

A Study of Surface Interactions on γ -Alumina, Silica-Alumina, and Silica-Magnesia using the EPR Spectra of Adsorbed Nitric Oxide

JACK H. LUNSFORD

From the Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received February 4, 1969

The EPR spectrum of the adsorbed NO molecule was used to determine crystal and magnetic field interactions on the surface of γ -alumina, silica-alumina, and silica-magnesia. The crystal-field splitting, Δ , of the $2p\pi^*$ levels of NO was found to be 0.75 eV on dehydrated γ -alumina and 0.60 eV on dehydrated silica-alumina. The spectrum on silica-magnesia indicated two adsorption sites with Δ equal to 0.60 and 0.33 eV. Spectra of NO on γ -alumina and silica-alumina show considerable hyperfine coupling with an ^{27}Al atom at the adsorption site. The spectra were very similar to the spectrum of NO on a decationated Y zeolite. The maximum number of adsorption sites (as indicated by the spin concentration) was found to be $4(\pm 1) \times 10^{12}$ sites/cm² for γ -alumina and two types of silica-alumina. Silica-magnesia had $1.1(\pm 0.3) \times 10^{12}$ sites/cm². The number of sites and the shape of the spectra were a function of the degree of dehydration. Water added back to dehydrated γ -alumina and silica-alumina also affected the spectra. It appears that these adsorption sites are the α sites which Peri has studied using the IR spectra of adsorbed CO₂.

INTRODUCTION

Electron paramagnetic resonance spectra have been used to explore crystal and magnetic field interactions on the surface of a number of solids of catalytic interest (1-5). The crystal-field interaction may be determined from the spectra of certain adsorbed molecules including nitric oxide and the superoxide ion. In both of these species the $2p\pi^*$ orbital, which contains the unpaired electron, is split by a low symmetry crystal field. This splitting of energy levels is exhibited in the g tensor of the EPR spectrum. Any magnetic interaction between the unpaired electron and nuclei with magnetic moments is apparent in the spectrum as hyperfine structure. In the present work these spectroscopic techniques were extended to γ -alumina, silica-alumina, and silica-magnesia. The nitric oxide molecule was used as the paramagnetic probe.

A recent EPR study of surface interactions on decationated Y zeolites showed

that very large electrostatic fields exist on the surface and that the adsorption site is characterized by weak magnetic interactions from an ^{27}Al nucleus (4, 5). It was of particular interest to compare the spectra of NO on amorphous silica-alumina with crystalline zeolites in an effort to detect features which might explain the large differences in catalytic activity. Furthermore, it was significant to compare the EPR results with the infrared work of Peri (6) who used the spectra of CO₂ to study adsorption sites on γ -alumina and silica-alumina. By way of contrast, silica-magnesia was investigated as an example of an active cracking catalyst which does not contain alumina.

EXPERIMENTAL

Two commercial-grade silica-alumina catalysts were used in this experiment. One was Aerocat AAA (American Cyanamid) with 25% Al₂O₃ and a surface area of 430 m²/g. The other was Houdry M-46 which con-

tained 13% Al_2O_3 and had a surface area of 270 m^2/g . A base-exchanged sample of silica-alumina was prepared by soaking M-46 in a 1.5 M aqueous solution of potassium acetate for 1 week. The sample was then rinsed with distilled water and dried. The high-purity alumina (Catapal) was obtained from Continental Oil (7). It was essentially in the gamma form and had a surface area of 280 m^2/g . The silica-magnesia was an experimental Houdry cracking catalyst with a surface area of about 380 m^2/g . Fisher silica gel was used as a blank in these experiments.

The standard degassing procedure included heating the sample slowly to 600°C under vacuum and then maintaining this temperature for 14 hr. The catalysts were subsequently heated in 700 Torr of O_2 for 1 hr and evacuated for 30 min at 600°C. After these samples were studied they were degassed an additional 14 hr either at 700 or 800°C. An alternate treatment of an Aerocat AAA catalyst involved heating the sample under vacuum for 2 hr (including approximately 30 min to reach temperature) at 200°C increments beginning at 100°C. After each heating period the sample was studied.

