FTIR spectroscopic evidence of formation of geminal dinitrogen species during the low-temperature N_2 adsorption on NaY zeolites

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Adsorption of N_2 on NaY zeolites at 85 K and equilibrium pressures higher than 1 kPa results in the formation of geminal dinitrogen complexes characterized by an IR band at 2333.5 cm^{-1} (2255.4 cm^{-1} after adsorption of $^{15}N_2$). With decreasing equilibrium pressure the complexes tend to loose one N_2 ligand, thus forming linear species characterized by an IR band at 2336.8 cm^{-1} (2258.7 cm^{-1} after adsorption of $^{15}N_2$). All species disappear completely after evacuation. Co-adsorption of N_2 and CO revealed that the dinitrogen complexes are formed on Na^+ cations. The changes in the concentrations of the linear and geminal N_2 species with the changes in the equilibrium pressure are excellently described by equations of adsorption isotherms proposed earlier for mono- and di-carbonyls.

Keywords: adsorption, adsorption isotherms, dinitrogen, FTIR spectroscopy, geminal species, NaY, nitrogen, zeolites

1. Introduction

A recent tendency in the characterization of surface acidity by IR spectroscopy is the utilization of very weak bases as probe molecules [1]. Carbon monoxide is mostly applied for this purpose since it interacts weakly with base metal cations. However, CO forms a strong π-back bond with transition metal cations possessing a high d-electron density, and as a result the adsorption heat strongly increases. Recently, it was proposed that dinitrogen, being a weaker base than CO, could be very useful for testing surface acidity [1–4]. As a homonuclear diatomic molecule N_2 has no IR active mode [5]. However, after adsorption of N_2, the N–N stretching frequency (2331 cm^{-1}) may become IR active due to reduction of the molecular symmetry. An important advantage of the dinitrogen molecule, when compared to CO, is that N_2 is very inert, whereas reactive adsorption of CO often occurs and the (bi)carbonate and/or carboxylate structures formed affect the acidity of the adjacent metal cation [6,7]. Another benefit of N_2 is that there is no need to subtract the gas-phase spectrum.

The N_2 molecule is a very weak Lewis base and is only weakly bound to surfaces. For this reason the adsorption of dinitrogen is studied at low temperatures. It has been established that N_2 can be bound both to OH groups and Lewis acid sites [1–4]. In general, the N–N stretching mode is shifted by up to 30 cm^{-1} towards higher frequencies (reaching the value of 2360 cm^{-1}) due to σ-donation of electrons from N_2 to the surface acid site. The stronger the adsorption, the larger is the frequency shift. The origin of the IR band has been proven by experiments using $^{15}N_2$. There are only few reported cases when N_2 is strongly adsorbed on cationic sites: this concerns Cu^+ [8,9] and Rh^+ [10,11] cations in zeolites, where bands of adsorbed $^{14}N_2$ have been detected at ambient temperature in the 2300–2188 cm^{-1} region. In the present paper, we report on FTIR studies of dinitrogen adsorption on NaY zeolites. We infer from the experimental results that two N_2 molecules are bound to a single site.

2. Experimental

2.1. Samples and reagents

Two NaY samples were studied: one supplied from Union Carbide Corp. (USA), Si/Al ratio of 2.6, and another obtained by Grace Davison (SP No. 6-5257.0101). Prior to the IR measurements the powders were pressed into self-supporting wafers at a pressure of 10^4 kPa. Their areal density was ca. 10 mg cm^{-2}. The samples were activated *in situ* for 1 h in a flow of oxygen at 673 K followed by 1 h evacuation at the same temperature.

Nitrogen (>99.999) and carbon monoxide (>99.997) were supplied by Linde AG. Labeled nitrogen ($^{15}N_2$) was provided by Isotec Inc. A. Matheson (USA) and had an isotopic purity of 99.7%.

2.2. Methods

FTIR spectroscopy studies were carried out with a Bruker IFS-66 apparatus at a spectral resolution of 1 cm^{-1} accumulating 128 scans. The *in situ* IR cell was connected to a vacuum/sorption system with a residual pressure less than 10^{-3} Pa. The specially constructed cell allowed the IR measurements to be performed both at ambient temperature and 85 K.

