rium isotope effect); (iv) regular (type A) isotope effects usually have **r** *vs.* log T curves confined to the 1.33–1.55 range and exhibiting relatively little structure [occasional exceptions were manifested in small negative deviations appearing in the high-temperature region ($T \approx 1000°K$) where, if exhibited by $\mathbf{r}_{QM}$ for *rates*, they would probably be washed out of **r** by **n**]; (v) in both anomalous and regular cases, the infinite-temperature asymptotic limit to **r** is 1.333, as demanded by theory[4] (this limit, however, can be approached from either above or below). Representative samples of the **r** *vs.* log T plots for the equilibrium isotope effect cases are shown in Figure 11.

It can be concluded from the work described in this report that one may use the usual estimates of **r** to calculate deuterium isotope effects from measured tritium effects, or *vice versa*, only if one is sure that the individual isotope effects are in the normal direction ($k_{\text{light}} > k_{\text{heavy}}$), reflect significant force constant changes at the isotopic position(s) between reactant and transition state, and exhibit regular (type A[10]) temperature behavior throughout the entire temperature range ($0 < T < \infty$). Present indications[2,12,28] are that one can only be so assured if one is dealing with sizable magnitude, pure primary, normal direction isotope effects and mixed primary–secondary normal isotope effects of sufficiently large magnitudes to be principally manifestations of the primary substitutions. Similarly, one should consider using relative tritium–deuterium isotope effects as indicators of quantum mechanical tunneling, or other factors not included in eq 1, only under the same conditions. Fortunately, these are the conditions most likely to be involved in a study of tunneling. We *estimate*, based on our studies, that if a primary or mixed primary–secondary deuterium isotope effect is at least as large as $\ln(k_H/k_D) = 1.0$ ($k_H/k_D \geqslant 2.7$) at 300°K, then the temperature-dependence behaviors of both the deuterium and corresponding tritium effects are most likely regular.

Acknowledgments. We thank Dr. Jacob Bigeleisen for helpful suggestions concerning the presentation of this work. We also thank Dr. Ralph E. Weston, Jr., for suggesting this problem to us.

A Study of Surface Structures of Submicron Metal Oxides by Vanadium Tetrachloride as a Paramagnetic Probe

James C. W. Chien

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01002.
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Abstract: The surface structures of annealed (n = 1.4OH/100 Å^2) and rehydrated (n = 4.6) Cabosils, γ-Al_2O_3, gibbsite, and boehmite have been studied by reactions with VCl_4. The vanadium atom becomes either singly or doubly attached depending upon whether the reaction consumes one or two hydroxyls as determined by HCl evolution. Reactions with annealed Cabosil have a stoichiometry of one. The incorporated vanadiums showed narrow epr lines at −195° which become significantly broadened at 25°. These species were readily reduced by heating the sample to above 150°. Therefore, nearly all of the paramagnetic probe molecules are singly attached and are within close approach to one another. Various alumina samples of different modifications react with VCl_4 to produce about 2HCl at 90°; the stoichiometry increases to 2.4 at higher temperatures. Therefore, all the vanadiums are doubly attached, and some of them even react with a third hydroxyl above 200°. The epr spectra of these species have line widths which are a function of degree of coverage alone but not of temperature. Heating to temperatures up to 450° caused no significant reductions. Reactions with rehydrated Cabosil consistently gave a stoichiometry of 1.5, suggesting that half of the vanadiums are singly attached and the remainder doubly attached. It is possible to deduce from the results of this study the approximate geometric distributions of hydroxyls on the surfaces of these submicron oxide particles.

The surfaces of solids, whether they are crystalline or amorphous, ionic or covalent, represent distinct states which differ chemically from the bulk states. The surface states may have unsaturated bonds (*i.e.*, the peripheral carbon atoms of a graphite crystal), or unsatisfied coordinations (*i.e.*, the Ti atoms along the c axis of the hexagonal α-$TiCl_3$), or polar functional groups. In the case of metal oxides, these groups are mostly hydroxyls. Ordinarily, the surface atoms only represent a minute fraction of the total. However, this fraction increases rapidly with the decrease of particle size. The surface hydroxyls (8OH/100 Å^2) of a typical sample of dried silica hydrogel with a surface area of 300 m^2 g^{-1}, amounts to 4% of the weight of the substance. Consequently, the surface groups largely determine the surface properties and usages of the substance. Submicron-sized oxides, which include fumed silica, alumina, TiO_2, mixed oxides, and also materials derived from them by appropriate chemical reactions, find diverse applications as adsorbents, reinforcing additives, processing aids, thixotropic agents, catalysts, and catalyst supports.

Many techniques have been employed in the past[1] to study the surface hydroxyls of metal oxides. These

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[1] H. P. Boehm, *Advan. Catal.*, **16**, 179 (1966).

include dehydration, neutralization, reactions with thionyl chloride and metal chlorides, and infrared and other forms of spectroscopy. However, these methods do not give information about the geometric distribution of the hydroxyl groups, nor do they reveal the state of the metal atoms in the surface. The central purpose of this work is to develop the use of VCl_4 to probe the surface structure of submicron oxide particles. From the amount of HCl evolved, the stoichiometry of its reaction with hydroxyls was determined. From the epr spectral parameters and widths it is possible to reveal further the geometrical disposition of these groups. In this capacity VCl_4 functions as a paramagnetic probe.

At first sight, VCl_4 seems to be an improbable molecule for the purpose assigned to it. Owing to short relaxation times, the epr spectrum of VCl_4 is too broad for detection[2] between 300 and 77°K. This is expected for a symmetric molecule with orbitally degenerate ground state. A broad epr spectrum can be observed[3–5] at 4°K ($g = 1.935$, line width 200–600 G). It is, however, possible to increase the relaxation time significantly by either replacement of one or more of the chlorine atoms with alkoxy groups or the complexing of VCl_4 with acetonitrile; both would remove the tetrahedral symmetry and the orbital degeneracy.[2] The vanadium atoms in these modified environments have epr spectra which can be readily observed even at room temperature. The same principle applies also to those vanadium atoms incorporated in the metal oxide surfaces. A simplifying feature of this technique is that unreacted VCl_4 molecules *do not* contribute to the observed spectra.

Experimental Section

Materials. The fumed silica and alumina are the products of Cabot Corp. The former, with the trade name Cabosil (M-5 grade) has a surface area of 150 m² g⁻¹ as received. The latter, with the trade name Alon, has an average particle diameter of 0.03 μ, a surface area of 100 $m^2\ g^{-1}$, and a bulk density of 63 $g\ l.^{-1}$ X-Ray patterns showed the material to contain 90% γ-Al_2O_3.

VCl_4 was purchased from Stauffer Chemical Co. and stored on a high-vacuum line in a blackened vessel maintained at −80°. VCl_4 was distilled fresh in each experiment.

Treatment of Cabosil. (a) Annealing. Cabosil, contained in a quartz vessel, was annealed at 700 ± 25° in a muffle furnace for 48 hr. This material has a bulk density of 33 $g\ l.^{-1}$, a surface area of 200 $m^2\ g^{-1}$, and contains 1.4OH/100 Å² ($n = 1.4$).[6]

(b) Rehydrating. Annealed Cabosil was rehydrated by reflux for about 3 hr in redistilled water. After filtration, the product was air dried overnight at room temperature and then vacuum dried at 70° to constant weight. The resulting brittle aggregates can be readily broken down by an agate mortar and pestle to a product having a surface area of 150 $m^2\ g^{-1}$, $n = 4.6$, and a bulk density of 60 $g\ l.^{-1}$.

