Paramagnetic Platinum and Oxygen Species on Supported Platinum

J. R. KATZER,[*,1] G. C. A. SCHUIT,[*] AND J. H. C. VAN HOOFF[†]

*Center for Catalytic Science and Technology, and
†Technische Hogeschool Eindhoven, The Netherlands

EPR was used to determine the paramagnetic platinum and oxygen species which are present at various stages in the genesis of a supported platinum catalyst and to determine the effect of the support on the formation of such species. Paramagnetic platinum centers, believed to be due to Pt^{3+}, are formed when $Pt(NH_3)_4^{+2}/Al_2O_3$ is calcined in O_2; for low metal contents a large fraction of the platinum is in the form of these species. Catalysts prepared by the same techniques with SiO_2 as a support show no paramagnetic platinum signals. Adsorption of O_2 on the Pt/Al_2O_3 catalysts results in the formation of a 3-g O_2^- signal and a second 2-g signal due to O^- and results in a corresponding reduction in the platinum signal. Again Pt/SiO_2 did not show comparable behavior. The results are interpreted in terms of electron transfer to the Al_2O_3.

INTRODUCTION

Although there has been a continuous increase in the number of spectroscopic techniques applied to the study of heterogeneous catalysts, no single technique provides sufficiently complete characterization. Combination of as many characterization techniques as appropriate and integration of all of the information obtained can provide a much better understanding of a heterogeneous catalyst, yet adequate catalyst characterization remains a most important need in our understanding of heterogeneous catalysis. Electron paramagnetic resonance (EPR) has been successfully applied to the study of transition metal oxide surfaces (1–7), but only limited EPR results have been reported on "more metallic" systems (8–14). EPR work on supported catalysts has been limited to O_2 on Ag/SiO_2 (8–10), Pd-Y zeolite (14),

and to chlorine-containing Pt, Pt–Ir, and Ir catalysts on Al_2O_3 (13).

There is an increasing body of evidence that even for metals as noble as platinum chemical interactions with the support may play an important role under many conditions. For example, Katzer et al. (15) have shown from EXAFS studies of supported Pt that there appears to be electron transfer from small Pt crystallites to alumina which increases with decreasing Pt crystallite size. Boudart and Gallezot (16) have observed no electron transfer from small Pt crystallites to monovalent Y zeolite but have observed electron transfer with multivalent (Ce) Y zeolites. Our EXAFS results as well as those of Lytle (17) show little electron transfer from supported Pt to silica.

Tauster et al. (18) have reported that Pt/TiO_2 chemisorbs H_2 normally after low-temperature reduction, but after high-temperature reduction it will not chemisorb H_2, although the Pt remains highly dispersed. Den Otter and Dautzenberg (19)

[1] Address correspondence to J. R. Katzer, Department of Chemical Engineering, Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19711.

Catalyst	Pt (wt%)	D^a	$d_p{}^b$ (nm)
Pt/Al$_2$O$_3$	0.40	1.00 (1.14)	<1.0
Pt/Al$_2$O$_3$	2.90	0.84	1.2
Pt/SiO$_2$	2.90	0.69	1.5

^{a} D = Dispersion = No. of Pt atoms on surface/
total No. of Pt atoms (chemisorption ratio greater
than 1.00 as shown in parentheses indicates devia-
tions from 1:1 Pt$_s$:H stoichiometry at very high
degrees of dispersion).

^{b} Average Pt crystallite size calculated from H$_2$
chemisorption, based on spherical geometry.

have proposed that with high-temperature
H$_2$ reduction of Pt/Al$_2$O$_3$ direct alloy type
bonding occurs between Pt and aluminum
of the partially reduced Al$_2$O$_3$. We have
shown that the specific catalytic activity
of Pt/Al$_2$O$_3$ for low-temperature NH$_3$ oxi-
dation decreases by over two orders of mag-
nitude with increasing Pt dispersion and
that highly dispersed Pt/SiO$_2$ has an order
of magnitude higher specific catalytic ac-
tivity than Pt/Al$_2$O$_3$ of similar dispersion
(20). The nature of the chemical interaction
with the support as indicated by the above
examples requires further refinement.

The objectives of this work were to de-
termine the paramagnetic platinum and
oxygen species which are present in the
various stages in the genesis of a supported
platinum catalyst and to determine how the
support is involved in the formation of
such species.

EXPERIMENTAL METHODS

The alumina and silica on which the
platinum was to be placed was crushed and
screened to the 14- to 20-mesh range,
washed in 20% nitric acid for 30 min, rinsed
with distilled water, dried, and calcined
at 973 K in air overnight. Platinum in the
form of Pt(NH$_3$)$_4$ (OH)$_2$ was then ion ex-
changed (adsorbed) onto the alumina and
silica. The support was allowed to stand

in contact with the exchange solution for
12 days to assure uniform distribution
throughout the particles, the water was
evaporated at 363 K over several days, and
the samples were dried at 393 K for 1 day.
Samples of Pt/Al$_2$O$_3$ and Pt/SiO$_2$ were
prepared containing 2.9 wt% Pt and 0.4
wt% Pt.

The resultant catalysts were typically
calcined in flowing oxygen by heating from
323 to 623 K at 1 K/min and then holding
at 623 K for 3 hr. For those samples that
were reduced, reduction was carried out
in flowing H$_2$ by heating from 323 to 623 K
at 1 K/min and holding at 623 K for 3 hr.
This procedure has been shown to give
highly dispersed Pt in Y zeolite (12) and
on these supports (13). The reduced
samples were amorphous to x-ray diffrac-
tion; dispersions determined by hydrogen
chemisorption and calculated Pt crystallite
sizes are given in Table 1. The 2.9 wt%
Pt/Al$_2$O$_3$ was shown by electron microscopy
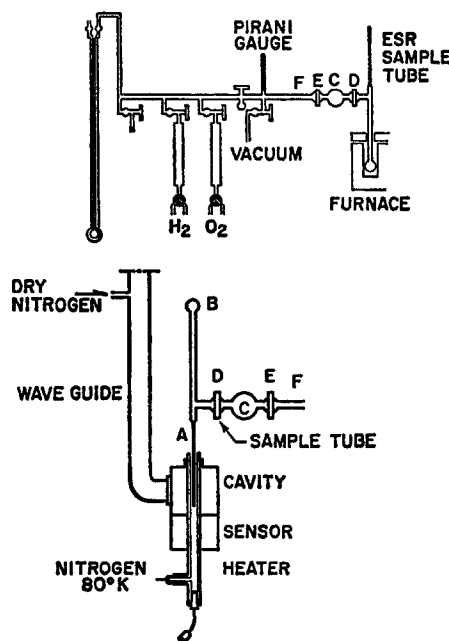to contain a narrow crystallite size distribu-

FIG. 1. Vacuum and gas dosing system with
sample tube and orientation in EPR spectrometer.

tion with all Pt crystallites between 2.0 and 3.2 nm for over 500 crystallites counted.