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3. Results

3.1. Low-temperature $^{14}N_2$ adsorption

In order to ascertain that the observed effects are not due to specific properties of a particular sample, two different NaY zeolites (see section 2) were studied. The results obtained were, however, essentially identical. For that reason we shall consider here only the Grace Davison sample.

The background spectrum of the activated NaY is typical of alkali-metal-exchanged Y-zeolites. In particular, no bands were detected in the ν(OH) region, which is consistent with the occupation of all cationic positions by sodium cations.

Exposure of the sample to 4 kPa of $^{14}N_2$ at 85 K results in the appearance of one narrow band (FWHM $= 4$ cm^{-1}) at 2333.5 cm^{-1}. Thus, the N–N stretching mode after the adsorption is shifted by only 2.5 cm^{-1} relative to the gas-phase frequency (Raman) at 2231 cm^{-1}. Lowering of the equilibrium pressure results in a decrease in intensity of the band without shifting the maximum. Simultaneously, a new narrow band at 2336.8 cm^{-1} (FWHM $= 2$ cm^{-1}) develops. This band reaches maximum intensity at a pressure of about 10 Pa. At still lower pressures the intensity begins to decrease and the band disappears completely after evacuation. The shift of the N–N modes relative to the gas-phase Raman stretching frequency is, in this case, 5.8 cm^{-1}, which implies a stronger interaction between the adsorbed N_2 molecules and the surface. This is in agreement with the higher stability of the corresponding surface species.

A temperature increase in the presence of 4 kPa N_2 leads to the same effects as the pressure decrease at 85 K. At temperatures higher than 210 K adsorbed dinitrogen can no longer be detected.

In order to obtain more information on the nature of the sites to which N_2 is bonded, we performed some CO–N_2 co-adsorption experiments. The results indicated competitive adsorption of both gases which implies that dinitrogen is coordinated to Na^+ cations.

3.2. Low-temperature adsorption of $^{15}N_2$

Since the positions of both $^{14}N_2$ bands fall in the region where gaseous CO_2 absorbs (2380–2280 cm^{-1}), even small changes in the air-CO_2 concentration in the spectrometer can affect the spectra. This renders the exact calculation of the band intensities ambiguous. In order to prevent such perturbation by CO_2 and to obtain better quality spectra, as well as to confirm the origin of the bands, we studied the adsorption of $^{15}N_2$.

Figure 1 shows a series of spectra recorded after adsorption of $^{15}N_2$ on NaY at 85 K at decreasing pressures starting at 4 kPa (spectrum (a)). The picture is essentially the same as observed after $^{14}N_2$ adsorption and the observed isotopic shifts coincide well with the theoretically calculated ones. At 4 kPa equilibrium pressure only one symmetric band at 2255.5 cm^{-1} (FWHM $= 4$ cm^{-1}) is detected in the $\nu(^{15}N–^{15}N)$ stretching region. As in the case of $^{14}N_2$ adsorption, a decrease of the equilibrium pressure results in a decrease of the intensity of this band and a simultaneous development of a new band at 2258.7 cm^{-1} (FWHM $= 2$ cm^{-1}). The intensity of the latter passes through a maximum and the band disappears completely after evacuation.

Experiments were also performed with $^{14}N_2$–$^{15}N_2$ isotopic mixtures. The already detected bands for adsorbed $^{14}N_2$ and $^{15}N_2$ were observed and they also showed the above mentioned changes with the equilibrium pressure. No additional bands were detected.