Treatment of Alon. In addition to experiments with "as received" Alon samples, two hydrated forms of alumina were prepared by hydrothermal reactions. The gibbsite structure is stable up to 200° and the boehmite structure is stable up to 500°. To obtain the former, Alon was dispersed in water and heated to 200° for 2 hr. After freeze drying, the product was found to have a surface area of 100 $m^2\ g^{-1}$ and 8.1 mmol/g of hydroxyl groups. Alumina with surface layers of boehmite was prepared by hydrothermal treatment of Alon to a higher temperature (250°) and for a longer period of time (6 hr). The freeze-dried product has a surface area of 100 $m^2\ g^{-1}$ and 4.56 mmol/g of OH.

Whereas only several surface layers of the γ-Al_2O_3 particle were converted to the hydrated forms, the samples will be referred to as gibbsite and boehmite for the sake of brevity.

Reaction with VCl_4. (a) For Epr Measurements. The reaction vessel is constructed from a 50-ml round-bottom flask fitted with an O ring joint and a 10-in. long 4-mm o.d. quartz epr sample tube. A sample of fumed oxide was weighed into the vessel together with four small Teflon-coated stirring bars (1/8 in. o.d., 1/4 in. long). A high-vacuum Teflon valve with two O ring joints as ends was fastened to the reaction vessel. Viton O rings were employed for both the joints and the valves. This complete assembly was connected to a grease-free vacuum line. The sample was agitated and degassed at 150° until a constant vacuum of 1 μ was attained. The sample was cooled to −195° and a predetermined amount of VCl_4 was introduced to the top portion of the vessel remote from the sample. The Teflon valves were securely closed and the assembly was removed from the vacuum line. The vessel was brought to 90° slowly while its contents were thoroughly mixed by vigorous shaking. The total reaction time at 90° was 1 hr. For epr measurement, a sample of the material was transferred into the side arm and spectra were recorded at several temperatures. Evacuation of the sample caused no spectral changes.

(b) Determination of Stoichiometry. Two methods were used to determine the amount of HCl produced for each VCl_4 reacted. The choice was governed by the sample material and the degree of coverage. The first method (A) was applied to samples of large hydroxyl content and high degrees of coverage. The determination was made in conjunction with the epr measurement. After all the spectra had been recorded, the reaction vessel was connected to an absorption train. HCl was flushed out by a stream of predried N_2 and absorbed in traps containing standard NaOH solution. The scrubber was changed several times until no more HCl came through by titration of the contents. Finally, the amounts of hydrolyzable chloride and vanadium in the reaction vessel were determined.[7] No vanadium was ever detected in the scrubbers.

The metering of VCl_4 on vacuum line is based on the approximation that VCl_4 and $TiCl_4$[8] have the same vapor pressures at the same temperatures; the two compounds have very similar melting points and boiling points. The calculated quantity agreed with analysis to better than 15%.

When the hydroxyl content and the coverage are both low, an alternative method (B) was employed. A large quantity of metal oxide was placed in a cylindrical reactor fitted with steam-heated jacket and flushed with predried nitrogen for 1 hr. An evaporating bulb was connected to the inlet and scrubbers were connected to the outlet of the reactor. VCl_4 was introduced into the former to be carried into the reactor by nitrogen. A slight warming of the bulb was necessary to aid the evaporation. The HCl evolved was determined by titration.

Both methods have been applied to samples having intermediate hydroxyl contents and VCl_4 coverages. Their results agreed to better than 20%.

The concentration of those surface vanadium atoms which contribute toward the epr spectral intensity was calculated by the first moment method with an accuracy of about ±10%. The first moment computer program also included base-line justification.

Interpretation of Spectra. Most of the vanadium epr spectra obtained in this work are characteristic for powder samples having axial symmetry for the spin Hamiltonian. The condition for resonance is [9]

$$\omega_0 = g\beta_0 H/\hbar + AM + \frac{A_\perp{}^2(A_{||}{}^2 + A^2)}{4A^2 g\beta_0 H/\hbar}[I(I+1) - M^2] \quad (1)$$

where

$$g^2 = g_{||}{}^2 \cos^2\theta + g_\perp{}^2 \sin^2\theta \quad (2)$$

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(2) J. C. W. Chien and C. R. Boss, *J. Amer. Chem. Soc.*, **83**, 3767 (1961).

(3) D. W. Pratt, Ph.D. Thesis, University of California, Berkeley, Calif., 1967.

(4) R. B. Johannesen, G. A. Candela, and T. Tsang, *J. Chem. Phys.*, **48**, 5544 (1968).

(5) J. C. W. Chien, unpublished results.

(6) The surface area was measured by the Brunauer–Emmett–Teller method; *n* was calculated from thermogravimetric loss of water between 20 and 1100°. Both determinations were made under the supervision of Dr. R. D. Mair of the Hercules Research Center.

(7) Total vanadium content was measured spectrophotometrically at 415 mμ following the oxidation of all vanadium species by H_2O_2. The oxidation state assay was based on the liberation of I_2 from KI–KIO_3 solution by V^{2+} and V^{3+} species and the oxidation of I_2 by V^{5+}. These analyses were done by Mrs. E. L. Dalton of the Hercules Research Center.

(8) R. C. Weast, Ed., "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p D-101.

(9) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

and

$$(gA)^2 = g_{||}^2 A_{||}^2 \cos^2\theta + g_\perp^2 A_\perp^2 \sin^2\theta \quad (3)$$

Values of $A_\perp$ and $g_{||}$ are easily obtained, for the perpendicular bands are the stronger features[10] of an axial powder spectrum. Equation 1 for the perpendicular signals is obtained by setting $\theta = 90°$

$$\omega_0 = g_\perp \beta H(M_I)/h + A_\perp M_I + \frac{(A_{||}^2 + A_\perp^2)\hbar}{4g_\perp \beta H(M_I)}[I(I+1) - M_I^2] \quad (4)$$

The hyperfine fine coupling parameter has been predicted[11] to be negative[12] for vanadium. Consequently, the low-field line belongs to $M_I = -{}^7/_2$ and the high-field line to $M_I = +{}^7/_2$. Values of $A_\perp$ and $g_\perp$ are readily obtained from the field positions and the spacings of the set of eight perpendicular signals. Similar relations can be developed for the parallel signals and values of $A_{||}$ and $g_{||}$ obtained in much the same way. Spectral interpretation is further aided by the fact that the parallel and the perpendicular signals have opposite phases. Therefore, if the three low-field signals and the five high-field signals belonging to the perpendicular set have positive and negative phases, respectively, then the three low-field signals are negative and the remaining high-field signals are positive for the parallel set. Applying the above method to Figure 1 gives $A_\perp = 79.3$ G, $A_{||} = 189.9$ G, $g_\perp = 2.0250$, and $g_{||} = 1.9699$.

