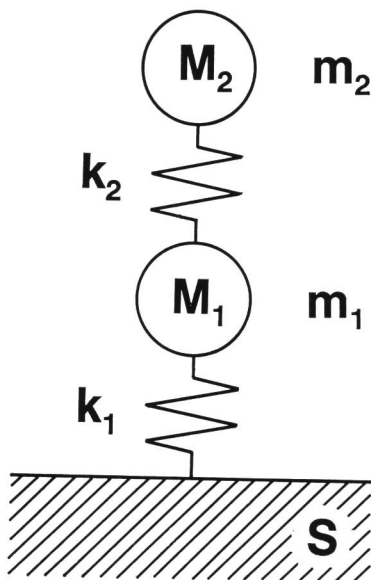


Figure 2. A simple coupled oscillation model for end-on type adsorption of diatomic molecule on surface.

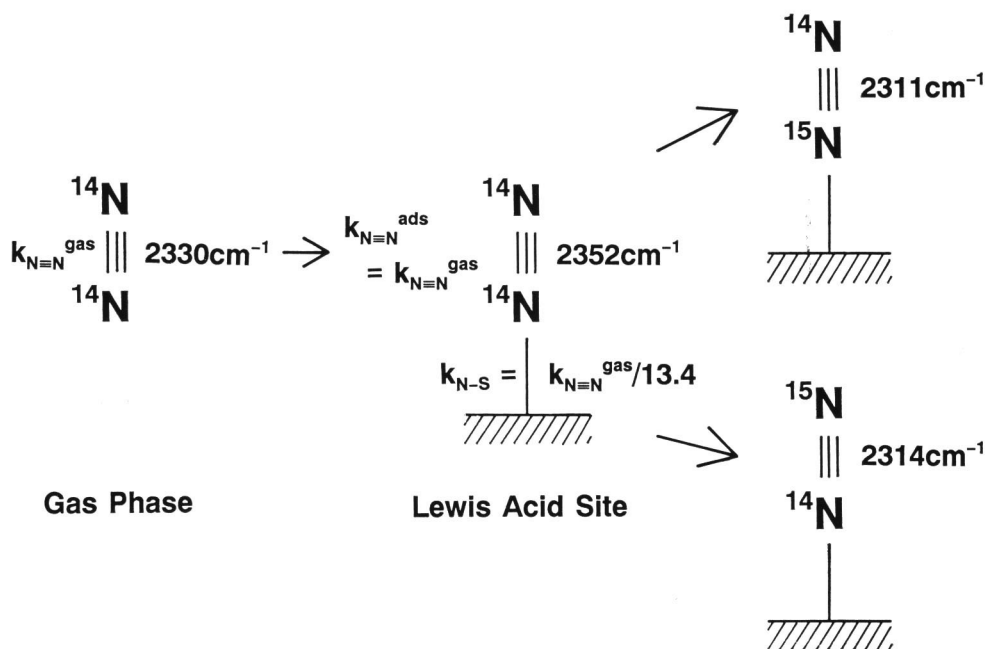
M_1, M_2 : Particle S : Substrate
 m_1, m_2 : Mass of M_1 and M_2 , respectively
 k_1, k_2 : Force constants between S and M_1 , M_1 and M_2 , respectively

$$\omega^2 = 1/2 \{ k_1/m_1 + k_2/\mu \pm \sqrt{(k_1/m_1 + k_2/\mu)^2 - 4k_1k_2/m_1m_2} \} \quad (\text{Eq. 1})$$

where $1/\mu = 1/m_1 + 1/m_2$ (μ : reduced mass of M_1 - M_2 system).

As a first approximation, we assumed that the force constant of $\text{N}\equiv\text{N}$ bond was not influenced by adsorption on the zeolite, that is $k_{\text{N}\equiv\text{N}}^{\text{ads}} (=k_2) = k_{\text{N}\equiv\text{N}}^{\text{gas}}$ (where $k_{\text{N}\equiv\text{N}}^{\text{ads}}$ and $k_{\text{N}\equiv\text{N}}^{\text{gas}}$ represent the bond constant of $\text{N}\equiv\text{N}$ bond of adsorbed N_2 species and that of N_2 in gas phase, respectively). This assumption and the experimental results, $\nu(^{14}\text{N}\equiv^{14}\text{N})$ in gas phase is 2330 cm^{-1} (BENDTSEN, 1974; BRODERSEN, 1979) and $\nu(^{14}\text{N}\equiv^{14}\text{N})$ of adsorbed species on LAS is 2352 cm^{-1} (WAKABAYASHI *et al.*, 1992), lead to the conclusion that $k_{\text{S-N}} (=k_1)$ is equal to $0.0745k_{\text{N}\equiv\text{N}}^{\text{gas}}$ and that peak splitting of $^{14}\text{N}^{15}\text{N}$ species on LAS is about 3 cm^{-1} as shown in Scheme 1, if this species is adsorbed in end-on fashion. But this k_1 value is rather large for the weak adsorption of N_2 on the zeolite. This assumption may limit the maximum value of the peak splitting.