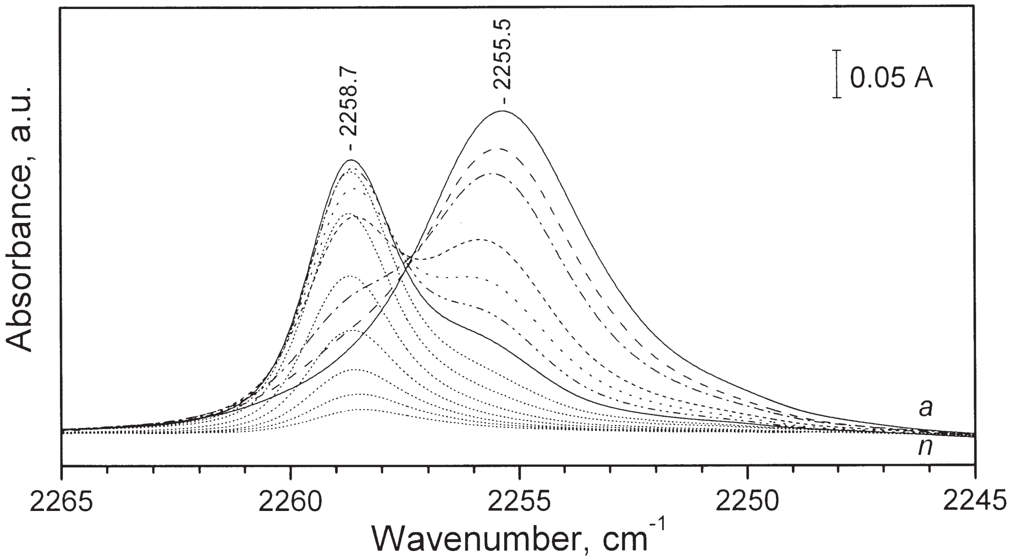

Figure 1. FTIR spectra of $^{15}N_2$ adsorbed at 85 K on NaY-1 sample: equilibrium pressure of (a) 4000; (b) 300; (c) 150; (d) 50; (e) ca. 40; (f) ca. 25; (g) ca. 15 Pa $^{15}N_2$; after a short evacuation (e); and time evolution of the spectra in dynamic vacuum (f)–(n).

4. Discussion

4.1. Low-temperature dinitrogen adsorption on NaY zeolites

The results presented in this work clearly demonstrate the existence of two different N_2 adsorption species on NaY zeolite, which can be interconverted depending on the equilibrium pressure. Usually, when one species is converted to another, the IR bands pass through an isosbestic point. Inspection of figure 1 shows that, although slightly changing in position, an isosbestic point is indeed observed in the series of spectra (a)–(f) (until the band at 2258.7 cm^{-1} rises in intensity). The gradual weakening of the 2258.7 cm^{-1} band during evacuation is the reason for the disappearance of the isosbestic point.

There are several possibilities to assign the two IR bands. First, the higher frequency band (prevailing at low coverages) may correspond to bridging N_2 molecules bound simultaneously to two Na^+ cations. At higher coverage these would be converted into linear species (the lower frequency band). This hypothesis is unlikely, because of several reasons: (i) bridging N_2 molecules should be only weakly polarized and are thus expected to show lower frequency than the linear species; (ii) grouping of all Na^+ cations in suitable pairs is unlikely.

Secondly, linear species (the higher frequency band) might be converted into mono- or multi-dinitrogen layers. This is also improbable, because the physically adsorbed dinitrogen is expected to be IR inactive.

Thirdly, the presented spectra can be explained by assuming the formation, at low pressures, of linear dinitrogen complexes ($^{14}N_2$ band at 2336.8 cm^{-1}) which are converted, at high pressures, to geminal species ($^{14}N_2$ band at 2333.5 cm^{-1}). Usually, when more than one adsorbate molecule are coordinated to one site, the adsorption of the first molecule is very strong. Typical examples are the di- and tri-carbonyls formed on Rh^+ [11,12], Ir^+ [13], Ru^{n+} [14], Os^{n+} [15], Cu^+ [16] and Ag^+ [17]. In the present case, however, the N_2 molecules (when forming linear species) are only weakly polarized by Na^+ cations; these complexes decompose on evacuation even at 85 K. This weak interaction suggests a small effect of N_2 on the properties of the Na^+ ions to which it is bonded. Thus, a suitable space arrangement would allow a coordination of a second N_2 molecule to the same sodium cation, both ligands becoming equivalent. Similar suggestions have already been made for CO weakly adsorbed to CaNaY [18] and LiZSM-5 [19] zeolites.

