

NOTES

ESR Studies of Aluminas

INTRODUCTION

Turkevich and co-workers (1) have recently reported electron spin resonance (ESR) studies of commercial palladium-on-alumina catalysts. They observed a broad line resonance that changed both in linewidth and g factor when the catalysts were subjected to reduction in hydrogen. The origin of this broad line was not elucidated. We have been conducting ESR studies of cupric oxide supported on a commercial alumina (results to be reported at a later date) and have found that the alumina support itself gives rise to a broad line qualitatively similar to that observed by Turkevich and co-workers. Therefore, we have investigated the ESR spectra of various alumina supports under a variety of conditions. Measurements have been made on three aluminas obtained from commercial sources and on a high-purity alumina prepared in this laboratory. The commercial aluminas all produced spectra that are attributed directly or indirectly to the presence of paramagnetic impurities. The high-purity sample gave no ESR absorption spectra, presumably because of its low level of paramagnetic impurities (transition metals). Some studies have been made on the effects of evacuation, hydrogen treatment, and subsequent oxidative treatment. Narrow lines with g value near that of the free electron can be observed in all samples after evacuation at high temperature.

EXPERIMENTAL

The aluminas obtained from commercial sources were Davison high-purity eta alu-

mina (η), Harshaw 0104 (γ), and Kaiser experimental XA 331 (γ) alumina. High-purity γ alumina was prepared from triply distilled aluminum isopropoxide (J. T. Baker Chemical Company) according to Bridges *et al.* (2). It was found to be principally γ alumina. The indicated structures of all four aluminas were determined by X-ray diffraction analysis using for structure assignment the diffraction patterns given by Newsome and co-workers (3).

The impurity contents were evaluated by emission analysis with a Jarrell-Ash 3.4 Ebert Model 19-300 emission spectrograph (Table 1). It should be noted that 1 ppm of, e.g., iron (as oxide) corresponded to about 10^{14} spins in the cavity.

TABLE 1
MAIN IMPURITIES DETERMINED BY
EMISSION ANALYSIS^a

	Kaiser XA 331	Harshaw 0104	High-purity γ alumina	Davison Eta
Cr	N.D.	N.D.	N.D.	10-50
Mn	5-10	5-10	N.D.	5-10
Fe	50-100	10-50	<1	~100
Co	N.D.	N.D.	N.D.	N.D.
Ni	N.D.	1-5	N.D.	~50
Cu	5-10	100-500	N.D.	~100

^a Numbers indicate ppm.

The ESR spectra were recorded at 9.5 Gc/sec on a Varian V4502 X-band spectrometer in a TE₀₁₂ cavity. The apparatus was equipped with the Fieldial calibrated sweep system and a 6-inch magnet. Measurements in the range of -175° to $+300^{\circ}$ C were made using Varian's variable temperature accessory V4557. All measurements were made at a power level of

30 mW. No saturation effects were observed. Samples were contained in standard quartz tubes obtained from Varian. These tubes were connected to a conventional vacuum system for the various treatments and were sealed prior to transfer to the cavity. The g values were measured by comparison with crystalline diphenylpicrylhydrazyl (DPPH) ($g = 2.0036 \pm 0.0003$).

RESULTS AND DISCUSSION

No ESR absorption was observed for the high-purity γ -alumina sample when examined without further treatment. However, the Kaiser and Davison aluminas gave rise to a broad anisotropic absorption when measured in air at room temperature, with linewidths of 650 and 550 gauss, respectively, and g factors 2.49 and 2.09 ($\pm 3\%$). The linewidth of this absorption had a strong dependence on the surrounding atmosphere and on temperature (Table 2). The reduction in linewidth observed in

TABLE 2
LINewidths OF BROAD ESR ABSORPTION
($\Delta H \pm 2\%$)

Sequential treatments	Davison Eta	Kaiser XA 331
Air ^a	540	660
10 ⁻⁵ Torr, 500°C ^a	500	575 ^b
10 ⁻⁵ Torr, 500°C ^c	706	1260 ^b
260 Torr, H ₂ ^d	—	—
-170°C	727	1167 ^b
-160°C	685	—
-100°C	—	1178 ^b
-10°C	573	1157 ^b
+50°C	491	1024 ^b
+150°C	325	850 ^b
+300°C	1331	491
10 ⁻⁵ Torr, 500°C ^a	^b	809
Air, 500°C ^a	543	696

^a Spectra recorded at room temperature.

