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Studies of the ESR Spectra of Alumina

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The ESR spectra of a number of samples of η- and γ-alumina have been studied after a variety of pretreatments. A triplet in the spectrum of some commercial aluminas has been identified as NO_2 strongly bound to the alumina. The triplet can also be generated by treatment with HNO_3 of alumina not initially showing the triplet, or by decomposition of $Al(NO_3)_3 \cdot 9H_2O$. Treatment with D_2O at 550°C does not affect the triplet. Treatment with H_2 at 550°C converts the triplet to an intense singlet. Reoxidation regenerates the triplet, though with reduced intensity. The NO_2 is probably reduced by H_2 to NO, which is also relatively strongly bound to the alumina and can be reoxidized to NO_2.

INTRODUCTION

Studies of the electron spin resonance (ESR) spectra of catalytic grade alumina (Al_2O_3) have been used to investigate the products of high energy irradiation (*1, 2*) and the formation of radicals (*3, 4*). The importance of the purity of the Al_2O_3 for ESR studies was illustrated by Berger and Roth (*5*). Their work shows that the presence of paramagnetic impurities in most commercial samples tends to confuse and even prevent the study of catalytic processes on the surface of alumina. Iron (probably in the form of Fe^{3+}) is the most common impurity and its resonance is usually in the region of most interest. Sancier and Inami (*6*) have observed a broad resonance at $g = 2.1$ only on reduction of Fe^{3+}-containing Al_2O_3 with H_2, while Berger and Roth (*5*) have observed a similar (but not necessarily identical) resonance under oxidizing conditions in some aluminas. Berger and Roth also noted a triplet ESR absorption and attributed this to a possible trapped electron or hole. The triplet was shown to disappear or be masked on reduction with H_2 but to reappear on oxidation with O_2. This triplet did not appear in high purity Al_2O_3 even when it was heated in air at 500°C. An extensive study has been undertaken here which indicates that the triplet can be attributed to the presence of NO_2 on the alumina surface. The presence of nitrogen on the surface of Al_2O_3 has previously been demonstrated by Rosenblatt and Dienes (*7*) by mass spectroscopic measurements.

EXPERIMENTAL

Commercial alumina. Two samples of η-Al_2O_3 and one of γ-Al_2O_3 were obtained from the Houdry Laboratories of Air Products and Chemicals. A different sample of η-Al_2O_3 was supplied by the Davison Chemical Division of W. R. Grace. A sample of high purity γ-Al_2O_3 (*5*) was graciously supplied by Dr. J. F. Roth of the Monsanto Co. The analysis of the samples is given in Table 1.

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TABLE 1

ANALYSIS OF ALUMINA SAMPLES

Type	η	η	η	γ	γ	$Al(NO_3)_3$	$Al(NO_3)_3$
Source	Houdry	Houdry	Davison	Houdry	Monsanto	Baker	Fisher
Supplier's sample No.	110J91-3Z	110J91-2Z	—	—	NPB593750	62246	744300
Our identification	A	B	C	D	E	F	G
BET surface area, m^2/g	250	235	—	195	186	—	—
Fe_2O_3, %	0.001	<0.001	0.011	<0.005	<0.0001	0.0005	0.001
Other transition elements as the oxides, %	0.014 max	0.0005	0.00005	—	—	0.0005	0.001
Nontransition elements as oxides, %	0.3350 max	0.21 max	~0.0335	0.03	—	0.04	0.05

$Al(NO_3)_3 \cdot 9H_2O$. Three sources of $Al(NO_3)_3 \cdot 9H_2O$ (Baker, Fisher, and Merck) were used for the preparation of amorphous Al_2O_3. The latter was prepared in each case by thermal decomposition at 550°C for 12 hr in air. The analytical data on the Merck nitrate are not known, but the others are given in Table 1.

ESR measurements. The ESR spectra of all samples were determined on a Varian V 4502-19 X-band (9.5 GHz) spectrometer. The g values and splitting parameters were measured from precise field determinations using a Magnion proton-oscillator gaussmeter. Measurements of the cavity frequency were carried out using a Hewlett-Packard frequency meter. The spin numbers were estimated by comparison with Varian standard pitch samples. The field dependence of a few samples was determined by comparing the X-band measurements with those obtained on a Varian V 4502-09 Q band (35 GHz) spectrometer. ESR grade quartz sample tubes (3-mm i.d.) supplied by Wilmad, Buena, N. J., were used for all determinations.