Results

Cabosil. A. Rehydrated Cabosil. Upon the reaction of rehydrated Cabosil with small amounts of VCl_4 (between 5 and 7% coverage), there was obtained a spectrum (Figure 1 and 2a) at both 25 and −195°. The spectral parameters are $g_\perp = 2.0250$, $g_{||} = 1.9699$, $A_\perp = 79.3$ G, and $A_{||} = 189.9$ G. This resonance spectrum is attributed to those vanadiums which are attached to the surface through the reaction with two "vicinal" hydroxyl groups with the evolution of 2HCl. The spectral intensity at −195° is about three times greater than that at 25°.

Different spectra (Figures 2b and 2c) were obtained at a coverage of 10% which are apparently the combined resonances of doubly attached vanadiums (*vide supra*) and singly attached vanadiums (Figure 4c, *vide infra*). At the higher coverages, the 25° spectrum contains a broad component, whereas the corresponding −195° spectrum does not. The latter is about ten times more intense than the former for a 20% coverage sample.

Above 20% coverage both the room-temperature and the liquid-nitrogen-temperature spectra have a broad component (Figures 2d–h). When rehydrated Cabosil was saturated with one monolayer of VCl_4, there was obtained at −195° only a broad epr spectrum (Figure 2h) ($g = 1.894$, $\Delta H = 480$ G); no room-temperature spectrum could be observed.

At less than 20% coverage, the concentration of tetravalent vanadium, as calculated from the −195° epr spectra, agreed very well with the amount of VCl_4 introduced. In these samples all the vanadium in the surface contributes to the epr intensity. This is not the case above 20% coverage. The total epr signal intensity begins to decrease as the coverage exceeds 40%. Figure 3 summarizes the results; each point in this figure is the average of two or three runs.

The use of CH_3CN is also helpful to spectral interpretation here. For instance, the epr spectra of a sample with 11.8% VCl_4 were altered by the addition of CH_3CN vapor in two ways. The original spectrum (Figure 2c) was converted to one like Figure 2a. The broad component present in the 25° spectrum before treatment disappeared after the treatment. These changes are reversible.

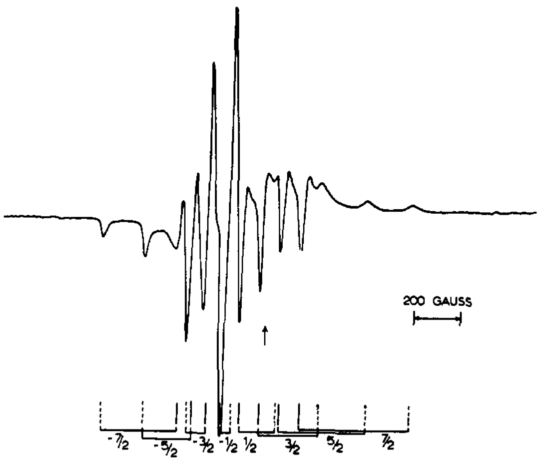

Figure 1. Epr spectrum of 5% vanadium on rehydrated Cabosil. Marker is 3370 G.

B. Annealed Cabosil. Because of the low hydroxyl content ($n = 1.4$) and low bulk density of this material, the epr spectral intensities are relatively weak. Though the spectra have definitely axial appearance, it is not possible to resolve the parallel and the perpendicular signals.

Between 10 and 30% coverage, the room-temperature epr spectra are devoid of hyperfine structure (Figure 4b). The resonance intensity varies from sample to sample taken from the same reaction mixture. The line width ranges from 340 to 580 G. Sometimes the line shape is symmetric, other times it is not. At 40% and higher coverages, no spectrum could be seen at room temperature owing to excessive line broadening even though the sample exhibited an epr spectrum at −195°. Addition of CH_3CN to a beige-colored sample of annealed Cabosil (23.5% coverage), which was characterized by a weak and broad spectrum at 25°, was changed to a pinkish orange colored material which displays a strong room-temperature epr spectrum (Figure 5) with $g_0 = 1.980$ and $A_0 = 114$ G. Upon evacuation, the sample resumed its original color with a tenfold reduction of the epr absorption. This process is reversible and quite reproducible.

The variegated changing patterns observed at room temperature were contrasted by the reproducible spectra recorded for the same specimen at −195°. These powder spectra for 10, 20, and 30% coverage were identical apart from intensity differences (Figure 4d) ($g_0 = 1.953 \pm 0.001$; $A_0 = 120 \pm 2$ G).

At 40% coverage, the low-temperature spectra showed a broad component (Figure 4d) which became the dominant feature at higher coverages (Figure 4e). When the VCl_4 introduced corresponded to 80% of the available silanol groups, it was apparent that some VCl_4 remained unreacted and can be pumped off.

In Figure 6 the vanadium concentration calculated from the epr intensities at −195° is plotted against coverage (curve A). Two points are noteworthy. At

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[10] J. A. McMillan, "Electron Paramagnetism," Reinhold, New York, N. Y., 1967, p 158.

[11] A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, 230, 169 (1955).

[12] A will be assumed to be negative here but the sign will not be shown explicitly in the text.