In most cases, geminal species exhibit symmetric and antisymmetric IR modes [11–13,16,20]. However, we have observed only one band. A possible explanation of this phenomenon is that the angle between both N_2 molecules is near 180°, as a result only the antisymmetric modes are IR active. This hypothesis, however, can be ruled out because of the following reasons: In NaY zeolites the Na^+ cations occupy S_I, $S_{I'}$ and S_{II} sites. The S_I and $S_{I'}$ sites are located in the hexagonal prisms and the sodalite cages, respectively, where they are not accessible to N_2 at low temperature [21]. Hence, the only accessible Na^+ cations are located in S_{II} positions, in a six-ring window. This localization requires the bond angle between adsorbed geminal species to be less than 180°.

Another explanation for the appearance of only one stretching mode for the geminal species is that the interaction between Na^+ and N_2 is too weak to produce splitting of the stretching modes (i.e., the interaction constant between Na^+–N and N–N modes is close to zero). In this case both N_2 molecules behave as isolated species and independent oscillators. Indeed, the complexes observed in this study had low stability and were decomposed during evacuation even at 85 K. The lack of vibrational interaction between the dinitrogen molecules is supported also by the fact that the bands characterizing geminal species were essentially the same after adsorption of pure isotopes and isotopic mixtures (where mixed $Na^+(^{14}N_2)(^{15}N_2)$ complexes are expected). It should be noted that only one band (at 2188 cm^{-1}) has been observed for surface $Rh(N_2)_2$ species [11] and this phenomenon has also been explained by the lack of vibrational coupling between both N_2 ligands.

When the geminal complexes are formed the nitrogen molecules are affected by the O^{2-} surrounding of the Na^+ cation. As a result, an inhomogeneous broadening of the N–N stretching band due to intermolecular interaction is expected. This explains the higher FWHM of the bands due to geminal species as compared to the bands characterizing linear complexes.

The lower (by 3 cm^{-1}) frequency of the geminal species can be explained by the so-called chemical shift: the first adsorbed dinitrogen molecule is polarized by the Na^+ cation and also polarizes it. As a result, the Lewis acidity of the latter slightly decreases and the second N_2 molecule is more weakly polarized. After formation of the geminal complex, however, both ligands become equivalent.

To verify the assignment of the observed bands to linear and geminal species we compared the experimental data with a mathematical model proposed earlier [22].

4.2. Mathematical model

The mathematical model describes the change in the concentration of adsorbed mono- and di-carbonyl species during the change in the equilibrium CO pressure [22]. It was noted, however, that the derived adsorption isotherms are generally valid for mono- and di-adspecies. The equations proposed were:

$$\Theta_1 = \frac{bP}{P^2 + 2bP + ab}, \tag{1}$$

$$\Theta_2 = \frac{P^2}{P^2 + 2bP + ab}, \tag{2}$$

$$\Theta = \frac{P(P + b)}{P^2 + 2bP + ab}, \tag{3}$$

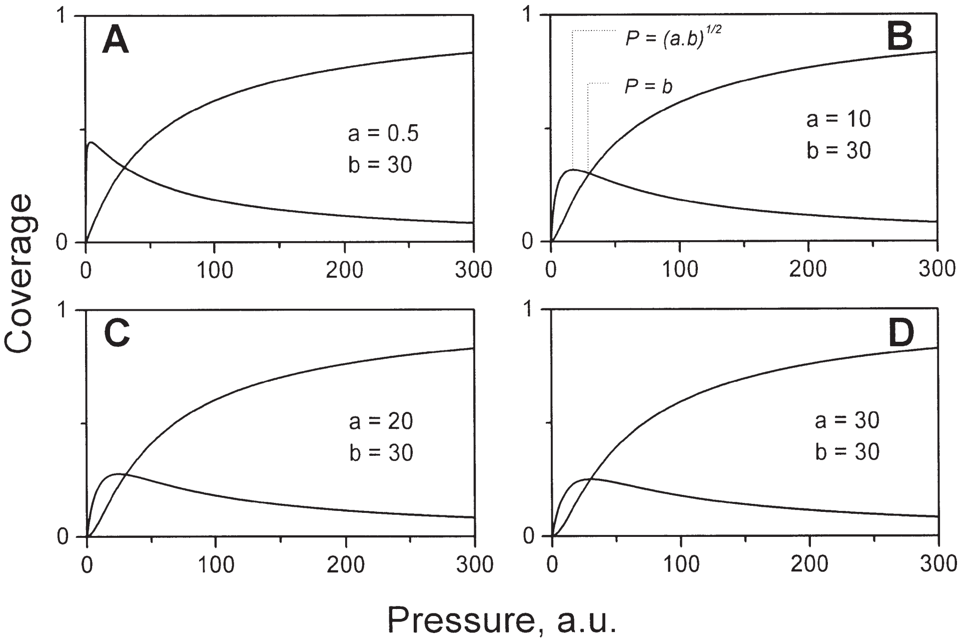

Figure 2. Plots of the adsorption isotherms (equations (1) and (2)) at different ratios between the parameters a and b.

where Θ_1 is the surface coverage by mono-species, Θ_2 is the surface coverage by di-species, Θ is the total surface coverage ($\Theta = 1$ when all sites are occupied by two admolecules), P is the equilibrium pressure, a and b are constants (having a pressure dimension). The constant a represents the ratio between the rate constants of decomposition and formation of mono-species, whereas b represents the respective ratio for the di-species.

Figure 2 shows plots of the theoretical adsorption isotherms (1) and (2) at different ratios between the coefficients a and b. Plot (A) presents the case when the mono-species are very strongly adsorbed ($a \to 0$), whereas plot (D) concerns a situation when the mono- and di-species have the same strength of adsorption. Intermediate cases (e.g., plots (B) and (C)) are expected in practice.

It is evident that the curves in plots (B) and (C) of figure 2 resemble the behavior of both kinds of N_2 species detected on the NaY samples. Therefore, we tried to fit the experimental data to the theoretical curves. It was proposed [22] that the coefficients a and b can be easily extracted from the experimental data based on the two relations (see figure 2(B)):

- $b = P$, at the crossing point of the two isotherms, Θ_1 and Θ_2; and
- $a = P^2/b$, at the maximum of the isotherm Θ_1 of the mono-species.

However, the accuracy of our pressure measurement was only 10 Pa which did not allow the exact determination of low equilibrium pressures (below ca. 50 Pa). Therefore, we adopted the following procedure, which is characterized by smaller error, to calculate the coefficients a and b: At high pressures equations (1) and (2) can be written as

$$\Theta_1 = \frac{b}{P + 2b}, \tag{4}$$

$$\Theta_2 = \frac{P}{P + 2b}. \tag{5}$$

Since the coverage is proportional to the absorption in the IR spectra, one may write

$$A_1 = k_1 \frac{b}{P + 2b}, \tag{6}$$

$$A_2 = k_2 \frac{P}{P + 2b}, \tag{7}$$

where A_1 and A_2 are the absorptions of the bands characterizing mono- and di-species, respectively, whereas k_1 and k_2 are constants, depending on the extinction coefficients.

The fitting procedure at higher pressures for both curves gave $b = 20$ Pa, $k_1 = 2.55$ and $k_2 = 2.60$. The slightly higher value of k_2 as compared to k_1 indicates a little lower extinction coefficient of the band characterizing geminal species. This is consistent with their lower stretching frequency (compared to that of linear species). Taking into account very close wavenumbers of both bands, the difference between the extinction coefficients is expected to be very small.

It follows from equations (1) and (3) for the maximum of isotherm Θ_1 ($P = \sqrt{ab}$):

$$\Theta_{1,\mathrm{max}} = \frac{\sqrt{ab}}{2a + 2\sqrt{ab}}. \tag{8}$$

Moreover,

$$\Theta_{1,\mathrm{max}} = \frac{A_{1,\mathrm{max}}}{A_{\mathrm{max}}} = \frac{A_{1,\mathrm{max}}}{A_{2,\mathrm{max}}} \tag{9}$$

(because $\Theta_{\mathrm{max}} = 1$ and $A_{\mathrm{max}} = A_{2,\mathrm{max}}$).