The treatment of the samples with gases (H_2, O_2, H_2O, and D_2O) was carried out by preevacuating at 550°C for 1 hr prior to admission of H_2 or 3 hr for the other gases. The sample tubes were sealed in the appropriate atmosphere while heated at 550°C. The D_2O-treated samples were heated at 300°C for 4 hr to insure complete exchange (*8*, *9*).

Results and Discussion

The spectra of the Houdry A sample as received or after preevacuation at 550°C for 3 hr were identical. The spectrum is illustrated in Fig. 1, and the ESR data are summarized in Table 2. The g, A (splitting), and ΔH (width) values of the triplet were found to be independent of the field by comparison of the X-band and Q-band data. This clearly indicates that the observed triplet arises from the nuclear splitting of an isotope with a nuclear spin $I = 1$. Of the common isotopes only ^{14}N

TABLE 2
ESR Data

Sample	g	ΔH (G)[a]	A (G)	Fig.
A evacuated at 550°C	1.999	15.3	56.2	1
A treated with H_2 8 times at 550°C	1.99[b]	81.7	—	2
A + D_2O at 550°C	1.999	15.3	53.1	
C as received	2.04	95.0	—	3a
C washed in HCl	2.04	138.5	—	3b
C washed in HCl, treated with HNO_3	1.998	16.2	56.1	3c
Al_2O_3 from Baker $Al(NO_3)_3 \cdot 9H_2O$	2.000	20.7	53.3	4

Note: All values to ±1 last significant figure.

[a] Center signal for triplet resonances, width at baseline for $g = 2.04$ resonances.

[b] Average value $g_{\parallel} = 1.96$, $g_{\perp} = 2.00$.

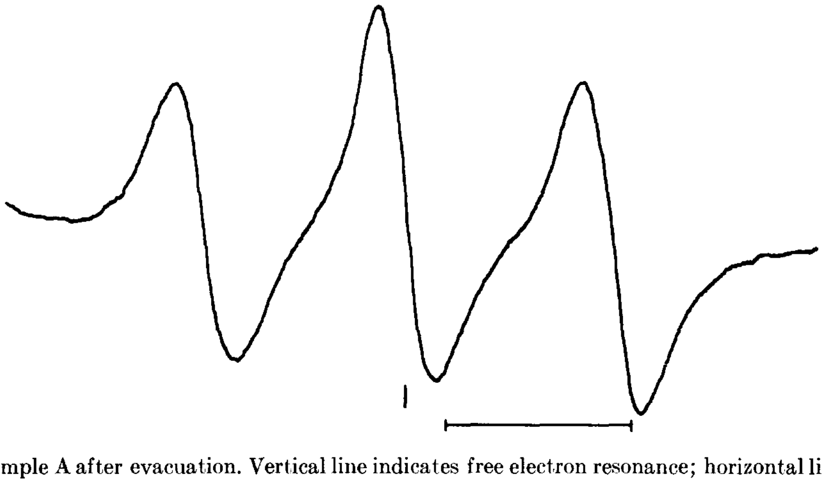

Fig. 1. Sample A after evacuation. Vertical line indicates free electron resonance; horizontal line indicates 50 G.

has $I = 1$; thus, the triplet apparently arises from an unpaired electron on nitrogen.

Treatment of the Houdry A sample three times with H_2 at 550°C for 15 min each time followed by evacuation for 15 min changes the triplet to a more intense singlet, which is illustrated in Fig. 2 and summarized in Table 2. If the H_2-reduced sample is oxidized with O_2 gas at 550°C for 12 hr, the triplet reappears but with 60% of its former intensity. Thus the triplet arises from an oxidized species. Further treatment of the samples with H_2O or D_2O gas does not alter the triplet signal (Table 2), which indicates that the paramagnetic species is not associated with H atoms, since an alteration of the triplet would be expected on deuterium exchange. The g, A and ΔH values of the triplet are nearly identical with those of NO_2 adsorbed on Linde Na-X Molecular sieve (*10*) and on other solid matrices (*11*). Thus, the evidence seems convincing that the triplet signal observed on the Houdry sample arises from NO_2 on the surface of the Al_2O_3.

The intensity of the triplet signal as a function of the surface area of two Houdry η-Al_2O_3 samples and one Houdry γ-Al_2O_3 sample was also studied. The observations are given in Table 3, and they suggest that in the case of η-Al_2O_3 a correlation of the spin density and the surface area may exist. The sample of γ-Al_2O_3 does not correlate with the η-Al_2O_3 samples, however, and presumably the γ-Al_2O_3 contains less adsorbed NO_2.