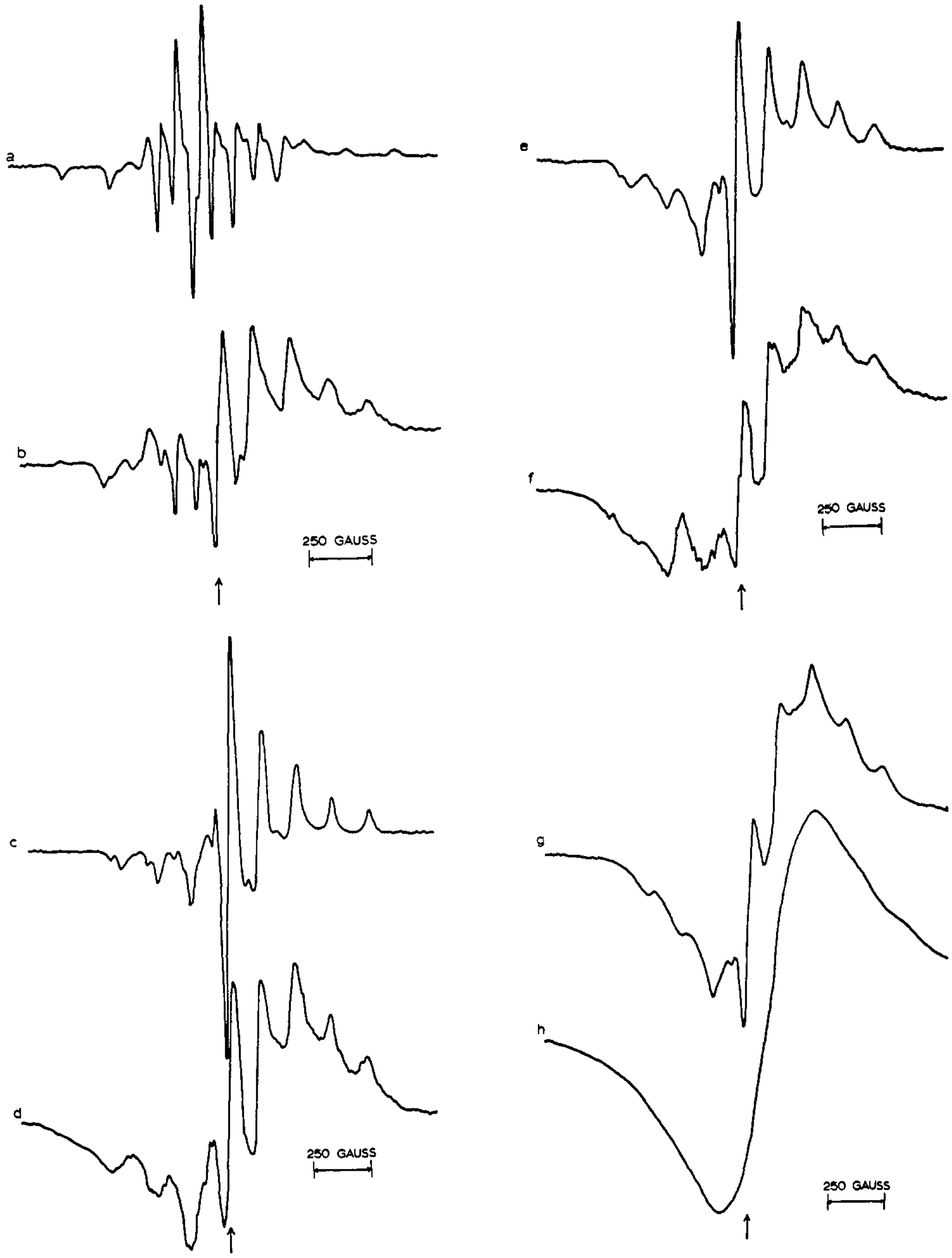

Figure 2. Epr spectra of vanadium-labeled rehydrated Cabosil obtained at various coverages and temperatures: (a) 5%, 25 and −195°; (b) 10%, 25°; (c) 10%, −195°; (d) 20%, 25°; (e) 20%, −195°; (f) 40%, 25°; (g) 40%, −195°; (h) 80%, −195°. Marker is 3280 G.

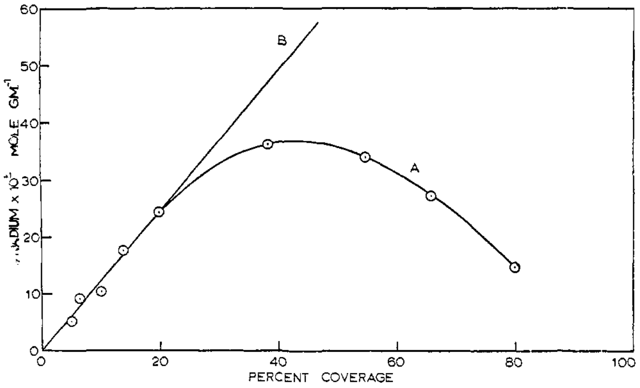

Figure 3. Variation of vanadium signal intensity with coverage on rehydrated Cabosil: (A) experimental curve, (B) theoretical line.

low coverages this concentration is considerably lower than the amount reacted; the latter is given by line B. The epr intensity begins to decline with coverage above 40%. The data indicate that a fraction of the vanadium atoms in the surface must be sufficiently close to neighboring vanadium atoms so that their broadened resonances fail to contribute to the observed spectral intensity.

C. Stoichiometry of VCl_4 Reaction with Cabosil. The amount of HCl produced by the reactions of VCl_4 with Cabosils was determined by both methods A and B. The results are summarized in Table I.

Method A, when used on annealed Cabosil, gave somewhat scattered results. However, the average value of the stoichiometric ratio is in agreement with that obtained with the more precise method B. About

Table I. Stoichiometry of Reaction between VCl_4 and Cabosil

Cabosil Type	Cabosil Weight, g	Coverage, %	VCl_4 added, mmol	HCl titer, mequiv	Method used	Stoichiometric ratio
Annealed	2.03	51	0.41	0.458	A	1.10
	0.98	28	0.11	0.097	A	0.89
	0.906	38	0.14	0.169	A	1.24
	11.8	26	1.21	1.305	B	1.08
	10.9	12	0.54	0.562	B	1.04
Rehydrated	2.12	13	0.35	0.537	A	1.54
	1.31	66	0.11	0.168	A	1.53
	0.83	40	0.43	0.658	A	1.53
	1.58	20	0.41	0.635	A	1.55
	3.42	14	0.62	0.967	A	1.56
	2.50	10	0.32	0.498	A	1.55
	40.2	11.5	6.02	9.31	B	1.55
	40.4	38.5	20.10	31.4	B	1.56

94% of the VCl_4 is singly attached to the surface *via* reaction with one silanol group.

Much more HCl was evolved for each VCl_4 reacted with rehydrated Cabosil. At a stoichiometry of 1.55 about half of the VCl_4 must be incorporated by reaction with two silanol groups. The fact that the same stoichiometric ratio of 1.55 was obtained under all kinds of experimental conditions is believed to be significant. First, there appear to be two kinds of sites. One kind consists of adjacent hydroxyls, both of which react with one VCl_4 to incorporate the probe molecule by double attachment; a second kind permits only single attachment of VCl_4. Secondly, the VCl_4 reaction was uniform and there was no chromatographic effect. The fact that this reaction is a slow one even at room temperature is undoubtedly helpful. Either one of the

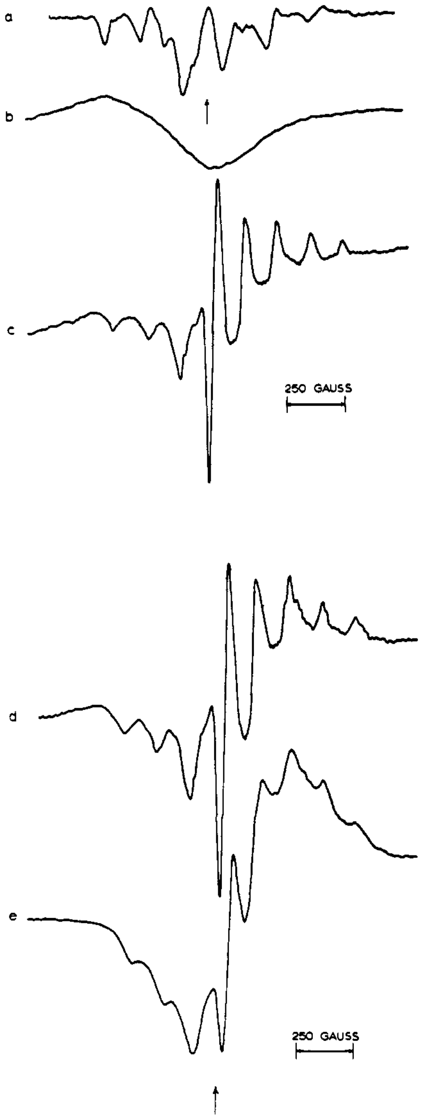

Figure 4. Epr spectra of vanadium on annealed Cabosil obtained at various coverages and temperatures: (a) 5%, −195°; (b) 10, 20, 30%, 25°; (c) 10, 20, 30%, −195°; (d) 40%, −195°; (e) 80%, −195°. Marker is 3300 G.