The ^{14}NO , which had a minimum purity of 98.5% as received from a commercial source, was further purified by the freeze-pump technique. Liquid nitrogen was used to freeze the nitric oxide. The ^{15}NO , enriched to 99.3% ^{15}N , was purified in the same manner. Upon each addition of the gas to the sample the nitric oxide was sublimed to minimize contamination from other oxides of nitrogen.

The NO was admitted onto the sample at room temperature and at pressures ranging from 0.4 to 100 Torr. The Vycor sample tube was sealed at room temperature by means of a stopcock, and the catalyst was tapped into a 4-mm diameter quartz sidearm. The sidearm with the catalyst was then cooled in liquid nitrogen.

A conventional X-band EPR spectrometer with a TE_{102} -mode microwave cavity was employed. All spectra were recorded with the sample at 77°K. The technique used to determine the g values and the absolute spin concentration have been described elsewhere (4, 8).

RESULTS

Analysis of the Spectra

NO spectra on γ -alumina. The spectrum shown in Fig. 1a was observed when ^{14}NO was adsorbed on γ -alumina that had been degassed at 600°C. The initial pressure of NO on this sample was 0.5 Torr at 23°C. Upon increasing the pressure to 10 Torr the amplitude of the spectrum approximately doubled but there was less resolution. This paramagnetic species could be easily removed by degassing the sample for 1 min at 23°C.

Comparison of the spectrum of Fig. 1a with the very similar spectrum of NO on a decationated Y-type zeolite (4) provides convincing evidence that the adsorption site for the NO molecule is essentially the same on both surfaces. The analysis of the spectrum, therefore, is the same as that carried out previously. The unpaired electron on ^{14}NO interacts magnetically with its ^{14}N nucleus which has a nuclear spin of 1 and with an ^{27}Al nucleus which has a spin of 5/2. This leads to a total of 18 hyperfine lines. In the resulting spectrum there may be an overlap of some of these lines. A theoretical stick figure is shown in Fig. 1b to demonstrate how the experimental spectrum could be generated. The ^{14}N splitting and the relative amplitude of the lines were taken from the spectrum of ^{14}NO on MgO (2).

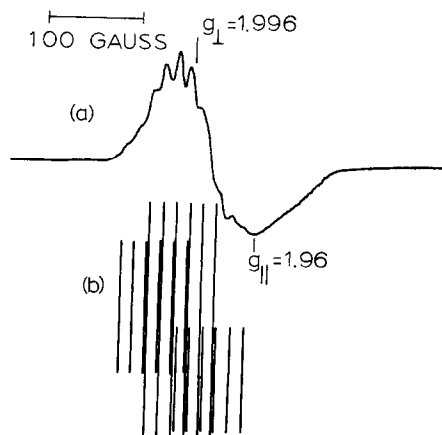


FIG. 1. (a) EPR spectrum of ^{14}NO on γ -alumina dehydrated at 600°C; (b) stick-figure representation of six equally spaced EPR spectra of ^{14}NO on MgO.

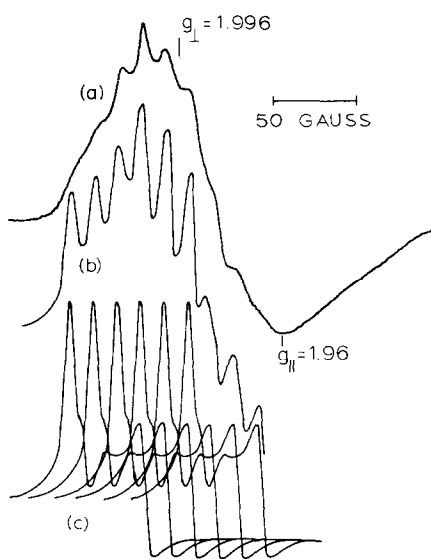


FIG. 2. (a) EPR spectrum of ^{15}NO on dehydrated γ -alumina; (b) theoretical spectrum that resulted from the summation of the six curves (amplitude reduced) in (c); (c) six equally spaced EPR spectra of ^{15}NO on MgO .