Samples of Pt/Al_2O_3 and of Pt/SiO_2 at several stages of pretreatment were introduced into the sample holder with an attached EPR tube (Fig. 1) where further controlled-atmosphere treatments and gas dosing were carried out. The sample could be heated and evacuated in bulb B which promoted effective removal of gases released by the sample. The sample could then be transferred into the 4-mm EPR tube without environmental contact; gas for later dosing could be stored in bulb C. Evacuation was typically to less than 10^{-4} Torr during the later stages of heating the sample and after cooling to room temperature.

EPR spectra were taken on an AEG (Model No. 533) spectrometer with an X-band microwave bridge and low-temperature accessory for measurements at temperatures to 77 K. Measurement techniques were standard. Instrument parameters were varied over a broad range to define conditions under which operating parameters adversely affected line shape and intensity, and these operating regions were avoided.

To quantify the EPR spectra, suitable quality spectra were divided into segments, with very fine grids being used where the rate of change of the derivative was large. The data were then integrated using a computerized trapazoidal integration technique. If the absorption curve did not close to zero, a baseline correction technique was applied, and the derivative curve was integrated again. The absorption curve typically closed to better than $\pm 15\%$ on the first integration and closed almost exactly after application of baseline correction. Curves that did not close well on the first integration and required large baseline corrections were not used. Integration of the absorption curve gave the desired area. A sharp signal superimposed on a much broader signal was observed in the presence of O_2; the two lines were not separable in the derivative mode. Integration of the derivative spectra gave a broad absorption peak with a narrower peak superimposed on it. Smooth interpolation of the curve for the broad peak gave the baseline for the narrow peak and permitted accurate determination of its area.

The alumina was high purity η-Al_2O_3 (Harshaw No. AL-0104) and had a surface area of ~ 140 m^2/g; the silica was from W. R. Grace, Davison Chemical Division (Grade 59) and had a surface area of ~ 290 m^2/g. Gases were high purity from Linde. A weak pitch from Varian containing 1×10^{13} spins/cm was used to determine the concentration of paramagnetic centers in the Pt samples.

RESULTS

The alumina support had a weak paramagnetic signal with a g value of 4.26. No other signals appeared either before or after evacuation or upon calcining to 623 K in O_2 using the same procedures used for the Pt-containing samples. Addition of 10-Torr O_2 to the calcined, evacuated support sample did not result in any new signals or other changes; neither did heating in H_2 to 623 K or subsequent addition of O_2. The silica support also contained a weak signal with an approximate g value of 4.26. The silica did not show any other signals after calcination in O_2 or after heating in H_2 at 623 K; no new signals appeared upon addition of 10-Torr O_2 to either the calcined or reduced SiO_2.

For the Pt/Al_2O_3 the majority of the work was done with a sample of 2.9 wt% Pt/Al_2O_3. The results obtained were confirmed identically on a second sample, and similar results were obtained on a sample of 0.4 wt% Pt/Al_2O_3. The EPR line with a g value of 4.26 was also present in all Pt/Al_2O_3 and Pt/SiO_2 samples and was independent of pretreatment or adsorption conditions. Since it did not change in in-
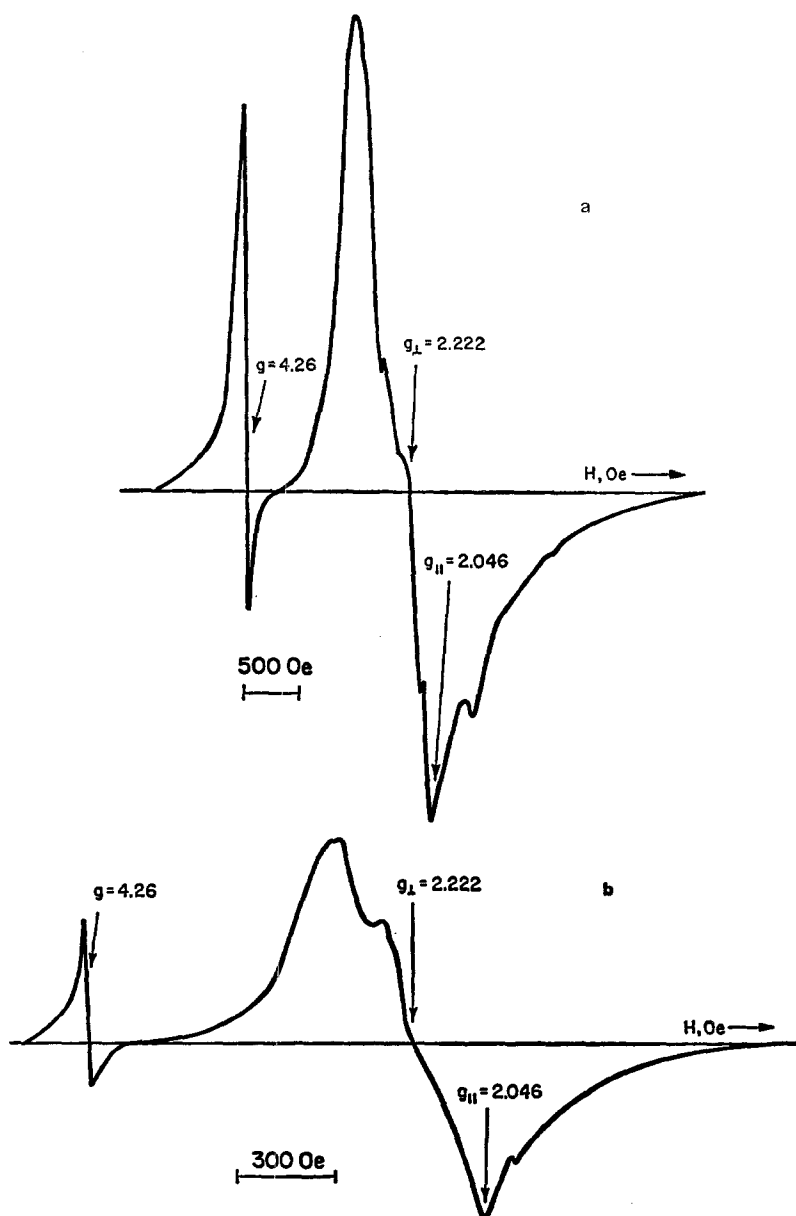
FIG. 2. EPR spectra of 2.9 wt% Pt/Al_2O_3 after calcination in O_2 at 623 K followed by evacuation to $<10^{-4}$ Torr at 623 K. (a) spectrum taken at 298 K; (b) spectrum taken at 80 K.

tensity, it could be used to gauge the relative peak heights on the spectra presented below.

