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# An ESR Study of Nitric Oxide Adsorbed on Silica Gel

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Nitric oxide adsorbed on silica gel was investigated by ESR. It was found that there are at least two adsorption sites for nitric oxide; one of them is on the silica gel which has been pretreated at low temperatures (below *ca.* 500 °C) (Site L), while the other is predominantly on the silica gel which has been pretreated at high temperatures (above *ca.* 500 °C) (Site H). The crystal-field splitting of the $\Pi_X^*$ and $\Pi_Y^*$ states, which are originally degenerate, was determined to be 0.26 eV for the nitric oxide adsorbed on Site L and 0.52 eV for the nitric oxide on Site H. The temperature dependence of the ESR spectrum was also examined, and the average crystal field acting on nitric oxide was found to decrease with an increase in the temperature.

Previously, the magnetic properties of nitric oxide adsorbed on silica gel surfaces have been studied by Solbakken *et al.*[1] by the measurement of the magnetic susceptibility. They reported that, at 181 and 193 K, nitric oxide is adsorbed entirely in a state with a magnetic moment the same as in the excited $^2\Pi_{3/2}$ state, while at 273 and 293 K it is adsorbed in the same average magnetic state of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$as in the gas phase. On the other hand, the ESR of nitric oxide adsorbed on solid surfaces has been observed in several adsorbent systems at the temperature of liquid nitrogen and at −180 °C.[2–10] In the ESR studies, it has been shown that, when nitric oxide is adsorbed on the solid surfaces, the orbital degeneracy of the $2p\pi^*$ level, which an odd number of electron occupy, is lifted by the surface field and the orbital angular momentum is quenched; that is, the ESR of nitric oxide in the adsorbed state can be explained by a spin-only paramagnetism and well reflects the nature of the interaction with the surfaces. A few attempts have been made to observe the ESR of nitric oxide adsorbed on the silica-gel surface.[5,7] However, no successful observation has yet been reported, although the ESR investigation of nitric oxide in the silica-gel system seemed to be interesting in connection with Solbakken's work and also for purposes of comparison with other adsorbent systems. In the course of studies of radicals trapped on solid surfaces, we could observe the ESR of nitric oxide adsorbed on silica gel. In this paper we will present the ESR observed for nitric oxide on silica gel and will discuss the interaction of nitric oxide with the surface.

## Experimental

The nitric oxide was obtained commercially from the Takachiho Chem. Ind. Co., Ltd., and was dried with $P_2O_5$. The silica gel used was a Tokyo Chem. Ind. Co. product for chromatography, with a surface area of 422 $m^2/g$. The gel was heated *in vacuo* at $10^{-6}$ Torr overnight prior to the adsorption of nitric oxide. The heating *in vacuo* was attempted at several temperatures between 300 °C and 600 °C. After the pretreatment of the silica gel, the nitric oxide was adsorbed onto the silica gel at −60 °C and at pressures ranging from 2 to 60 Torr. When the silica gel was evacuated at low temperatures (below 450 °C), an appreciable decrease of radical concentration was observed when the sample was left standing at room temperature. All the samples for ESR measurements, therefore, were immediately immersed in the liquid nitrogen after the nitric oxide had been adsorbed and the sample tube had been sealed off from the vacuum line.

The measurements of the ESR were carried out with a Hitachi model 771 ESR spectrometer with 100 kHz field modulation. The number of nitric-oxide molecules responsible for the ESR was determined by using a freshly-crystallized $CuSO_4 \cdot 5H_2O$ crystal as the standard.

## Results and Discussion

The ESR of nitric oxide observed at −196 °C are shown in Fig. 1. The hyperfine pattern observed is similar to those observed for the other adsorbent systems,[2–10] except that the linewidth is rather broader and the nitrogen hyperfine splitting is observed only as a shoulder. In Fig. 1, the sharp line with a *g*-value of 2.004 (indicated by A) is a background spectrum of silica gel which is produced by heating *in vacuo*. When the silica gel is preheated at temperatures higher than 550 °C, as Fig. 1b shows, a new additional absorption is observed on the low-field side of the nitric oxide spectrum (marked with B). This new absorption may be considered to be due to a paramagnetic center produced on the surface by the reaction with nitric oxide.