In Fig. 2 this same analysis was carried out for ^{15}NO adsorbed on γ -alumina. In this case only 12 hyperfine lines are expected since ^{15}N has a nuclear spin of $1/2$. The resulting theoretical spectra (Fig. 2b) generated by summing the six spectra of ^{15}NO on MgO (Fig. 2c) is in good agreement with the experimental curve (Fig. 2a). From this work a value of 14 ± 2 G for the hyperfine coupling with ^{27}Al has been determined.

The spectrum of the O_2^- species on a deca-cationated zeolite (5) lends additional support for the interpretation that the hyperfine structure is indeed that of ^{27}Al . The O_2^- spectrum unambiguously showed the six-line hyperfine structure which is characteristic of aluminum.

From the spectra in Figs. 1 and 2, values of $g_{\perp} = 1.996 \pm 0.002$ and $g_{\parallel} = 1.96 \pm 0.01$ were determined. The high-field minimum, which is used to determine g_{\perp} , was shifted to a slightly lower field when compared with the deca-cationated zeolite.

The maximum spin concentration of paramagnetic NO species was found to be 1.4×10^{19} spins/g or 4.9×10^{12} spins/cm 2 for γ -alumina that had been degassed at 600 or

700°C. A sample degassed at 500°C showed a spin concentration which was about 25% less than these values.

Approximately 10^{20} water molecules per gram of alumina were added back at 300°C to a previously degassed sample. After the sample was briefly evacuated (~ 15 sec) at 300°C and cooled to room temperature, the shape of the nitric oxide spectrum was considerably altered as shown in Fig. 3. In addition, the spin concentration was decreased by a factor of ten. One should note that the value of g_{\parallel} has changed to 1.94 and the aluminum hyperfine structure is no longer apparent. A degassed sample was also exposed to carbon dioxide at 23°C, but unlike water, most of the CO_2 could be reversibly desorbed. After subjecting the sample to 450 Torr of CO_2 and then evacuating for 30 min at 23°C the NO spectrum returned to 80% of its original amplitude.

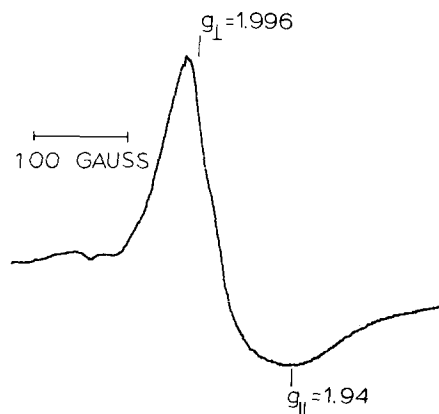


FIG. 3. EPR spectrum of ^{14}NO on γ -alumina after water was added back at 300°C.

NO spectra on silica-alumina. The spectra of ^{14}NO on Houdry M-46 and Aerocat AAA silica-alumina degassed at 600°C are shown in Fig. 4a. In general, the basic features of the spectra are nearly identical. They reveal less hyperfine resolution than the spectrum of NO on γ -alumina, but the similar features confirm that the ^{27}Al interaction was still present. The resolution was unaffected by the room temperature pressure of nitric oxide; however, the amplitude of the spectrum went through a broad maximum at a pressure of 1 Torr. The value of g_{\parallel} was 1.95

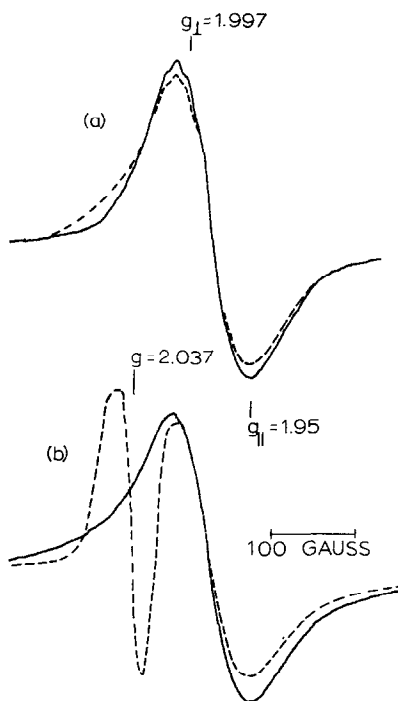


Fig. 4. EPR spectra of ^{14}NO on silica-alumina: (a) Dehydrated at 600°C , (b) dehydrated at 800°C ; (—) Aerocat AAA; (---) Houdry M-46.