In order to estimate realistic $k_{\text{S-N}} (=k_1)$ and $k_{\text{N}\equiv\text{N}}^{\text{ads}} (=k_2)$ values, we have applied Eq. 1 to N_2 -metal single crystal surface systems, such as N_2/Ni (110) (BANDY *et al.*, 1982; KUWAHARA *et al.*, 1988; HORN *et al.*, 1982), N_2/Pd (110) (KUWAHARA *et al.*, 1987) and N_2/Pd (111) (BERTOLO *et al.*, 1992) where two normal mode frequencies are available from the experimental data of electron energy loss spectroscopy (EELS).



Scheme 1 A simulation of peak splitting of $^{14}\text{N}^{15}\text{N}$ species adsorbed on the Lewis acid site of H-mordenite in the case of end-on type adsorption without any change of N-N bond constant compared with gas phase.

The results are tabulated in Table 2, which suggests that $k_{\text{S-N}}/k_{\text{N}=\text{N}}^{\text{gas}}$ is between 0.087 and 0.033, and that the peak splitting is between 3.7 cm^{-1} and 1.3 cm^{-1} , depending on $k_{\text{S-N}}/k_{\text{N}=\text{N}}^{\text{gas}}$ value, that is, on the bond strength between adsorbed N_2 species and substrate.

N_2 is held rather strongly on Ni (110), and weakly on Pd (110) and Pd (111). So, $k_{\text{S-N}}$ value of N_2 species on H-mordenite would be resemble to or smaller than that of Pd (110) or Pd (111). Considering these results, $k_{\text{S-N}}/k_{\text{N}=\text{N}}^{\text{gas}}$ is changed systematically between 0.0745 and 0, and $k_{\text{N}=\text{N}}^{\text{ads}}$ is determined so that $\nu(^{14}\text{N}\equiv^{14}\text{N})$ of adsorbed species is equal to 2352 cm^{-1} according to our IR data. The results are tabulated in Table 3.

From these results, we can see that peak splitting ($\Delta\nu$) almost linearly changes with the value of $k_{\text{S-N}}/k_{\text{N}=\text{N}}^{\text{gas}}$, suggesting that peak splitting is strongly dependent on $k_{\text{S-N}}/k_{\text{N}=\text{N}}^{\text{gas}}$, that is, on the bond strength between adsorbed N_2 species and substrate. If the bond strength between N_2 species and LAS of H-mordenite is as weak as, or weaker than that of N_2/Pd (110), the peak splitting of $^{14}\text{N}^{15}\text{N}$ species would be less than 1.8 cm^{-1} , which is difficult to resolve under our experimental condition because the best resolution achieved by our spectrometer is 2 cm^{-1} . There exists the probability that the splitting is less than 1 cm^{-1} . If so, it is difficult to observe even

Table 2. An Estimation of the Peak Splitting of $^{14}\text{N}^{15}\text{N}$ Species Adsorbed on Ni (110), Pd (110) and Pd (111) Based on the Electron Energy Loss Spectroscopy (EELS) data

System	EELS Data/cm $^{-1}$		Estimated Values			Estimated Values/cm $^{-1}$			$\Delta\nu$
	$\nu(\text{S}^{14}\text{N}\equiv^{14}\text{N})$	$\nu(\text{S}-^{14}\text{N}_2)$	$k_{\text{N}\equiv\text{N}^{\text{ads}}}/k_{\text{N}\equiv\text{N}^{\text{gas}}}$	$k_{\text{S}-\text{N}}/k_{\text{N}\equiv\text{N}^{\text{gas}}}$	$\nu(\text{S}^{14}\text{N}\equiv^{15}\text{N})$	$\nu(\text{S}^{15}\text{N}\equiv^{14}\text{N})$	$\nu(\text{S}^{15}\text{N}\equiv^{15}\text{N})$		
N_2/Ni (110)	2194 ^a	339 ^a	0.864	0.0869	2159.0	2155.3	2155.3	3.7	
N_2/Ni (110)	2186 ^b	323 ^b	0.860	0.0787	2151.0	2147.6	2147.6	3.4	
N_2/Pd (110)	2242 ^c	242 ^c	0.915	0.0437	2205.2	2203.4	2203.4	1.8	
N_2/Pd (111)	2258 ^d	210 ^d	0.931	0.0328	2220.7	2219.4	2219.4	1.3	

S: Substrate

$\nu(\text{SN}\equiv\text{N})$: Wavenumber of $\text{N}\equiv\text{N}$ stretching Mode

$\nu(\text{S}-\text{N}_2)$: Wavenumber of $\text{S}-\text{N}$ stretching Mode

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d. M. Bertolo and K. Jacobi, *Surf. Sci.*, **265**, 1 (1992)