^b Very strong absorption at zero magnetic field.

^c Spectra recorded at -170°C.

^d Spectra recorded at indicated temperatures.

the evacuated samples at room temperature was accompanied by an increase of intensity by a factor of about 1.7. This suggests that part of the paramagnetic impurity ions are located on or near the surface and interact with adsorbed oxygen by way of a dipolar relaxation mechanism.

When the evacuated samples were kept under 260 Torr of hydrogen at temperatures ranging from -170° to 300°C and measured under these conditions, changes in linewidths and absorption at zero magnetic field were observed. These spectra in Table 2 are, of course, not intrinsic to alumina. Differences in the behavior of the two samples were certainly due to differences in the content and the environment of impurities.

The same argument applies with respect to Harshaw alumina, which has a completely different impurity composition and ESR spectra. An absorption with g value varying from 3.9 to 4.5 was particularly noticeable in the Kaiser and Davison aluminas. It might be a component of the powder spectrum of an impurity and associated with the broad line.

Narrow signals were observed that appear to be due to some form of trapped electrons or holes (Table 3). In air, only the Davison sample exhibited three lines of equal intensity with g values 2.034, 2.001, and 1.967 ($\pm 0.1\%$). When this sample was evacuated to 10⁻⁵ Torr at 500°C for several hours, only a line with $g = 2.003 \pm 0.002$ remained. Under the same treatment, a narrow line with $g = 2.003$ appeared in all the aluminas. In the case of the high-purity γ alumina, this narrow absorption was of very low intensity at room temperature, but was readily detected at -170°C.

The sharp signal remained throughout all the further treatments except the reoxidation. On reoxidation, the three lines in the Davison sample were identically restored and the other samples no longer contained the sharp signal.

Except for an investigation on irradiated γ alumina (4) no systematic study of trapped electrons or holes in transition aluminas is known to us. Comparison of our results with work published on ZnO (5) and TiO₂ (6) under similar experimental conditions suggests that the narrow signal with $g = 2.003$ is due to mobile electrons. In fact, transition aluminas exhibit semiconductor properties (7). The absence of g -factor anisotropy and hyper-

TABLE 3
 g VALUES OF LINES ATTRIBUTED TO FREE ELECTRONS AND/OR ADSORBED OXYGEN SPECIES^a

Sequential treatments	Davison Eta	Kaiser XA 331	Harshaw 0104	High-purity γ alumina
Air	2.034 \pm 0.002	—	—	—
	2.001 \pm 0.002	—	—	—
	1.967 \pm 0.002	—	—	—
10 ⁻⁵ Torr, 500°C } 330 Torr H ₂ , 500°C } 10 ⁻⁵ Torr, 500°C }	2.003 \pm 0.002	2.003 \pm 0.002	2.003 \pm 0.002	2.003 \pm 0.002
Air, 500°C	2.034 \pm 0.002	—	—	—
	2.001 \pm 0.002	—	—	—
	1.967 \pm 0.002	—	—	—

^a g values measured at room temperature.

fine structure points to a mobile species of charge carrier. Kazanskii *et al.* (7) have also assigned a line with $g = 2.002$ to free electrons captured in the conduction band.

A relation seems to exist between impurity content (as measured by the broad absorption) and the presence of the $g = 2.003$ signal. Introduction of extraneous cations will, of course, help to establish color centers and give semiconducting properties to the alumina.

In conclusion, we attribute the broad lines to impurities and not to adsorbed oxygen species. Impurities may also be responsible for the broad line found in palladium-alumina catalysts (1). The narrow line with $g = 2.003$ is thought to be due to mobile electrons.

These results illustrate spectra that may arise directly or indirectly from impurities in, or from, high-temperature evacuation of aluminas.

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Infrared Emission Spectra of Surfaces—An Interferometric Approach

Techniques for measuring infrared emission spectra of solid surfaces have recently been described (1). Conventional spec-

trometers were employed, and useful emission spectra were obtained. However, in order to obtain enough emitted radiation to