± 0.01 , the same as was observed for the NO spectrum on decationated zeolites. A spin concentration of 1.0×10^{19} spins/g or 3.7×10^{12} spins/cm 2 was calculated for the Houdry M-46 sample, while a spin concentration of 1.4×10^{19} spins/g or 3.3×10^{12} spins/cm 2 was calculated for the Aerocat AAA sample.

No nitric oxide spectrum was observed following rehydration of the Houdry M-46 sample with 10^{20} water molecules per gram of sample at 150°C . After a brief evacuation at 300°C the nitric oxide spectrum could be detected again, but the amplitude was reduced by almost an order of magnitude. The value of g_{\parallel} remained the same.

The spectra shown in Fig. 4b were detected for the two silica-alumina samples after overnight under vacuum at 800°C and the subsequent addition of ^{14}NO at 23°C . It is evident that the hyperfine resolution has been reduced still further. The spectrum of NO on the Houdry M-46 sample is distinguished by a new resonance line with an

apparent g value of 2.037 ± 0.002 . Like the NO spectrum, the species responsible for this line could easily be removed by evacuation at 23°C . The amplitude of the new line was much more sensitive to NO pressure than the usual NO line. It was hardly discernible at 1 Torr of NO (23°C) but quite apparent at 10 Torr of NO (23°C).

In an effort to further show the effect of dehydration temperature upon the active sites of interest, a sample of Aerocat AAA silica-alumina was heated to progressively higher temperatures. The NO spectrum was recorded after each 200°C temperature increment. The spin concentration as a function of dehydration temperature is shown in Fig. 5. It should be noted that the different symbols in the figure represent different modifications of the spectra. The nitric oxide spectrum following the 100°C dehydration was characterized by a very broad high-field minimum with $g_{\parallel} = 1.87 \pm 0.01$. The hyperfine structure, though not well resolved, suggested interaction only with the nitrogen nucleus. The spectrum was very similar to that observed on a well-degassed NaY zeolite (4). After dehydration at 300°C the spectrum was essentially the same as that shown in Fig. 3 for NO on rehydrated alumina. Heating the sample under vacuum at 500 and 700°C lead to a spectrum like that in Fig. 4a while dehydration at 900°C resulted in a spectrum like that in Fig. 4b.

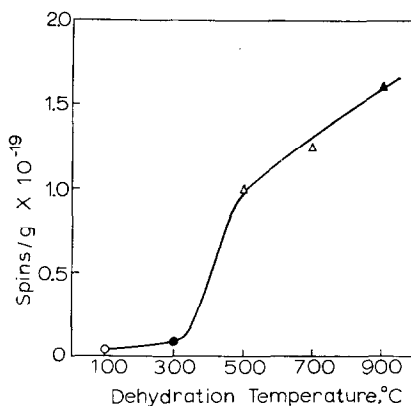


Fig. 5. Spin concentration as a function of dehydration temperature for Aerocat AAA silica-alumina; different symbols represent modifications in the spectra (see text).

The spectrum of NO on K-doped M-46 after overnight dehydration at 600°C indicated about the same spin concentration as was observed on the pure M-46. There was, however, a loss in hyperfine resolution, and the spectrum resembled more the curve shown in Fig. 4b for NO on AAA silica-alumina.

NO spectra on silica-magnesia. The spectrum of ^{14}NO on silica-magnesia that had been degassed at 600°C is shown in Fig. 6. The hyperfine structure reflects only the interaction with ^{14}N and is quite similar to that observed on magnesium oxide. A hyperfine splitting of 30 ± 2 G may be compared with 33 ± 1 G for ^{14}NO on MgO. The two high-field minima in Fig. 6 have g values of

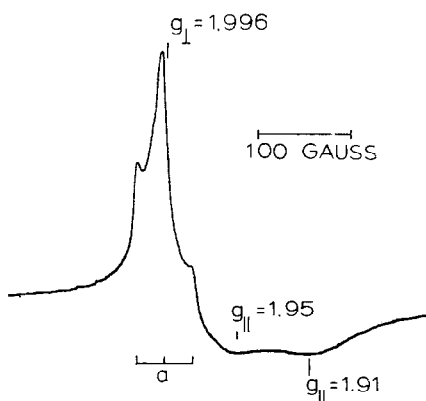


FIG. 6. EPR spectrum of ^{14}NO on silica-magnesia dehydrated at 600°C.