After drying the 2.9 wt% Pt/Al_2O_3 sample at 393 K for 3 hr the sample had a very weak signal with a peak-to-peak width (ΔH_{pp}) of 58 Oe and a g value of about 2.01. Evacuation for 0.25 hr at 373 K resulted in a 70% increase in the $g = 2.01$ signal, but no other changes were observed. Calcining in O_2 to 623 K with evacuation to $<10^{-4}$ Torr at 623 K as outlined above lead to a very strong, broad EPR signal with a linewidth (ΔH_{pp}) of 750 Oe and a main g value of 2.222. This signal was about 200 times more intense than any other

signals previously observed. Figure 2a shows the characteristic shape of this line at 298 K. Cooling to 80 K resulted in a reduction in the linewidth to about 600 Oe and an increase in the measured signal intensity which followed very well that predicted by the Curie–Weiss law (Fig. 2b). The line with the g value of 2.01 was also present in the 298 K spectrum although it was very weak. The $g = 2.01$ line was not present in all calcined evacuated samples of Pt/Al_2O_3. The main signal ($g = 2.222$) will hereafter be referred to as the *platinum signal;* this signal has a fine structure, which will be discussed below.

The addition of 10-Torr O_2 to the EPR tube resulted in the rapid formation of a new, strong, and more complex EPR signal with a peak-to-peak width (ΔH_{pp}) of about 70 Oe and a g value of 2.010 for the main line (Fig. 3). Associated with the formation of this new line there was a simultaneous,

marked reduction in the intensity of the platinum ($g = 2.222$) signal. This new line ($g = 2.010$) will hereafter be referred to as the *oxygen signal.* Reduction in the oxygen pressure resulted in both a reduction in the intensity of the oxygen signal and a significant increase in the amount of detail visible in the signal (Fig. 4). This fine structure will be discussed below. More complete evacuation to pressures below 10^{-4} Torr at room temperature resulted in complete removal of the oxygen signal and return of the platinum signal to its original intensity. Readdition of O_2 resulted in reappearance of the oxygen signal, and evacuation removed it again. This cycle was repeated six or seven times and was also repeated several times on other samples with no change in either the resultant oxygen or platinum signals with respect to either their shapes or intensities. Observed changes in signal intensity ($\sim$15–20%)
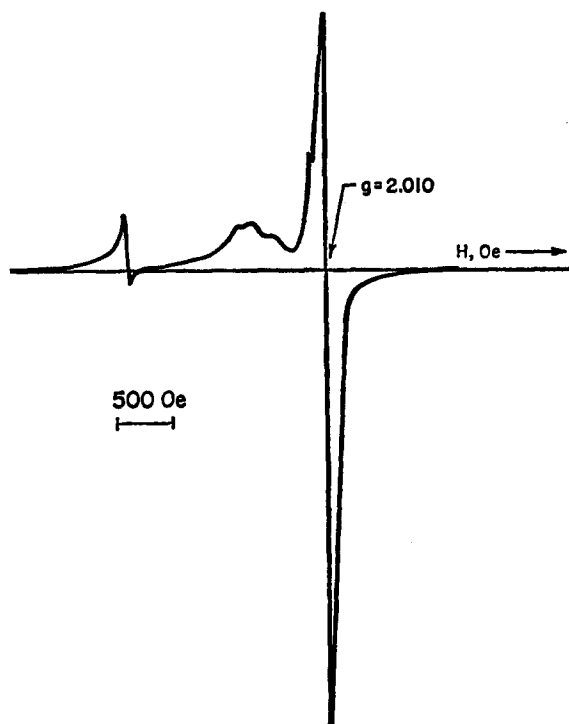

FIG. 3. EPR spectrum obtained at 298 K upon addition of 10-Torr O_2 to the sample whose spectrum is shown in Fig. 2
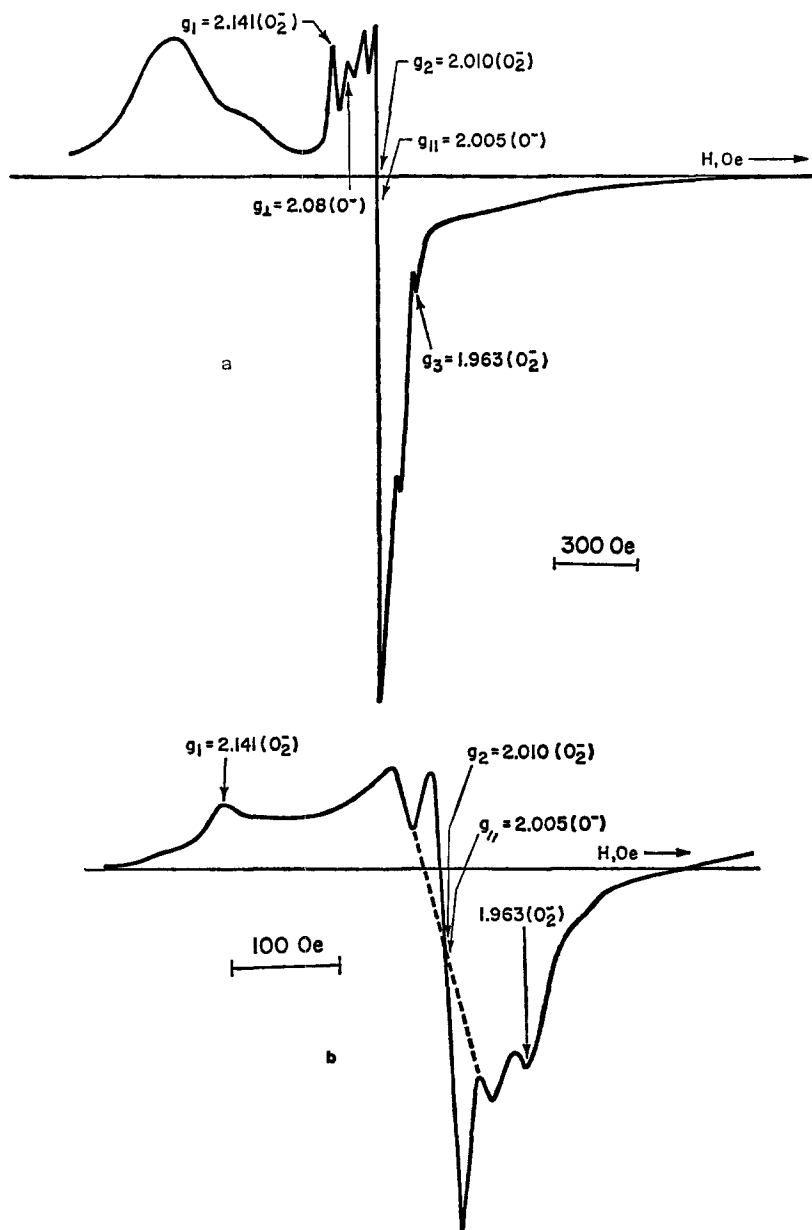
FIG. 4. EPR spectra of O_2 adsorbed on calcined, evacuated Pt/Al_2O_3 sample whose spectrum is shown in Fig. 2. Conditions: (a) 0.010-Torr O_2, spectrum taken at 298 K; (b) 0.10-Torr O_2, spectrum taken at 80 K.