The ESR absorption due to nitric oxide changes appreciably with the preheating temperature of the silica gel. As Fig. 1 shows, when the silica gel is

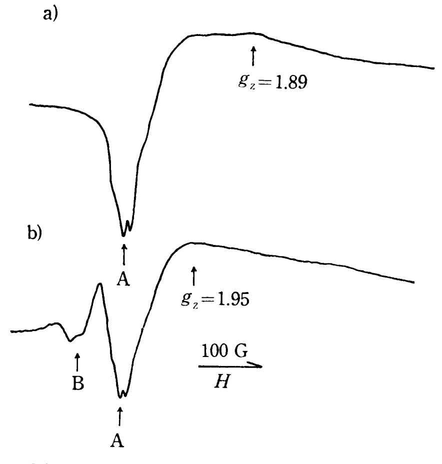

Fig. 1. ESR spectra, recorded at −196 °C, of nitric oxide on silica gel preheated at 500 °C (a), and at 600 °C (b).

pretreated at low temperatures (below *ca.* 500 °C), nitric oxide shows a spectrum with $g_z$ value of 1.89,[11] whereas when the silica gel is pretreated at temperatures above *ca.* 500 °C, the signal intensity at the absorption maximum corresponding to the $g_z$ value weakens appreciably and the maximum appears on the low-field side corresponding to $g_z=1.95$. These facts indicate that there are at least two different adsorption sites for nitric oxide on the silica-gel surface; one of the sites is on the silica gel which has been preheated at low temperatures (Site L), while the other is predominantly on the silica gel preheated at high temperatures (Site H). However, it is imagined that there may still be some small variety in these two adsorption sites, since the spectra show broad absorption bands.

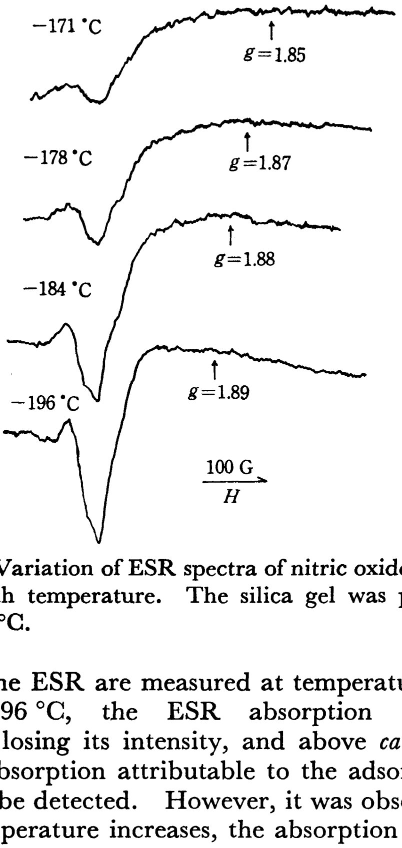

Fig. 2. Variation of ESR spectra of nitric oxide on silica gel with temperature. The silica gel was preheated at 550 °C.

When the ESR are measured at temperatures higher than −196 °C, the ESR absorption extensively broadens, losing its intensity, and above *ca.* −160 °C no ESR absorption attributable to the adsorbed nitric oxide can be detected. However, it was observed that, as the temperature increases, the absorption maximum in the $g_z$ region gradually shifts toward the high-field side (Fig. 2). In a way similar to that reported by Kanzig *et al.* for the $O_2^-$ molecule,[12] the following expression is derived for the $g_z$-value of nitric oxide:

$$g_z = g_e - 2\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2}. \qquad (1)$$

Here, $\lambda$ is the spin-orbit coupling constant and is estimated to be ~0.01 eV from the interval between the $^2\Pi_{3/2}$ and and $^2\Pi_{1/2}$ states, while $\Delta$ is the crystal-field splitting of the $\Pi_X{}^*$ and $\Pi_Y{}^*$ states. According to the equation, the increase in the $g_z$ value with the elevation of the temperature indicates that the effective surface field acting on the nitric oxide molecule weakens as the temperature is elevated and as the molecular motion becomes more active, implying that the orbital angular momentum, quenched by the interaction with the surface, recovers as the temperature is elevated. The marked linewidth broadening observed with the elevation of the temperature may be attributed to the large spin-orbit coupling, the magnitude of which is modulated with the fluctuation in the interaction of nitric oxide with the surface by the thermal agitation of nitric oxide.