1.95 ± 0.01 and 1.91 ± 0.01 . The shape of the spectrum was not a function of the NO concentration, but it was observed that the amplitude of the spectrum continued to increase as the room temperature pressure of NO was increased to about 100 Torr. The spin concentration at the higher pressure was 4.0×10^{18} spins/g or 1.1×10^{12} spins/cm². Following dehydration of silica-magnesia at 800°C and subsequent addition of nitric oxide, no spectrum was observed. This was apparently the result of surface sintering since the surface area of silica-magnesia becomes very small after heat treatment at 800° (9).

NO spectra on silica gel. Nitric oxide adsorption on a sample of silica gel which had received the standard pretreatment at

600°C resulted in a very weak spectrum with a g value of 2.033 ± 0.002 . Though the amplitude was much less, the position and shape of this line was similar to the low-field line observed on Houdry M-46. No nitric oxide spectrum was detected.

DISCUSSION

Nature of the active site. The splitting Δ of the $2p\pi^*$ orbitals of NO by the crystal field at the adsorption site is given by (3, 4):

$$\Delta = \frac{2\lambda}{g_e - g_{\parallel}}$$

where g_e is the free-electron g value and λ is the spin-orbit coupling constant. For the NO molecule, $\lambda = 0.0150$ eV. It was calculated from the experimentally determined values of g_{\parallel} that $\Delta = 0.75$ eV for NO on dehydrated γ -alumina and $\Delta = 0.60$ eV for NO on dehydrated silica-alumina. The value of Δ for NO on silica-alumina degassed at 100°C was 0.23 eV which may be compared with 0.21 eV for NO on a dehydrated NaY zeolite (4). The results on silica-alumina clearly demonstrated that the crystal and magnetic field interactions, as well as the concentration of sites, strongly depended upon the degree of dehydration. Water added back to the samples at moderate temperatures likewise had an effect on the characteristics of the site.

The spectrum of nitric oxide on silica-magnesia showed two minima which denotes two values for g_{\parallel} or two types of adsorption sites. A similar situation was observed for the spectrum of NO on dehydrated magnesium oxide (2) where, at higher NO concentrations, three minima were observed with g_{\parallel} values of 1.95, 1.92, and 1.89. At lower concentrations only the minimum with $g_{\parallel} = 1.89$ was detected, and it was concluded earlier that the other two minima were only adjuncts to the main spectrum. It may be, however, that the other two minima were actually the g_{\parallel} components of the NO spectrum at other adsorption sites. If this is true, then the comparable values of g_{\parallel} on magnesium oxide and silica-magnesia suggest that similar adsorption sites exist on these two materials. The adsorbed state with $g_{\parallel} = 1.95$ confirms that the crystal field

interaction ($\Delta = 0.60$ eV) was as strong as that observed on silica-alumina. The value of $g_{\parallel} = 1.91$ corresponds to a Δ of 0.33 eV.

The characteristics of the sites for NO adsorption on γ -alumina and silica-alumina are remarkably similar to the α sites which Peri (6) has identified by means of the infrared spectra of adsorbed CO_2 . The surface concentration of sites on γ -alumina was essentially the same; 4.9×10^{12} sites/cm² as determined by the NO spectrum compared with 5.2×10^{12} sites/cm² as determined by 1-butene titration of the CO_2 spectrum. On silica-alumina a site concentration of $4(\pm 1) \times 10^{12}$ sites/cm² was found in the present work, whereas Peri observed a range of concentrations from 3×10^{12} to 9×10^{12} sites/cm², depending on the particular sample used. Comparable amounts of water added back prevented the formation of the NO(EPR) and CO_2 (IR) spectra; yet, CO_2 could be reversibly desorbed at room temperature. In addition, according to both techniques the number of adsorption sites on silica-alumina increased somewhat upon dehydration at 800°C as compared to dehydration at 600°C. Peri states that the adsorption of CO_2 on α sites is probably best explained by ion-quadrupole interaction. In a like manner it appears that the NO molecule is held by crystal field interactions. The α sites, according to Peri, are formed upon loss of hydroxyl groups from the aluminum atoms. The resulting structure appears to be an $\text{Al}^+\text{O}^{2-}\text{Al}^+$ group. If the sites are indeed the same, the hyperfine structure indicated that the paramagnetic species was interacting with only one Al^+ during a period which was long compared to 10^{-9} sec. It may be that the loss in hyperfine resolution for certain samples was due to rapid motion of the molecule from one aluminum ion to the other.