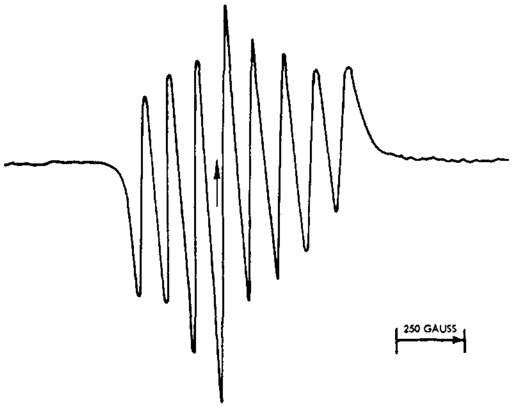

Figure 5. Vanadium on annealed Cabosil after exposure to CH_3CN. Spectrum recorded at 25° and 23.5% coverage. Marker is 3351 G.

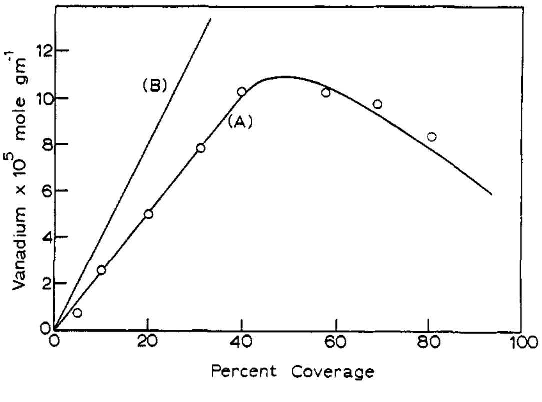

Figure 6. Variation of vanadium signal intensity with coverage on annealed Cabosil: (A) experimental curve, (B) theoretical line.

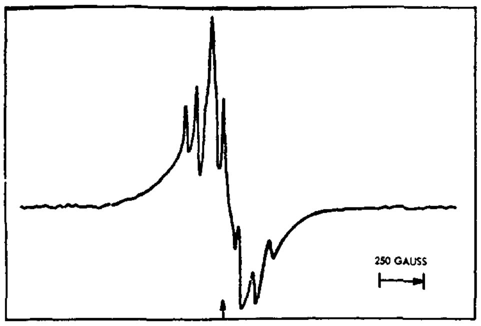

Figure 7. Vanadium on rehydrated Cabosil after heating at 350°. Marker is 3260 G.

above effects could render the method without quantitative value.

D. Migration of Vanadium on Silica Surface. The interconversion equilibria at various temperatures between vanadium halides of different oxidation states are complicated but well understood.[13] The conditions under which these processes occur on the silica surface are of interest for two reasons. It would define the limiting temperature above which V^{4+} is converted to V^{3+}; the latter species are not easily detected by epr because of a large zero-field splitting. Furthermore, one would have the means to study the propensity with which the attached vanadium can migrate on such surfaces.

The possibility that the reaction

$$2V^{4+}Cl_x \rightleftharpoons 2V^{3+}Cl_{x-1} + Cl_2 \qquad (5)$$

may occur under normal reaction conditions was first examined. In one experiment 0.65 g of rehydrated Cabosil was allowed to react with 0.11 mmol of VCl_4 at 90° for 1 hr. The thiosulfate titer of the volatile product was 0.0153 mequiv, indicating that a maximum 15% of vanadium could have reacted to give chlorine. Another experiment using 0.5 g of rehydrated Cabosil and 7×10^{-5} mol of VCl_4 reacting at 110° for 1 hr produced a 6.8×10^{-3} mequiv thiosulfate titer. About 9.7% of the vanadium may have reacted to form chlorine. Similar low titers were obtained for reactions with annealed Cabosil at 90°.

Reactions at elevated temperatures were next studied. After treating a sample of rehydrated Cabosil with VCl_4 to 10% coverage, the sample was brought up to 150, 250, 350, and 450° for 1 hr at each temperature. Epr spectra were recorded at −195° following each heat treatment. The initial spectrum was nearly the same as that shown in Figure 2c. After 1 hr at 150°, the spectral intensity was reduced threefold. Heating at 250° caused further lowering of observed signal intensity with concomitant decrease in hyperfine splitting. The spectrum obtained after an hour at 350° (Figure 7) appears to consist of a broad component with a width of 280 G and a narrow eight-line component with A_0 = 91.7 G; the g values are 1.980 and 2.009, respectively. A third narrow single-line component could also be present, which perhaps caused the poor resolution of the $M = -^3/_2$ and $-^1/_2$ lines. The narrow component disappeared after continued heating at 450°; only the broad line remained.

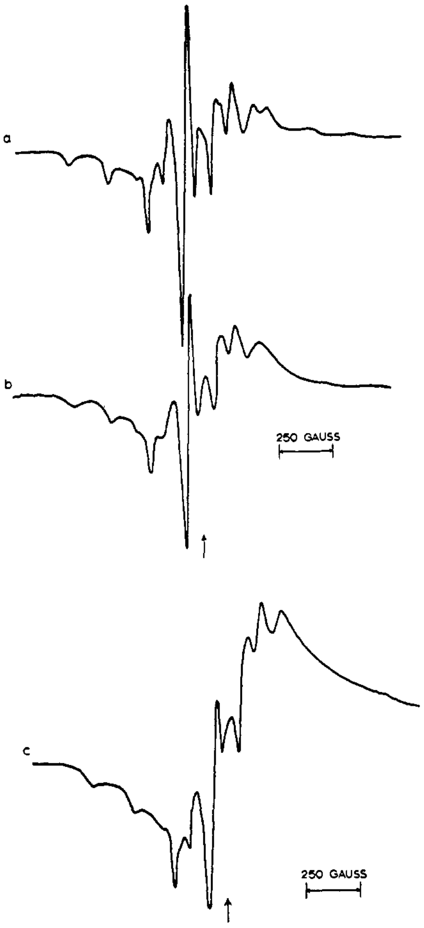

Figure 8. Epr spectra of vanadium on γ-Al_2O_3 with varying amounts of VCl_4 reacted: (a) 0.144 mmol g^{-1}, (b) 0.288 mmol g^{-1}, (c) 1.136 mmol g^{-1}. Marker is 3300 G.

The result of a similar experiment for annealed Cabosil is straightforward. Regardless of the amount of coverage, all of the vanadium(IV) epr signal disappeared upon heating to 150° or higher; no other new signal was produced. Analysis of the sample showed that about 80% of the vanadium has valence less than four.

Alumina. A. Stoichiometry of the Reaction between VCl_4 and Alumina. Because of the high bulk densities of the alumina samples, the stoichiometry was determined by method A. In several triplicate experiments, 0.25–1.0 g of alumina was evacuated at 150° for 2 hr, after which time 0.023–0.336 mmol of VCl_4 was admitted. Following 1 hr of reaction at 90°, the HCl formed was determined. The titer ranged from 0.175 to 0.790 mequiv. The stoichiometries found for reactions on γ-Al_2O_3, boehmite, and gibbsite surfaces are 2.16 ± 0.05, 1.94 ± 0.03, and 2.08 ± 0.05, respectively. Therefore, all the VCl_4 molecules are incorporated by double attachment on these surfaces.