Recetnly, Huang and Van Vleck tried to explain Solbakken's magnetic-susceptibility measurements by theoretical calculations.[13] They showed that Solbakken's observation may be explained by assuming that the average crystal field per molecule increases as the temperature is elevated. Our observation indicates, however, that the average crystal field acting on nitric oxide, rather, decreases as the temperature is elevated. It seems likely that the average magnetic moment of nitric oxide at low temperatures in the adsorbed state is much higher than that of nitric oxide in the gas phase at the same temperature, because the orbital angular momentum is quenched by the interaction with the surface and the molecule in the ground state, $^2\Pi_{1/2}$, which originally has no magnetic moment because of the cancellation of the orbital magnetic moment and the spin magnetic moment, comes to show paramagnetism due to electron spin.

Table 1. Values of $\Delta$ for nitric oxide

| Solid | (eV) | Ref. |
|---|---|---|
| Silica gel { site L | 0.26 | This work |
| Silica gel { site H | 0.52 | |
| MgO | 0.30 | 2 |
| ZnS | 0.33 | 3 |
| ZnO | 0.50 | 3 |
| Silica–alumina | 0.60 | 5 |
| Silica–magnesia | {0.33<br>0.60 | 5 |
| γ-Alumina | 0.75 | 5 |

The crystal-field splitting of the $\Pi_X{}^*$ and $\Pi_Y{}^*$ states, $\Delta$, was evaluated as 0.26 eV for nitric oxide on Site L and 0.52 eV for nitric oxide on Site H by means of Eq. (1). These $\Delta$ values are compared with those obtained in the other systems in Table 1. It should be noticed here that the value relates to the field gradient in the X or Y direction of the nitric oxide molecule;[9] therefore, it relates also to the adsorbed structure of nitric oxide. It is not necessarily proportional to the field strength primarily existing on the surface if there is any difference in the adsorbed structure in the solid systems.

The maximum concentration of nitric oxide responsible for the ESR absorption was obtained for the sample pretreated at temperatures higher than 500 °C as $0.9\times10^{18}$ spin/g, which corresponds to $2\times10^{11}$ spin/cm², with an error of ±30%, while for the sample pretreated at *ca.* 300 °C the spin concentration was much less (1/3~1/4), suggesting that the sites for adsorption were produced by the loss of a hydroxyl group, such as a siloxane group. The presence of the two adsorption sites, Site L and Site H, may be due to a difference in the surroundings of the two sites; Site L may be the siloxane group, with silanol groups surrounding it, while Site H may be the siloxane group, with no silanol groups surrounding it. The increase in the pressure of nitric oxide over 30 Torr at the adsorption process in the sample preparation did not seem to result in any appreciable increase in the radical concentration. This may be mainly due to the formation of the diamagnetic dimer of nitric oxide, $N_2O_2$, on the surface.

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**References**

1) A. Solbakken and L. H. Reyerson, *J. Phys. Chem.*, **63**, 1622 (1959).
2) J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967).
3) J. H. Lunsford, *J. Phys. Chem.*, **72**, 2141 (1968).
4) J. H. Lunsford, *ibid.*, **72**, 4163 (1968).
5) J. H. Lunsford, *J. Catal.*, **14**, 379 (1969).
6) B. M. Hoffman and N. J. Nelson, *J. Chem. Phys.*, **50**, 2598 (1969).
7) M. Shelef, *J. Catal.*, **15**, 289 (1969).
8) J. H. Lunsford, *J. Phys. Chem.*, **74**, 1518 (1970).
9) C. L. Gardner and M. A. Weinberger, *Can. J. Chem.*, **48**, 1317 (1970).
10) P. H. Kasai and R. J. Bishop, Jr., *J. Amer. Chem. Soc.*, **94**, 5560 (1972).
11) z Axis coincides with N–O bond axis.
12) W. Kanzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).
13) N. L. Huang and J. H. Van Vleck, *J. Chem. Phys.*, **50**, 2932 (1969).