could be attributed mainly to effects resulting from removing and repositioning the sample tube in the EPR cavity

The presence of four peaks in the EPR spectra of oxygen adsorbed on 2.9 wt% Pt/Al_2O_3 which had been calcined and

evacuated at 623 K suggests that the oxygen signal is actually composed of two different signals. There is further indication of this in the effect of O_2 pressure on the signal. The intensity of the center line of the oxygen signal increased relative to the

other portions of the signal with decreasing O_2 pressure.

Addition of 10-Torr O_2 at 80 K resulted in only a moderately strong oxygen signal with a relatively weaker line in its center, although the detailed structure was substantially missing due to physically adsorbed oxygen. It is not clear whether the reduced oxygen peak intensity resulted because of the reduced reactivity of O_2 at 80 K and thus its inability to dissociate or because the oxygen was condensed on the porous Al_2O_3 in the upper portion of the tube and never reached the Pt/Al_2O_3 in the lower portion of the tube. The oxygen signal intensity relative to the platinum signal intensity was approximately equivalent to that observed for 0.02-Torr O_2 at 298 K.

At 298 K with the O_2 pressure reduced to 0.10 Torr, 100-Torr H_2 was added to the EPR tube in the spectrometer, and a spectrum was taken immediately thereafter. There was no evidence of any remaining oxygen signal in this spectrum, and the platinum signal had returned to its normal intensity. The adsorbed oxygen species had reacted rapidly with added H_2 at room temperature. After evacuation, addition of 10-Torr O_2 resulted in the reappearance of the oxygen signal along with reduction in the intensity of the platinum signal. Both the oxygen and platinum signals were significantly more intense ($\sim 25\%$) than observed previously; this was probably due to surface changes produced by reaction with H_2 since an increase to this level had not been observed in any of the other experiments.

If the relaxation time is rapid relative to the frequency of the microwave radiation the signal intensity will be proportional to the microwave power applied, and the number of spins determined from the peak intensity will be accurate. If saturation of the signal with increasing power occurs, the calculated spin concentration will be in error. Room temperature spectra of the calcined and evacuated 2.9 wt% Pt/Al_2O_3 and of the sample in the presence of 0.2-Torr O_2 showed the desired variation in signal intensity with microwave power, indicating lack of saturation effects.

The 0.4 wt% Pt/Al_2O_3 calcined at 623 K in O_2 and evacuated to $<10^{-4}$ Torr at 623 K had a platinum signal which had a lineshape equivalent to that observed for the 2.9 wt% Pt/Al_2O_3 and a peak intensity which was about 70% of the value for the 2.9 wt% Pt/Al_2O_3. Thus the number of paramagnetic centers formed appears to be only weakly dependent on the platinum content in the range studied. The number of paramagnetic centers formed may therefore be more a function of sites on the Al_2O_3 surface which interact with the platinum. Addition of O_2 produced an oxygen signal which had a line shape that was identical to that for O_2 on the 2.9 wt% Pt/Al_2O_3 suggesting that the species formed were the same. The intensity in the presence of 10-Torr O_2 was less than that for the 2.9 wt% Pt/Al_2O_3 suggesting that the paramagnetic platinum centers formed did not pick up O_2 as readily.

When the calcined Pt/Al_2O_3 was reduced in flowing H_2 at 623 K, the platinum signal was eliminated, but a new, strong symmetric signal of broad linewidth (ΔH_{pp} = 1420 Oe) appeared. The intensity of this spectrum was proportional to the metal content of the catalyst, and its linewidth (ΔH_{pp}) was reduced to about 250 Oe by cooling to 80 K. It had an approximate g value of 2.28. This signal will not be considered further here.

Addition of 10-Torr O_2 to the reduced Pt/Al_2O_3 did not result in the formation of of an oxygen signal. Heating the reduced Pt/Al_2O_3 in 50-Torr O_2 overnight at 698 K with subsequent evacuation to $<10^{-4}$ Torr at 623 K and addition of 10-Torr O_2 at 298 K resulted in the appearance of a weak oxygen signal identical in line shape to that observed for the unreduced, calcined Pt/Al_2O_3 with 10-Torr O_2. However, the mag-

nitude of the oxygen signal on this material was only about 1% of the magnitude of the oxygen signal for the unreduced, calcined samples.

The sample of 2.9 wt% Pt/SiO_2 was calcined and evacuated in a manner identical to that for the Pt/Al_2O_3, and EPR spectra were taken. Although a signal appeared to be present, it was very weak, very broad, and very asymmetric, not at all characteristic of the platinum signal observed for Pt/Al_2O_3. The lineshape was only slightly different and only slightly more intense than the spectrum observed for an empty, evacuated quartz EPR tube. Addition of 10-Torr O_2 to the calcined, evacuated Pt/SiO_2 sample did not result in a distinguishable oxygen signal or any other significant change in the spectrum, again in marked contrast to the behavior observed upon addition of O_2 to calcined, evacuated Pt/Al_2O_3.

Reduction of the Pt/SiO_2 at 623 K in flowing H_2 produced at most a slight reduction of the broad line in the spectrum; the resultant spectrum was essentially that for the empty, evacuated quartz EPR tube. There was no similarity between the EPR spectra for reduced Pt/SiO_2 and Pt/Al_2O_3 although the Pt crystallite sizes as determined by H_2 chemisorption were similar.