B. Epr Spectra of Vanadium in Surfaces of Alumina. The spectra obtained with γ-Al_2O_3 at 25 and −195° are identical aside from a 3.5-fold intensity difference, in accord with the Curie dependence. Furthermore, spectra of samples with different coverages have the same features. These statements are also valid for gibbsite and boehmite samples.

In the case of γ-Al_2O_3 and gibbsite, the epr spectra obtained at 5% coverage are the same as the spectrum

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[13] R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 50, 54, 60 (1964).

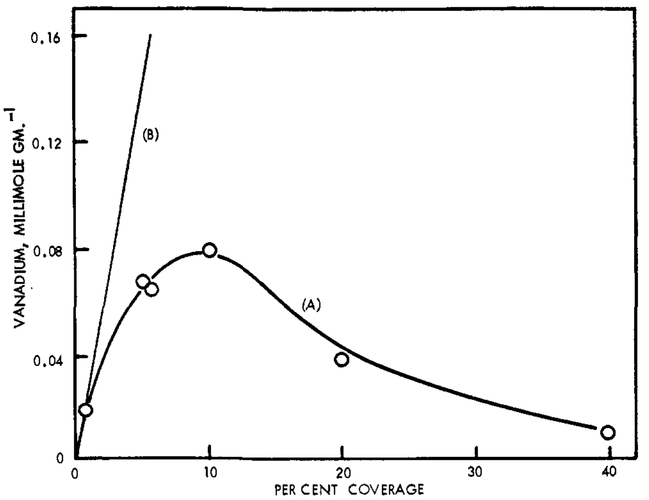

Figure 9. Variation of vanadium spectral intensity with degree of coverage on α-Al_2O_3: (A) experimental curve, (B) theoretical curve.

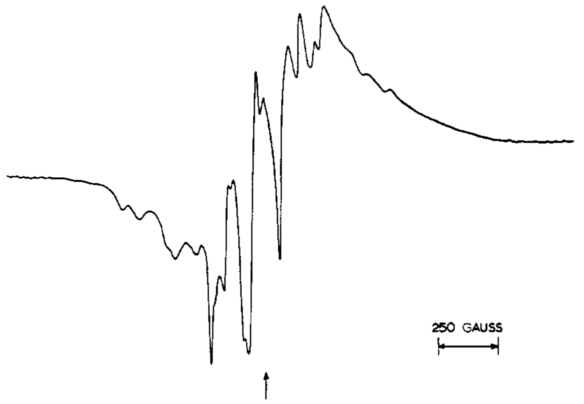

Figure 10. Vanadium spectrum on boehmite surface, 0.495 mmol of V g^{-1}. Marker is 3300 G.

shown in Figure 1a, except the resolutions are inferior for the high-field signals. A broad component is present at all other coverages (Figure 8). The spectral intensity approaches a maximum at 10% coverage and declines with the addition of more VCl_4 (Figure 9).

With 0.066 mmol of VCl_4 reacted per gram of gibbsite, the spectra is identical with Figure 8a aside from the absolute intensities. The same can be said about spectra obtained at 0.45 and 0.86 mmol of VCl_4 per gram of gibbsite.

On the other hand, with comparable amounts of VCl_4, the boehmite samples have more complicated spectra (Figure 10) containing more than 16 lines. Two interpretations are possible: either the spin Hamiltonian has rhombic symmetry or the vanadium atoms in this surface experience more than one type of ligand environment. If the former is assumed, one obtains g_1 = 1.905, g_2 = 1.974, g_3 = 1.986; A_1 = 192.6 G, A_2 = 161.1 G, and A_3 = 82.3 G.

C. **Migration Studies.** In this experiment, 0.25 g of γ-Al_2O_3 (as received) was covered with 0.072 mmol of VCl_4. Epr spectra were recorded at $-195°$ after each 1-hr heating at various temperatures. It was found that 150° heating caused only a slight change in the original spectrum and a moderate reduction in intensity. The new spectral parameters (Figure 11) are:

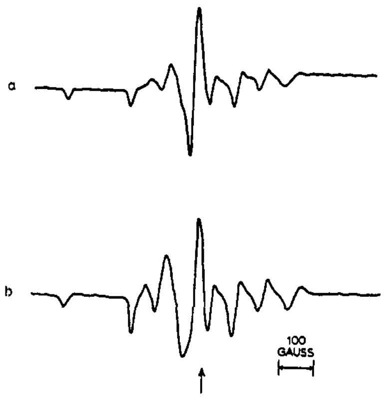

Figure 11. Change of vanadium spectra on γ-Al_2O_3 with heating: (a) 1 hr at 150°, (b) 1 hr at 250 and 450°. Marker is 3275 G.

$g_{\parallel}$ = 1.966, $g_{\perp}$ = 2.004, $A_{\parallel}$ = 180.5 G, $A_{\perp}$ = 60.9 G. During this period of heating, additional HCl was evolved to increase the overall stoichiometry to 2.4. Heating to temperatures higher than 150° caused only minor broadening of the resonance lines without either the loss of intensity or further evolution of HCl. No visible changes of any kind were observed by heating to 450°.

Discussion of Results

In the subsequent discussion there will be frequent references to several types of hydroxyls. There are geminal pairs with two hydroxyls on the same silicon atom. There are "vicinal" pairs, where the two hydroxyls are separated by a distance of 3.2 ± 0.1 Å and are thus ideal for reaction with the two Cl atoms of VCl_4.[14] There are single or isolated hydroxyls which are situated more than 4 Å from another hydroxyl group. Finally, the typical hydroxyls in the surface of γ-Al_2O_3 are close-packed hydroxyls.

Cabosils. The choice to study two particular surface-modified forms of Cabosil has several reasons. Fumed silica and dried hydrogel of silica are the earliest known and most widely studied members of submicron metal oxides. The annealed and the rehydrated forms are the most reproducible surface-modified materials. Even though fumed silica has long been thought to be an entirely amorphous substance, recent investigators believe otherwise. The constant value of n = 4.6 found for rehydrated Cabosil led DeBoer and Vleeskens[15] to propose that its surface is essentially that of the [0001] face of β-tridymite. Others believe[16] that the surface of silica gel (n = 7.85) is the same as the [100] face of β-cristobalite and that the subsequent dehydration is a random process.[17] Snyder and Ward,[18] on the other hand, argued that the surface is not modified during dehydration and that only bulk hydroxyls are removed in the process. There are also unsettled questions regarding the presence of vicinal and geminal hydroxyls. VCl_4 will react only with one member of the geminal pair under our mild experimental conditions. Reac-

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tions with both members would require the sharing of an edge for the two tetrahedra, which is an improbable event. Of course, the reaction of a VCl_4 molecule with two hydroxyl groups, one of each from different categories, is entirely possible.

Two points of general interest are noteworthy. Whereas a singly attached vanadium probe is free to rotate about the Si–O–V bonds, the doubly attached probe is immobile. Secondly, since each attached vanadium occupies an area of at least 46.1 Å^2, the maximum permissible surface density of the paramagnetic probe is 2.1/100 Å^2.