Table 3. An Estimation of the Peak Splitting of $^{14}\text{N}\equiv^{15}\text{N}$ Species Adsorbed on the Lewis Acid Sites of H-Mordenite
(Tabulated values of $k_{\text{N}\equiv\text{N}}^{\text{ads}}$ and $k_{\text{S}-\text{N}}$ are determined so that $\nu(\text{S}^{14}\text{N}\equiv^{14}\text{N})$ equals to 2352 cm^{-1} according to our IR data)

Assumed Values		Estimated Values/ cm^{-1}			
$k_{\text{N}\equiv\text{N}}^{\text{ads}}/k_{\text{N}\equiv\text{N}}^{\text{gas}}$	$k_{\text{S}-\text{N}}/k_{\text{N}\equiv\text{N}}^{\text{gas}}$	$\nu(\text{S}^{14}\text{N}\equiv^{15}\text{N})$	$\nu(\text{S}^{15}\text{N}\equiv^{14}\text{N})$	$\Delta\nu$	$\nu(\text{S}-^{14}\text{N}_2)$
1.000	0.0745	2314.0	2311.0	3.0	315.1
1.006	0.0500	2313.5	2311.5	2.0	258.9
1.011	0.0333	2313.1	2311.8	1.3	211.8
1.013	0.0250	2313.0	2312.0	1.0	183.6
1.014	0.0200	2312.9	2312.1	0.8	164.4
1.017	0.0100	2312.7	2312.3	0.4	116.4
1.019	0.0000	2312.5	2312.5	0.0	0.0

S: Substrate

$\nu(\text{SN}\equiv\text{N})$: Wavenumber of $\text{N}\equiv\text{N}$ stretching Mode

$\nu(\text{S}-\text{N}_2)$: Wavenumber of $\text{S}-\text{N}$ stretching Mode

the peak broadening clearly. Considering these results, the slight broadening (from 0.6 to 0.8 cm^{-1}) observed here may imply that dinitrogen species on LAS of H-mordenite is adsorbed in end-on fashion and that the peak splitting of $^{14}\text{N}^{15}\text{N}$ species is less than 1 cm^{-1} . But this result is not conclusive, and it is necessary to carry the experiment under more high resolution conditions to get more information.

This result also indicates that $\nu(\text{S}-\text{N}_2)$ is correlated with the bond strength between substrate and nitrogen species, so that we could estimate the peak splitting of $^{14}\text{N}^{15}\text{N}$ species more precisely if we knew the wavenumber of $\text{S}-\text{N}$ stretching mode. But it is very difficult to observe such low wavenumber region, due to the very low sensitivity of infrared spectroscopy itself and MCT detector in this region and to the strong absorption band of zeolite lattice under 1400 cm^{-1} . It requires another method to estimate the bond strength between dinitrogen species and zeolite substrate.

From Table 3, we can get also the information about the bond strength of $\text{N}\equiv\text{N}$ bond, suggesting that $k_{\text{N}\equiv\text{N}}^{\text{ads}}/k_{\text{N}\equiv\text{N}}^{\text{gas}}$ would be greater than 1, that is, $\text{N}\equiv\text{N}$ bond is strengthened by adsorption on Lewis acid site of H-mordenite compared with the gas phase. This result strongly suggests that dinitrogen species on LAS of the zeolite are adsorbed mainly through σ donation from nitrogen to Lewis acid site (electron acceptor site), which indicates, in turn, N_2 species on LAS is probably adsorbed in end-on fashion. It is well recognized that σ bonding plays a major role in N_2 adsorption on metal surfaces (HORN *et al.*, 1982; DE PAOLA *et al.*, 1987; RAO *et al.*, 1991) in which end-on type adsorption of N_2 species are well established, except for Fe (111) surface (GUNZE *et al.*, 1984; TSAI *et al.*, 1985) in which π bonding plays a dominant role to form side-on type N_2 species. HORN *et al.* (1982) reported that chemisorption of N_2 on Ni (110) occurs mainly through the donation of $\text{N}_2\ 2\sigma_u^*$ electron to Ni surface with a small amount of back donation of Ni d-electron to $\text{N}_2\ 1\pi_g^*$ orbital. Lacking d-electron in zeolite substrate, σ donation will be dominant in N_2/LAS of H-mordenite

system, which cause the strengthening of N–N bond because electron density of antibonding N_2 $2\sigma_u^*$ orbital is eliminated by donation to the substrate. These features will be discussed in more detail elsewhere (WAKABAYASHI *et al.*, 1992).

Acknowledgements

One of the authors (F. W.) wishes to express his thanks to Dr. Akihiko OKADA of the Institute of Physical and Chemical Research for providing him the opportunity to survey literatures at his Institute's library.

This work was partially supported by Grant-in-Aid for Scientific Research Nos. 02740414 and 03740247 from the Ministry of Education, Science and Culture, Japan, to one of the authors (F. W.).

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