When the reduced sample of Pt/SiO_2 was calcined in O_2 at 623 K for 1.5 hr and evacuated to $<10^{-4}$ Torr, there was again a slight increase in the intensity of the broad line, similar to the lineshape of the initially calcined Pt/SiO_2. Addition of 10-Torr O_2 to the sample of Pt/SiO_2 which was calcined in O_2 after reduction produced a weak and very narrow (ΔH_{pp} = 11 Oe) line occurring at about $g = 2.01$ which was apparently a $1-g$ signal resulting from an adsorbed oxygen species. This signal was completely eliminated by evacuation for 2 hr at 623 K with $P < 10^{-4}$ Torr. This oxygen signal could be reversibly added and removed and was reduced by

about a factor of 2 by reducing the O_2 pressure to 0.01 Torr.

DISCUSSION OF RESULTS

The absorption peak with $g = 4.26$ is probably due to impurity iron in the Al_2O_3 and the SiO_2; this is the g value typically observed for iron in solids (21). The fact that the peak intensity was less than 1/100 that of either the platinum or oxygen signals and that it did not undergo any changes with calcination, reduction, or adsorption of O_2 either before or after Pt addition suggests that it is not responsible for or related to the other signals.

The appearance of the strong line at $g = 2.222$ upon calcination and evacuation of the Pt/Al_2O_3 samples suggests that this signal is due to an oxidized Pt species. The signal is a 2 g signal with $g_\perp = 2.222$ and $g_{||} = 2.046$. The fine structure in the spectrum is due to splitting by the isotope of platinum (^{195}Pt) having a nuclear spin $I = \frac{1}{2}$; this isotope is 34% abundant. The other isotope, which is 66% abundant and which has a nuclear spin $I = 0$, produces the major adsorption curve. The derivative of the EPR absorption curve is constructed in Fig. 5 by sketching in the summation of the adsorption spectra from the lower portion and represents well the observed lineshape (Fig. 2). The splitting parameters for the signal ($A_\perp$ and $A_{||}$) were assumed equal and equivalent to the splitting observed by Geschwind and Remeika (22) for Pt in α-Al_2O_3, $A = 150$ Oe. Šroubek, et al. (23) reported $A = 140$ Oe for Pt in Nb-doped $BaTiO_4$. The $g_\perp$ value obtained in this work agrees well with that reported by Geschwind and Remeika (22) for Pt in corundum (for temperatures greater than 79 K, $g = 2.220 \pm 0.001$). At 4.2 K the Pt signal had g values of $g_x = g_y = 2.328 \pm 0.004$ and $g_z = 2.011 \pm 0.006$. Šroubek et al. (23) reported $g_\perp = 2.51 \pm 0.02$ and
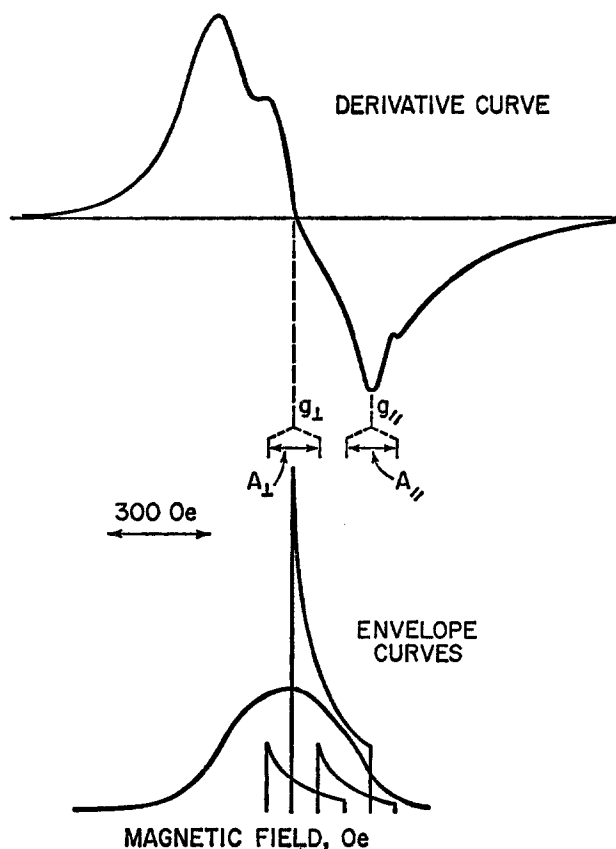
FIG. 5. Constructed paramagnetic platinum spectrum, using known parameters.

g_{11} = 1.935 ± 0.005 for Pt^{3+} in niobium-doped BaTiO$_3$.

Pt in the complex exchanged onto the Al$_2$O$_3$ (Pt(NH$_3$)$_4$(OH)$_2$) is Pt^{2+} which has a 5d^8 configuration and should give no EPR signal. Calcining should oxidize the Pt^{2+} to Pt^{4+}; our EXAFS work indicates that this is the case (24). We speculate that the platinum remains highly dispersed, possibly atomically, since the coulombic interactions between the original complex and the Al$_2$O$_3$ surface remain effective with oxidation. Therefore clusters of platinum oxide are almost certainly absent for the 0.4 wt% Pt/Al$_2$O$_3$ and are probably absent for the 2.9 wt% Pt/Al$_2$O$_3$ although we have no direct evidence for this. Evacuation at 623 K probably causes a partial reduction of the surface by removing oxygen anions

according to:

$$O^{2-}-Pt^{4+}-O^{2-} \rightarrow \Box Pt^{2+}-O^{2-} + \tfrac{1}{2}O_2. \quad (1)$$
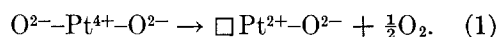
Neither Pt^{4+} (5d^6) nor Pt^{2+} (5d^8) is paramagnetic. However, if $\Box$Pt^{2+}-O^{2-} is in contact with a Lewis acid center on the surface of the calcined Al$_2$O$_3$, electron transfer to the Al$_2$O$_3$ could occur,

$$\Box Pt^{2+}-O^{2-} + L-Al_2O_3 \rightarrow$$
$$\Box Pt^{3+}-O^{2-} + L^{-}-Al_2O_3, \quad (2)$$

(Lewis acid center)
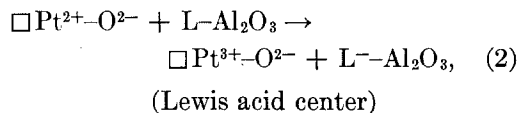
producing a paramagnetic Pt^{3+} (5d^7) ion. This would explain the formation of our observed paramagnetic platinum centers. This would also explain the observation that the intensity of the platinum signal was essentially independent of metal con-

tent. Ion exchange would probably occur at the strong sites first since we allowed 12 days for equilibration. Thus the number of paramagnetic centers formed should be a function of the support and not of metal content as long as sufficient metal is present. This is consistent with the observation that a 7.25-fold reduction in the Pt content resulted in only a 30% reduction in the platinum signal intensity.