Mechanism for Line Broadening. The data described above show both temperature-dependent and temperature-independent line broadenings. The former is most evident in silica samples at low coverages, while the latter dominates at high coverages as well as in γ-Al_2O_3 samples of all coverages. One can rule out those relaxation mechanisms due to incompletely averaged anisotropies and magnetic dipolar interaction because they should increase with the decrease of temperature contrary to the observed phenomenon. The −195° spectra have the best resolutions and narrowest line widths. Furthermore, broadening due to anisotropy should increase with the decrease of crystal-field symmetry. Instead, when CH_3CN is introduced to annealed Cabosil samples, there is often a marked reduction in line width of the vanadium resonance.

Two mechanisms which could be controlling the line width are relaxations through interaction with low-lying excited states and exchange interaction between adjacent paramagnetic species. The former is probably unimportant for the following reasons. The excited-state process is extremely temperature dependent and cannot conceivably account for the temperature-independent broadenings. Furthermore, the relaxation time is increased by lowering the crystal-field symmetry. In high-coverage samples, where the paramagnetic species could be within perturbation distances, the line widths are increased but not decreased.

By this process of elimination it is believed that exchange interaction probably determines the line broadening in the samples studied here. When the vanadium is doubly attached and is immobile, this interaction depends upon the proximity of attachment. It is independent of temperature. For singly attached species, this interaction at −195° is only possible among those vanadiums frozen in space close to each other. As motional freedom increases with elevation of temperature, rotation about the Si–O–V bonds should increase the probability of this interaction. The complexing of CH_3CN, aside from the effect on the crystal field, may also decrease exchange interaction by steric hindrance.

To account for indirect exchange interaction in chloroiridinate salts, Griffith, *et al.*,[19] proposed that a small admixture of an excited state could cause exchange interaction between the unpaired electron spin on each Ir^{4+} ion. Following these authors' treatment, we postulate an analogous admixture of structure B to structure A of the attached vanadium species.

V^{4+}–Cl^-–Cl^-–V^{4+}
A

V^{3+}–Cl–Cl–V^{3+}
B

The wave function is

$$\psi = a\varphi_A + b\varphi_B \tag{6}$$

where $a \gg b$. In the limit of negligible overlap, the simplified expression for the exchange integral, J, is

$$J = \langle \psi_1(1)\psi_2(2)|e^2/r_{12}|\psi_1(2)\psi_2(1)\rangle \tag{7}$$

The exchange term in the spin Hamiltonian is

$$H_{ex} = JS^iS^j = J/2[S(S + 1) - S^i(S^i + 1) - S^j(S^j + 1)] \tag{8}$$

where S is the total spin, which can take values of $S^i + S^j$, $S^i + S^j - 1, \ldots |S^i - S^j|$. An estimate of J is obtained by treating the system like an elongated Cl_2 molecule, with J corresponding to the splitting between the lowest singlet and the first excited triplet in such a molecule. An approximation of the Morse potential was used, and the following expression for J was given[19]

$$J \approx q^2D(1 - \{1 - \exp[-\beta(r - r_e)]\}^2) \tag{9}$$

where $D = 2 \times 10^4$ cm^{-1}, $\beta = 2.04 \times 10^8$ cm^{-1}, and $r_e = 1.99$ Å for Cl_2.[20] The quantity q is the density of unpaired spin on Cl. Pratt[3] reported a value of −1.422 MHz for the ^{35}Cl contact hyperfine coupling constant in VCl_4. The hyperfine structure of the $^2P_{3/2}$ ground state of the ^{35}Cl atom has been studied by atomic beam techniques.[21] The coupling constant was found to be 205 MHz, which is the A value for a "pure" p electron in a 3p orbital of the chlorine atom. From these values, q is estimated to be 6.9×10^{-3}. For the approximate calculations which follow, the same q will be assumed for Si–$OVCl_3$, since the oxygen and the chlorine atoms do not differ greatly in heir electronegativities.

We are interested in the Cl–Cl distance at which hyperfine structure disappears, *i.e.*, $J \approx A$. For J to be 1.725×10^{-2} cm^{-1}, the distance between the Cl atoms of the exchange-interacting vanadiums is about 4 Å. To this is added the V–Cl bond distance[14] of 2.03 Å. Therefore, when two vanadiums are separated by less than 8 Å, exchange interaction should obliterate the hyperfine structure.

This indirect hyperfine interaction was found[22] to fall off rapidly with distance according to

$$J \approx Ce^{-7r}$$

for the chloroiridate salts. If the same dependence is assumed for the species under consideration, then an increase of only 0.33 Å in the Cl–Cl distance reduces J by a factor of 10.

Whereas a V–V distance of about 8 Å is needed to obliterate hyperfine structure when the vanadiums are doubly attached, a greater separation would achieve the same broadening for singly attached vanadiums. At room temperature two vanadiums attached each singly to a surface silanol group separated by about 12 Å would approach one another sufficiently close to have $J \approx A$ when they rotate about the Si–O–V bonds. It is 10 Å for exchange interaction between a singly and a doubly attached vanadium.

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For $J \gg A$, the line width could be sufficiently great that the detection of the resonance could become impossible. Additional broadening due to moderation of zero-field splitting may also come into play.

Rehydrated Cabosil. Three points need to be made prior to the discussion of the surface structure of rehydrated Cabosil. If one considers the area occupied by each VCl_x to be about 46 Å^2, then only two such groups can be accommodated per 100 Å^2 of surface. At n = 4.5, all the surface hydroxyls are consumed if the groups are $>VCl_2$, *i.e.*, doubly attached. If they are all singly attached ($-VCl_3$), then half of the hydroxyls remain unreacted at maximum coverage. Intermediate cases are also possible.

Secondly, DeBoer and Vleekens[15] proposed that this surface contains single hydroxyls separated by 5 Å from one another. At this distance, it is not possible for the vanadiums to be doubly attached. The model is incompatible with the observed stoichiometry of 1.55.

Thirdly, the stoichiometry of 1.55 was found for any coverage, implying the presence of two or more types of surface hydroxyls. These are the "vicinal" pairs of hydroxyls, with one member of a given pair situated about 3.2 Å from the other for ideal reaction of both with a VCl_4 molecule. Others include both geminal hydroxyl pairs and simple silanols, both of which can react only singly with a VCl_4 molecule.

At 5% coverage, the epr spectra showed no exchange broadening. None is expected at this low coverage. At twice that coverage, the epr spectrum (Figure 2c) is clearly the superposition of the doubly attached (Figure 2a) and the singly attached (Figure 4c) vanadium species. Some exchange broadening becomes evident at 25° (Figure 2b).

In the model proposed by Peri and Hensley,[17] they suggested for this surface that 70% of the hydroxyls are present as "vicinal" pairs and the remainder as geminal pairs both distributed randomly over the surface. The average separation between each pair is 12 Å. If the two types of vanadium species are equally abundant, as is indicated by the observed stoichiometry and epr spectra, then only the singly bounded vanadiums experience exchange interaction with one another. At this coverage there is no visible sign of exchange interaction in the $-195°$ epr spectrum (Figure 2c). Since J/k = 0.025°, the singly bounded vanadiums must be frozen at random orientations, most of which will be greater than 12 Å.