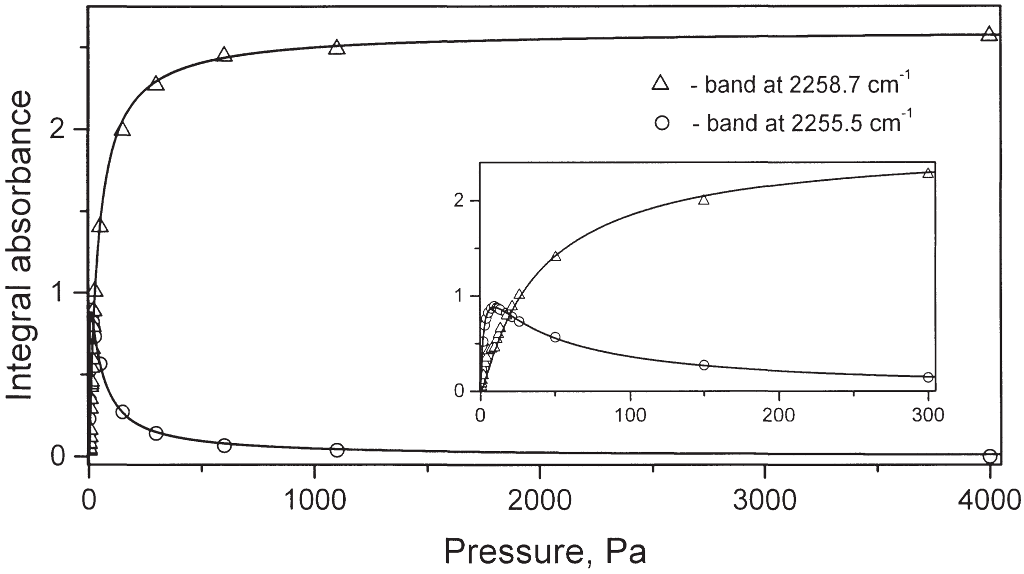

Figure 3. Experimental (data points) and theoretical (curves) adsorption isotherms for the formation of mono and geminal dinitrogen species at 85 K on NaY.

This allows an easy calculation of the coefficient a knowing $A_{1,\max}$, $A_{2,\max}$ and b. The resulting value is $a = 4$ Pa. This means that (assuming the same sticking coefficients for formation of linear and geminal species) the rate constant of desorption of the first molecule of the geminal complex is about five times higher than the respective constant for desorption of the second molecule. Figure 3 demonstrates that there is a very good fit between the theoretical curves and the experimental data.

It was already mentioned that the accuracy of the pressure measurements was low when $P < 50$ Pa. Therefore, the data points for A_1 (for pressures below 50 Pa) were placed on the theoretical curve for mono-species (inset figure 3). In this way the respective equilibrium pressure was determined. It is evident that the data points for A_2 (using the pressure values thus determined) fit well to the curve describing the adsorption isotherm of geminal complexes.

Thus, the results confirm the assignment of the band at 2258.7 cm^{-1} to linear $^{15}N_2$ species and of the band at 2255.5 cm^{-1} to geminal complexes.

5. Conclusions

- Adsorption of dinitrogen at 85 K on NaY zeolites results, at very low pressures, in formation of Na^+–$^{14}N_2$ complexes characterized by an IR band at 2336.8 cm^{-1} ($^{15}N_2$ at 2258.7 cm^{-1}). At higher pressures another molecule is coordinated to the same Na^+ site thus producing $Na^+(N_2)_2$ geminal dinitrogen complexes. The latter are characterized by an IR mode at 2333.5 cm^{-1} ($^{15}N_2$ at 2255.4 cm^{-1}).
- The changes of the mono- and di-species concentrations are excellently described by a mathematical model proposed earlier.

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