It is not readily possible to determine whether the platinum species responsible for the paramagnetic resonance is Pt^{1+} or Pt^{3+}; this is also the case in the work of Geschwind and Reimeka (22) and of Šroubek et al. (23). However, the chemistry of the system as outlined above strongly favors Pt^{3+}.

A typical absorption spectrum obtained by integration of a derivative platinum EPR spectrum was quite asymetric due to the 2-g signal. The area of this absorption peak was ratioed to that of the weak pitch sample, which for three scans reproduced to better than 5%, to obtain the number of paramagnetic centers. Table 2 gives the number of paramagnetic centers observed for a series of experiments starting with a freshly calcined, evacuated sample and then consecutively adding and removing oxygen, with spectra being taken after each addition and removal. Reproducibility was quite good. H_2 addition and evacuation produced an apparently significant increase in the concentration of paramagnetic centers. The low-temperature determinations are thought to be the most precise. If it is assumed that the average bulk density of the catalyst powder in the EPR tube is 1.0 g/cm³, the number of Pt atoms per centimeter is about $5 \times 10^{+18}$ for the 2.9 wt% Pt/Al_2O_3. Therefore, about one out of every 30 platinum atoms is paramagnetic. For the 0.4 wt% Pt/Al_2O_3 this ratio is about one out of every four platinum atoms. This density of paramagnetic centers is less than one center per 20 nm² of alumina surface area. This is in the site density range
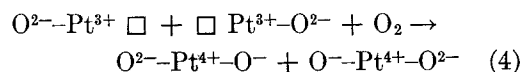
of strong Lewis acid centers on calcined Al_2O_3.

The fact that paramagnetic platinum centers were not formed for 2.9 wt% Pt/SiO_2 when it is calcined and evacuated by the same procedure suggests that the formation of the paramagnetic platinum species involves a specific interaction with the surface of the Al_2O_3 and that the interaction is markedly different from that which can occur with SiO_2. A probable type of interaction with Lewis acid centers on Al_2O_3 has been suggested above; similar Lewis acid centers should not form on SiO_2. Electron transfer to Al_2O_3 is indicated by our recent EXAFS studies of Pt/Al_2O_3; these results show that highly dispersed clusters of reduced platinum on Al_2O_3 are electron deficient suggesting electron transfer to Lewis acid centers (15). We do not see by EXAFS similar electron transfer from Pt of an equally high degree of dispersion to SiO_2 for Pt/SiO_2, consistent with our observed differences between Pt/Al_2O_3 and Pt/SiO_2 in this study. Small Pt clusters on Y zeolites do not exhibit electron transfer to the zeolite unless multivalent cations are exchanged into the zeolite (16).
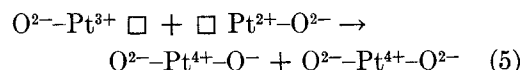
The addition of O_2 to these calcined, evacuated samples on Al_2O_3 can lead to the formation of O_2^- species by

$$\square \ Pt^{3+}\text{–}O^{2-} + O_2 \rightarrow O_2^-\text{–}Pt^{4+}\text{–}O^{2-}. \quad (3)$$
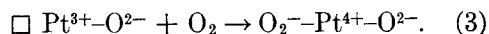
If site pairs are adjacent, O^- species could also be formed by:

$$O^{2-}\text{–}Pt^{3+} \ \square + \square \ Pt^{3+}\text{–}O^{2-} + O_2 \rightarrow$$
$$O^{2-}\text{–}Pt^{4+}\text{–}O^- + O^-\text{–}Pt^{4+}\text{–}O^{2-} \quad (4)$$
or

$$O^{2-}\text{–}Pt^{3+} \ \square + \square \ Pt^{2+}\text{–}O^{2-} \rightarrow$$
$$O^{2-}\text{–}Pt^{4+}\text{–}O^- + O^{2-}\text{–}Pt^{4+}\text{–}O^{2-} \quad (5)$$

Reactions (3), (4), and (5) provide a good explanation of the oxygen signal. The complex line that appears upon adsorption of O_2 involves one species having a 3-g signal and a second species clearly having a 1-g

signal. The 3-g signal is characteristic of the signal observed for O_2^- species which have been demonstrated to form on many outgassed oxide surfaces (1–7). This could be produced by reaction (3). The g values for the O_2^- signal are $g_1 = 2.141$, $g_2 = 2.010$, and $g_3 = 1.963$. These are in the range observed for other systems (1–7), but values of g_1 and g_3 this large and small, respectively, for adsorbed O_2^- have not been previously reported; further clarification of this signal is desirable.

The second species producing the sharp signal at the center of the oxygen spectrum is inferred to be O^- which would be formed by dissociation of O_2 in an environment not able to supply four electrons to form O^{2-}, for example, as indicated by Eqs. (4) and/or (5). It is possible that the O^- species is associated with Al^{3+} as proposed by Abdo et al. (25); however, it was reactive with H_2 at room temperature. The main g value of this species is 2.005 which is close to values previously reported (1–3, 7, 25). This species is more tightly bound than O_2^- (a) as would be expected and (b) as indicated by the fact that the intensity of this signal grows relative to that of the O_2^- signal with decreasing O_2 partial pressure. Similar behavior has been reported for O_2 adsorption on outgassed metal oxides (1, 2, 7, 25).

The 3-g signal indicates that there is no axial symmetry in the system for the O_2^- species. The large value for g_1 suggests that the metal ion to which the O_2^- is bound has a low change; this would favor Pt^{2+} rather than Pt^{4+} as postulated above. The large value would also suggest rather ionic character. Values of g_1 for O_2^- adsorbed on an aluminum ion at the surface of Al_2O_3 are characteristically 2.034 to 2.038 (1, 2, 25–27) establishing that the O_2^- species observed in this work is not interacting with Al^{3+} centers on the surface but is interacting with Pt centers. This is consistent with the observation that the platinum signal intensity decreased in proportion to the increase in the oxygen signal intensity. Values of g_3 for O_2^- less than 2.003 have been reported (1, 28–30).

The signal assigned to O^- is possibly a 2-g signal with g_1 at about 2.08; Fig. 4a shows a spectrum at low oxygen pressure which would appear to be composed of a 3-g O_2^- signal and a 2-g O^- signal. A value of $g_1 = 2.042$ has been reported for O^- on MgO (31, 32) and $g_1 = 2.024$ has been reported for O^- on Al^{3+} (25). Thus the O^- signal appears to also be associated with Pt and not with the support, consistent with Eqs. (4) and (5). We cannot derive more detailed information from the data about the nature of the paramagnetic oxygen species because the emphasis of the work was not to further quantify this aspect. Additional studies, particularly involving ^{17}O, would be useful.