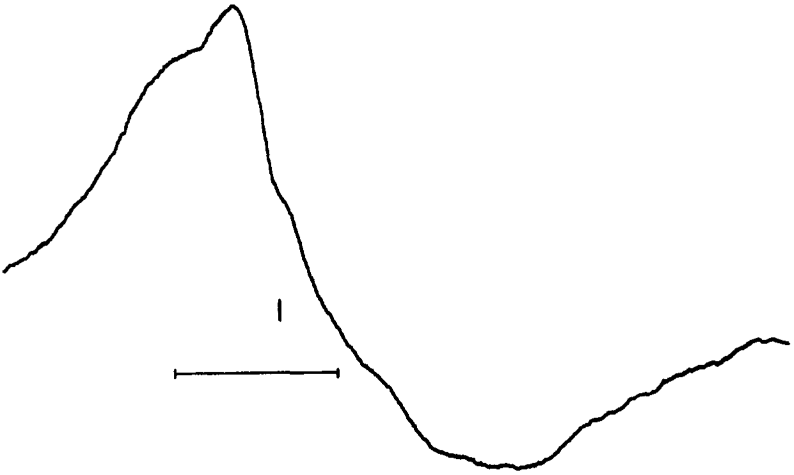

FIG. 2. Sample A treated with H_2 and evacuated. Vertical line indicates free electron resonance; horizontal line indicates 50 G.

TABLE 3
CORRELATION OF SURFACE AREA AND NUMBER OF SPINS

Sample	Surface area (m^2/g)	No. of spins (units of 10^{13})
A	250	56.6
B	235	51.0
D	195	1.0

The Davison sample C of η-Al_2O_3 has a broad ESR spectrum at $g = 2.04$ and a width of 95.0 G (Table 2, Fig. 3a). The width of the signal is sufficient to mask only one of the components of the NO_2 triplet. Since high field components of the triplet were not observed at maximum sensitivity of the spectrometer, it can be concluded that NO_2 is present to less than 10^{13} spins. The Monsanto sample E was found to be free of paramagnetic impurities to less than 10^{13} spins. The results on the Davison and Monsanto samples corroborate the previous findings of Berger and Roth (*5*).

In order to reduce the concentration of transition metal impurities, the Davison

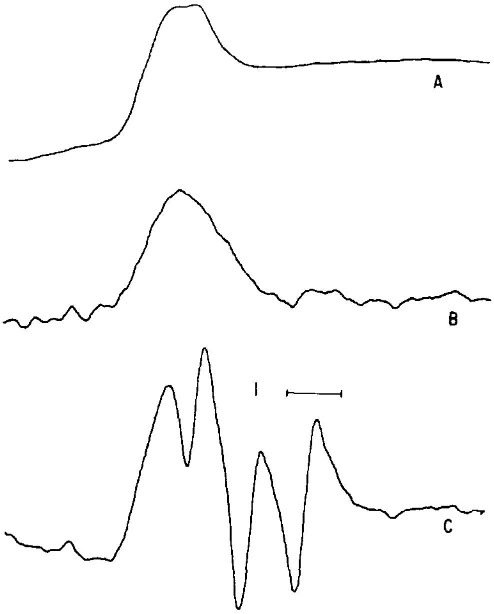

FIG. 3. Sample C. Curve (a): As received; recorder amplification 1×. Curve (b): Washed with HCl; recorder amplification 10×. Curve (c): Washed with HCl and treated with HNO_3; recorder amplification 10×.

sample was twice boiled in concentrated HCl (12 *N*, Baker) for 1 hr, filtered, and dried at 550°C for 12 hr. The ESR signal of the as-received sample was thus reduced tenfold in intensity and was detected at maximum sensitivity. This spectrum, shown in Fig. 3b, was recorded at tenfold higher recorder sensitivity. When this purified sample was further treated by boiling in concentrated in HNO_3 (16 *N*, Baker) and then dried at 550°C for 12 hr, the spectrum was a composite of the NO_2 triplet and the previous impurity singlet. This spectrum is shown in Fig. 3c, also at higher recorder sensitivity. Similar leaching of the as-received Davison sample directly with concentrated HNO_3 also reduced the broad signal and showed the NO_2 triplet.