Relationship to catalytic activity. One may conclude that a similar set of adsorption sites for nitric oxide exists on γ -alumina, silica-alumina, and decationated Y-type zeolites. These sites, which contain an aluminum atom or ion, are characterized by strong crystal field interactions with the adsorbed molecules. They begin to develop at about 400°C and increase in concentration as the dehydration temperature is increased, which

indicates that their formation is related to the loss of certain hydroxyl groups from the surface. The site concentration on decationated zeolites went through a maximum at 650°C, probably because of the annealing of unstable defects. A surprisingly consistent maximum site concentration of $4(\pm 1) \times 10^{12}$ sites/cm² was found for these materials. The sites are apparently not affected by the aluminum content (down to some lower limit) or the crystallinity of the sample.

One would like to evaluate the role of these sites in the catalytic activity; however, it is difficult to draw any general conclusions since the relative activity of each catalyst varies greatly with the particular reaction. For example, the cracking of 2,3-dimethylbutane goes with approximately the same ease on dehydrated silica-alumina and alumina (10). For this case the catalytic activity is at least consistent with the observation that the site concentration is essentially the same on both catalysts. On the other hand, the activity of silica-alumina is much higher than the activity of alumina for dealkylation of cumene (?). This difference in activity is usually explained in terms of greater Brønsted acidity for the silica-alumina. For this system it is clear that the NO adsorption site is not solely responsible for the activity; yet, it may be indirectly related through some mechanism whereby it causes a proton in a SiOH group to become acidic.

The unusually high activity of decationated zeolites for all reactions which are catalyzed by silica-alumina is also inconsistent with the constant concentration of adsorption sites. This difficulty can be explained by considering the higher degree of order in the zeolite which may (a) enhance the acid forming mechanism (11) or (b) result in a high ionic mobility that facilitates rapid desorption of the products (12). These conjectures, of course, only form the basis for a more detailed study on a given catalytic system.

ACKNOWLEDGMENT

The author acknowledges the support of this work by The Robert A. Welch Foundation under Grant No. A-257.

REFERENCES

1. KASAI, P. H., *J. Chem. Phys.* **43**, 3322 (1965).
2. LUNSFORD, J. H., *J. Chem. Phys.* **46**, 4347 (1967).
3. LUNSFORD, J. H., *J. Phys. Chem.* **72**, 2141 (1968).
4. LUNSFORD, J. H., *J. Phys. Chem.* **72**, 4163 (1968).
5. WANG, K. M., AND LUNSFORD, J. H., *J. Phys. Chem.* **73**, (1969).
6. PERI, J. B., *J. Phys. Chem.* **70**, 3168 (1966).
7. TUNG, S. E., AND McININCH, E., *J. Catalysis* **3**, 229 (1964); **4**, 586 (1965).
8. LUNSFORD, J. H., AND JAYNE, J. P., *J. Chem. Phys.* **44**, 1487 (1966).
9. RIES, H. E., MELIK, J. S., AND JOHNSON, M. F. L., *Disc. Faraday Soc.* **8**, 303 (1950).
10. HALL, W. K., LUTINSKI, F. E., AND GERBERICH, H. R., *J. Catalysis* **3**, 512 (1964).
11. RICHARDSON, J. T., *J. Catalysis* **9**, 182 (1967).
12. TUNG, S. E., AND McININCH, E., *J. Catalysis* **10**, 175 (1968).