Reactions (3), (4), and (5) indicate that for every O_2^- or O^- species formed one Pt^{3+} should be converted to Pt^{4+}. There should therefore be a corresponding reduction in the intensity of the platinum signal; such an intensity reduction was observed. The O_2^- plus O^- peak intensities, obtained by integrating the oxygen absorption peak on top of the platinum absorption peak, were converted into a number of paramagnetic oxygen centers by ratioing the oxygen absorption signal area to that of the weak pitch. Table 2 summarizes the values obtained for the experiments involving adsorbed oxygen for the same series of experiments summarized in the upper portions of the table for zero O_2 pressure. The precision is not as good as for the platinum signal alone because of the greater complexity of the spectra and the greater height and narrowness of the oxygen EPR signal. This reduces the platinum signal height as read out on the chart because of the change in the amplification required to accommodate the oxygen signal and thus reduces the precision of the platinum signal. Taking the best values from the table the average concentration of para-

TABLE 2

Concentration of Paramagnetic Centers for Supported Platinum Catalysts[a]

Sample	O_2 pressure (Torr)	Measurement temperature (°K)	Number of platinum centers per gram ($\times 10^{-18}$)	Number of oxygen centers per gram ($\times 10^{-18}$)
2.9 wt% Pt/Al$_2$O$_3$	0	298	1.8	—
2.9 wt% Pt/Al$_2$O$_3$	0	298	2.3[b]	—
2.9 wt% Pt/Al$_2$O$_3$	0	298	3.1[c]	—
2.9 wt% Pt/Al$_2$O$_3$	0	80	2.3	—
2.9 wt% Pt/Al$_2$O$_3$	0	80	2.4	—
2.9 wt% Pt/Al$_2$O$_3$	10	298	0.64[d]	0.80[d] (0.78)[e] [0.57][f]
2.9 wt% Pt/Al$_2$O$_3$	10	298	1.1	0.48 (0.57) [0.30]
2.9 wt% Pt/Al$_2$O$_3$	10	298	1.2	0.75 (0.61) [0.39]
2.9 wt% Pt/Al$_2$O$_3$	10	298	2.12[d]	1.3 [0.37]
2.9 wt% Pt/Al$_2$O$_3$	10	80	1.0	0.32 [0.15][g]
2.9 wt% Pt/Al$_2$O$_3$	0.01	298	1.4	0.17 [0.089]
0.4 wt% Pt/Al$_2$O$_3$	Low	298	1.0	0.06
2.9 wt% Pt/SiO$_2$	10	298	—	0.02

[a] Concentration of paramagnetic centers was obtained by double integrating the EPR derivative spectra, rationing the area, adjusted to consistent operating parameters, to that for a weak pitch sample containing 1×10^{13} spins/cm of sample measured at 298 and at 80 K, and assuming that the catalyst density in the EPR tube was 1 g/cm^3. For spectra containing both an oxygen and a platinum signal the entire line was doubly integrated to give the entire absorption area; interpolation of the platinum peak to form a baseline for the oxygen peak allowed the oxygen peak area to be obtained.

[b] After addition of 100-Torr H$_2$.

[c] Sample after addition of 100-Torr H$_2$ and evacuation.

[d] Indicated numbers are probably not as precise because the signal peaks which were integrated were small.

[e] Numbers in parentheses were obtained by double integration of only the derivative oxygen signal; since the oxygen signal also contains the negative portion of the platinum signal which could not be subtracted, it will contain a small but significant error.

[f] Numbers in brackets are the ratios of the oxygen absorption area to the total absorption area.

[g] O$_2$ adsorption at 80 K; oxygen signal much weaker than after adsorption at 298 K.

magnetic platinum centers if $1.2 \times 10^{18}/g$, and the average concentration of paramagnetic oxygen centers if $0.64 \times 10^{18}/g$. The average total number of paramagnetic centers in the presence of 10-Torr O_2 was $1.8 \times 10^{18}/g$. This is about 25% below the total number of paramagnetic platinum centers before oxygen addition. According to reactions (3), (4), and (5) for each paramagnetic oxygen species formed a paramagnetic platinum center should be eliminated. This behavior is approximately observed, supporting reactions (3), (4), and (5) as probable ones. It is also possible that a reaction such as

$$O^{2-}-Pt^{4+}-O^{-} + L^{-}-Al_2O_3 \rightarrow$$
$$O^{2-}-Pt^{4+}-O^{2-} + L-Al_2O_3 \quad (6)$$
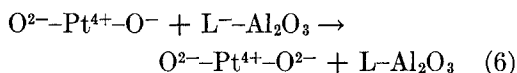
could occur during or following oxygen adsorption resulting in a reduction in the total number of paramagnetic (platinum plus oxygen) centers. The observed reduction in total number of paramagnetic centers could be explained by this type of reaction or could be due to experimental causes; we favor causes such as Eq. (6) over experimental causes. From the ratio of the total number of paramagnetic platinum centers plus oxygen centers (assumed to be the total number of paramagnetic platinum centers initially available) to the number of paramagnetic oxygen centers, about 30 to 35% of the paramagnetic platinum atoms adsorb oxygen forming paramagnetic oxygen species. The remaining paramagnetic platinum centers are not available, possibly due to steric reasons; some may be located in the near-surface region of the Al_2O_3.

The calcined 0.4 wt% Pt/Al_2O_3 behaved in the same manner and was not studied further.

In the presence of O_2 the Al_2O_3 again plays a vital role in the surface chemistry of the calcined catalyst. The 2.9 wt% Pt/SiO_2 after the same calcination and evacuation procedure formed no paramagnetic oxygen centers in the presence of 10-Torr O_2. This is consistent with the absence of a measurable concentration of paramagnetic platinum species for the calcined Pt/SiO_2.

Although there may have been little clustering induced by calcination, reduction results in marked clustering and the formation of small metal crystallites. These small crystallites of reduced Pt atoms can readily adsorb oxygen as demonstrated by oxygen chemisorption and the oxygen–hydrogen titration (33, 34). Reduced metal atoms readily dissociate oxygen molecules forming largely covalently chemisorbed species or O^{2-} ions. Thus O_2^{-} or O^{-} formation is not expected on reduced platinum surfaces and was not found. Clarkson and Cirillo (8, 9) have reported the formation of O_2^{-} species on silver supported on quartz; yet Abou-Kais et al. (10) could not find paramagnetic oxygen on silver supported on silica.