The ESR spectra of amorphous Al_2O_3 prepared by the thermal decomposition of Baker, Fisher, or Merck $Al(NO_3)\cdot 9H_2O$ were similar. The spectrum for the Baker sample is given in Fig. 4, and the data are summarized in Table 2. Each sample has the NO_2 triplet and a singlet at $g = 1.96$. The latter is most likely due to a Cr^{3+} impurity.

These results show that the ESR triplet spectrum previously observed on Al_2O_3 is not due to trapped electrons, holes, or transition metal impurities but is due to NO_2. The source of the NO_2 is not air since heating of pure Al_2O_3 in air does not give rise to the triplet (*5*). It would appear from this work that the probable source of NO_2 in the aluminas is the thermal decomposition of NO_3^- which may be present in the preparations. The intense singlet characteristic of H_2-treated Al_2O_3 (Fig. 2) is probably due to NO resulting from reduction of the

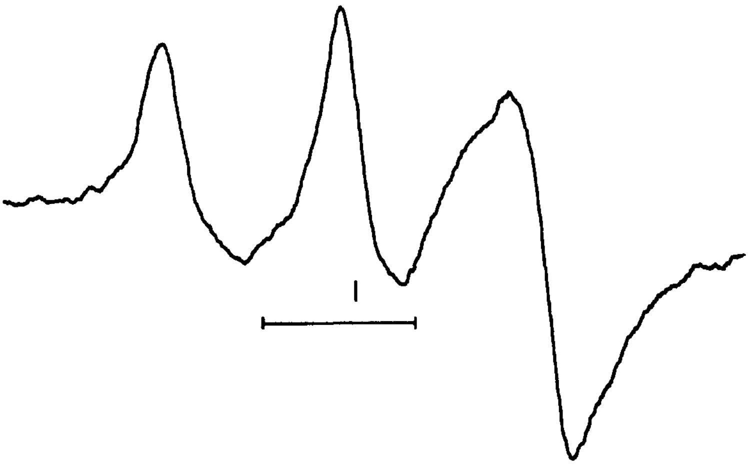

FIG. 4. Thermally decomposed $Al(NO_3)_3\cdot 9H_2O$ (Baker). Vertical line indicates free electron resonance; horizontal line indicates 50 G.

NO_2. Lunsford (*12*) has very recently shown that NO on Al_2O_3 gives a singlet nearly identical to ours, with $g_{\parallel} = 1.96$ and $g_{\perp} = 1.996$.

Oxidation of the reduced samples with O_2 restores the NO_2 triplet, indicating that some of the NO remains on the Al_2O_3. The loss of intensity of the triplet by 40% on such treatment indicates partial removal of the nitrogen in either the reduced or oxidized forms. Berger and Roth (*5*) noted that the triplet could be removed by evacuation for several hours at 500°C of their sample of Davison η-Al_2O_3. In this work the NO_2 was not removed from Houdry η-Al_2O_3 on evacuation for 3 hr at 550°C. This difference in the adsorption of the NO_2 may only be due to the difference in the nature of the samples.

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REFERENCES

1. ACRES, G. J. K., ELEY, D. D., AND TRILLO, J. M., *J. Catalysis* **4**, 12 (1965).

2. FOURNIER, J. T., AND BARTRAM, R. H., *J. Chem. Phys. Solids* **29**, 2029 (1968).

3. FLOCKHART, B. D., LEITH, I. R., AND PINK, R. C., *J. Catalysis* **9**, 45 (1967).

4. ONO, Y., AND KEII, T., *J. Phys. Chem.* **72**, 2851 (1968).

5. BERGER, P. A., AND ROTH, J. F., *J. Catalysis* **4**, 717 (1965).

6. SANCIER, K. M., AND INAMI, S. H., *J. Catalysis* **11**, 135 (1968).

7. ROSENBLATT, D. B., AND DIENES, G. J., *J. Catalysis* **4**, 271 (1965).

8. MILLS, G. A., AND HINDIN, S. G., *J. Am. Chem. Soc.* **72**, 5549 (1950).

9. HALDEMANN, R. G., AND EMMETT, P. H., *J. Am. Chem. Soc.* **78**, 2917 (1956).

10. COLBURN, C. B., ETTINGER, R., AND JOHNSON, F. A., *Inorg. Chem.* **2**, 1305 (1963).

11. FISHER, H., LANDOLT-BÖRNSTEIN, Neue Serie, Group II, Vol. 1 (K. H. Hellwege, ed.), p. 14, Springer-Verlag, Berlin, 1965.

12. LUNSFORD, J. H., *J. Catalysis* **14**, 379 (1969).