Limited studies on the effect of reoxidation showed that for Pt/Al_2O_3 the procedure used resulted in regeneration of limited capability to form paramagnetic oxygen species upon O_2 adsorption on the catalyst after evauation at 623 K. We speculate that appropriate reoxidation procedures could lead to recovery of a much larger fraction of the capability for formation of paramagnetic oxygen species.

For Pt/SiO_2, which did not form a measurable concentration of paramagnetic oxygen species after the original calcination and evacuation, a small concentration (Table 2) of paramagnetic oxygen species, presumably O^{-}, was formed when the reduced sample was reoxidized and evacuated followed by addition of 10-Torr O_2. There was no evidence for the formation of O_2^{-} species suggesting that in this case the platinum surface on which the paramagnetic oxygen species formed was a partially oxidized platinum crystallite which could provide a sufficiently high concentration of semireduced platinum atoms for reactions (4) and (5) to occur.

Reduction of Pt/Al_2O_3 replaced the paramagnetic platinum signal discussed

above with an intense, broad, symmetrical absorption line having approximately $g = 2.28$. This peak narrowed markedly at lower temperature (80 K) but was not studied further. The support again plays a primary role in the behavior observed. The reduced 2.9 wt% Pt/SiO_2 displayed no similar signal although the Pt crystallites formed with SiO_2 were similar in size to those formed with Al_2O_3 (Table 1). If the signal for reduced Pt/Al_2O_3 were due to odd electron effects as has recently been observed and discussed (35–38), then a similar signal should have been observed for Pt/SiO_2 since it had roughly the same Pt crystallite size (Table 1). Thus it can be concluded that the EPR signal observed for reduced Pt/Al_2O_3 is due to a direct involvement of platinum with the Al_2O_3; we have not studied this behavior sufficiently to speculate on its origin.

These results clearly show the extent and importance of interactions between platinum and alumina as compared to the platinum–silica system and point to the need to consider much more carefully the role of the support in the catalytic system even for a metal as noble as platinum. They also show that the chemistry of preparation and pretreatment can be quite important and probably plays a key role in determining the nature of the final catalyst; understanding the chemistry of the preparation and pretreatment of the catalyst should provide for a better understanding of the final catalyst.

ACKNOWLEDGMENTS

REFERENCES

1. Lunsford, J. H., *Advan. Catal.* 22, 265 (1975).
2. Derouane, E. G., and Vedrine, J. C., *Ind. Chim. Belg.* 38, 375 (1973).
3. Shvets, V. A., and Kazansky, V. B., *J. Catal.* 25, 123 (1972).
4. Lunsford, J. H., Zingery, L. W., and Rosynek, M. P., *J. Catal.* 38, 179 (1975).
5. Bielanski, A., and Najbar, M., *J. Catal.* 25, 398 (1972).
6. Hoang, van can, Ghorbel, A., and Teichner, S. J., *Bull. Soc. Chim. Fr.* (2), 437 (1972).
7. Van Hooff, J. H. C., "Formation of Surface-Peroxo Compounds" Ph.D. Thesis, Technische Hogeschool Eindhoven, Eindhoven, The Netherlands, 1968.
8. Clarkson, R. B., and Cirillo, A., Jr., *J. Vac. Sci. Technol.* 9, 1073 (1972).
9. Clarkson, R. B., and Cirillo, A., Jr., *J. Catal.* 33, 392 (1974).
10. Abdou-Kais, A., Jarjoui, M., Vedrine, J. C., and Gravelle, P. C., *J. Catal.* 47, 399 (1977).
11. Taupin, C., and Charvolin, J., in "Colloque Ampere XIV," p. 486 (Session 11, No. 8). North-Holland, Amsterdam, 1967.
12. Feher, G., and Kip, A. V., *Phys. Rev.* 98 (2), 337 (1955).
13. Sivasankar, S., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* 46, 420 (1977).
14. Naccache, C., Primet, M., and Mathieu, M. V., in "Proceedings of the Third International Conference on Molecular Sieves," Advances in Chemistry Series, No. 121, p. 266. American Chemical Society, Washington, D.C., 1973.
15. Katzer, J. R., Lorntson, J., Fukushima, T., and Schultz, J. M., submitted.
16. Boudart, M., and Gallezot, P., personal communication, 1978; paper presented at Spring Symposium at the Philadelphia Catalysis Club, May, 1978; paper presented at Roermond Conference on Catalysis, Roermond, The Netherlands, 1978.
17. Lytle, F., personal communication, 1978.
18. Tauster, S. J., Fung, S. C., and Garten, R. J., *J. Amer. Chem. Soc.* 100, 170 (1978).
19. Den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* 53, 116 (1978).
20. Krug, S. M., M. Ch. E. thesis, Department of Chemical Engineering, University of Delaware, Newark, Delaware, 1974.
21. Carnevale, et al., *J. Noncrystalline Solids* 22, 269 (1976).
22. Geschwind, S., and Remeika, J. P., *J. Appl. Phys.*, Supplement to Vol. 33 (1), 370 (1962).
23. Šroubek, Z., Ždánský, K., and Simánek, E., *Phys. Status Solidi* 3, K-1 (1963).
24. Fukushima, T., and Katzer, J. R., submitted.
25. Abdo, S., Howe, R. F., and Hall, W. K., *J. Phys. Chem.* 82, 969 (1978).

26. Gezalov, A. A., Zhabrova, G. M., Nikishia, V. V., Parasky, G. B., and Spiridonov, K. N., *Kin. Katal.* **9**, 462 (1968).

27. Wang, K. M., and Lunsford, J. H., *J. Phys. Chem.* **73**, 2069 (1969); **73**, 1165 (1971).

28. Bennett, J. E., Ingram, D. J. E., and Schonland, D., *Proc. Phys. Soc. Ser. A* **69**, 556 (1956).

29. Kanzig, W., and Cohen, M. H., *Phys. Rev. Lett.* **3**, 509 (1959).

30. Vedrine, J. C., and Naccache, C., *J. Phys. Chem.* **77**, 1606 (1973).

31. Williamson, W. B., Lunsford, J. H., and Naccache, C., *Chem. Phys. Lett.* **9**, 33 (1971).

32. Wong, N. B., and Lunsford, J. H., *J. Chem. Phys.* **55**, 3007 (1971).

33. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).

34. Wilson, G. R., and Hall, W. K., *J. Catal.* **17**, 190 (1970).

35. Kubo, R., *J. Phys. Soc. Japan* **17**, 975 (1962).

36. Gorkov, L. P., and Eliashberg, G. M., *Sov. Phys. JETP* **21**, 940 (1965).

37. Kawabata, A., *J. Phys. Soc. Japan* **29**, 902 (1970).

38. Elliott, R. J., *Phys. Rev.* **96**, 266 (1954).