At 20% coverage or greater, exchange broadening is discernible even in the $-195°$ epr spectra (Figures 2d–e). For all attached vanadiums to be separated by distances of 4 Å or less so that $J = A$, the number density should be 1.85/100 Å^2 or 1.85/2.25 = 82% coverage. Figure 2h shows that indeed at 80% coverage, there is no hyperfine structure.

At this level of approximation, the results obtained here are entirely consonant with the model advanced by Peri and Hensley[17] for random dehydration of surfaces which resemble the [100] face of β-cristobalite prior to heat treatment.

Finally, at 13% coverage, less than 10% of the attached V^{4+} species were reduced by heat treatment. The average separations for these species are 10.4 Å; they are not close enough for reduction according to eq 5. A corollary is that the covalently bonded vanadiums do not migrate under these conditions.

Annealed Cabosil. According to the model of Peri and Hensley[17] (case 1), most of the hydroxyls remaining after annealing are geminal pairs. The material has n = 1.4. Consequently, the surface density of geminal hydroxyl pairs is 0.7/100 Å^2. On the other hand, if all the hydroxyls remained as isolated silanol groups (case 2), the density is 1.4/100 Å^2. The stoichiometry of the VCl_4 reaction corresponds to 94% of the products as $-VCl_3$. Both geminal and isolated hydroxyls are expected to bond singly to the vanadium. If these groups are randomly distributed, the average separation between geminal hydroxyls is 13.5 Å; it is 9.5 Å for isolated hydroxyls. The distance will be intermediate between the two extremes if both types of hydroxyls are present.

At 10% or greater coverage no hyperfine structure was observed at 25° (Figure 4b). Furthermore, from 5% to 40% coverage, three-eights of the vanadiums have line widths too broad to be detected at $-195°$ (Figure 6). Let us consider first that only one OH of the geminal pair will react with VCl_4. Then the results imply an average separation between all hydroxyls to be less than 12 Å. For random distribution of hydroxyls according to either case 1 or 2, the average separations between surface-bound vanadiums at 10% coverage are 21.4 and 15 Å, respectively. If the observations were to be accounted for by the above assumptions, the hydroxyls which remain after annealing must be in clusters with local density as high as n = 8.8. Since this exceeds even the value of n = 7.85 for dried hydrogel of silica before any heat treatment,[16] an alternative explanation must be found.

The results given in Figure 6 for low coverages imply that three-eights of the vanadiums must be very close to at least one neighboring vanadium at $-195°$ on a surface of low hydroxyl concentration. Therefore, case 2 can be discounted. Returning to case 1 and assuming that both hydroxyls of the geminal pair can react with one VCl_4, one finds a plausible rationalization. The pair of vanadiums attached to the same geminal pair should have very broad line widths at all temperatures. The data indicate nearly equal probability for VCl_4 to react with either the first or the second hydroxyl of a geminal pair. This theory calls for decrease of epr spectral intensity for coverages exceeding 50%. Figure 6 shows that such is indeed the case.

Two other observations indicate that the geminal pairs are not randomly distributed in the surface. Firstly, the vanadiums in samples of coverages 10% or more were all reduced to valences $<+4$ upon heating. Secondly, introduction of CH_3CN significantly decreased the line width. Since CH_3CN is unlikely to interfere with the interaction of two vanadiums on the same geminal site, it must do so to vanadiums on neighboring sites. These results suggest the existence of clusters of geminal hydroxyl pairs with local density of about 2.6 pairs/100 Å^2 based on known dimensions of the VCl_4 molecule.[14]

These clusters could result from the annealing process. Dehydration of silanol groups, which are on the average 5 Å apart before heating, requires the rotation of neighboring SiO_4 tetrahedra to reduce markedly the separation of the Si atoms and to bring the bridging oxygen atom into line in order to link the tetrahedra through a corner and form a siloxane linkage. This deformation could conceivably produce islands of geminal hydroxyls which remain after annealing.

In conclusion, the results reported here for both the annealed and rehydrated Cabosils tend to support the model postulated by Peri and Henseley.[17] However, their picture for the former surface is probably an oversimplified view of the real structure.

Alumina. The unit cell of γ-Al_2O_3 can be represented as a cube of side 7.84 Å, presenting eight oxide ions at each face. It has a defect spinel structure,[23,24] with 21.33 Al atoms arranged at random in the 16 octahedral and 8 tetrahedral vacancies. Chemisorption of water molecules saturates all the available oxide ions, giving a surface equivalent to that of gibbsite. This is consistent with the X-ray findings.[25] There are 17 hydroxyls[26] per 100 Å^2 of surface; the average distance separating the hydroxyls here is particularly favorable for reaction of two neighboring groups with VCl_4. The actual observed hydroxyl content of the Alon sample is 2.8 mmol g^{-1}. The theoretical value is 2.17 mmol g^{-1} for 100 m^2 g^{-1} of surface area (n = 13.1), assuming each oxide ion at the surface reacts with H_2O to form a hydroxide ion. Therefore, nonsurface hydroxyls may be present in the sample.

The maximum epr intensity was attained at about 10% coverage on γ-Al_2O_3 as compared to about 40% on Cabosil. The surface concentration of vanadium atoms is nearly the same at 10% coverage on alumina as that at 30% coverage on rehydrated Cabosil.

All the paramagnetic probes are doubly attached to the alumina surface as shown by the stoichiometry of HCl evolution. Therefore, the vanadium atoms in this surface are immobile. In consonance with this conclusion, heating the samples to 450° causes no decrease in epr intensities and line broadening of the spectra is a function of coverage only and is independent of temperature.

That the surface of boehmite is different from those of gibbsite and γ-Al_2O_3 has already been demonstrated by adsorption experiments.[22] Both oxide and hydroxide ions are found on the surface of boehmite having layered patterns. The epr spectra indicate that the paramagnetic probe in this case has rhombic symmetry. It is possible that the presence of oxide ions in the surface provides weak additional ligand-field perturbations of the vanadium atoms.

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Salt Complexes of Cyclic Polyethers. Distribution Equilibria

H. K. Frensdorff

Contribution No. 251 from the Elastomer Chemicals Department,
E. I. du Pont de Nemours and Company, Inc., Experimental Station,
Wilmington, Delaware 19898.
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Abstract: Partition of salt complexes of cyclic polyethers between water and immiscible solvents has been used extensively as a measure of complexing tendency. It was the aim of the present work to establish the equilibria governing these processes and to analyze them in terms of the underlying molecular processes. Published data and new data on alkali–picrate complexes of two cyclic polyethers (18-membered polyether rings containing 6 oxygens) are utilized to establish the functional form of the overall equilibrium and the equilibrium constants. The overall equilibrium is analyzed in terms of three constituent equilibria: complex formation in the aqueous phase and partition of uncomplexed polyether and of complex. It has also been possible to deduce equilibrium constants for the dissociation of complex cation–picrate ion pairs in the organic solvent. Though the constants are small, they indicate considerably more dissociation for the complex ion pairs than for the corresponding uncomplexed salt ion pairs.

The cyclic polyethers described by Pedersen are of special interest because of their remarkable complexing properties.[1,2] They form complexes with many salts, especially those of alkali and alkaline earth cations, both in solution and in the crystalline state. In a complex of the typical polyether (Figure 1), the cation is located in the center of the main ring in the plane, or almost in the plane, of the oxygen atoms,[3] being held there principally by electrostatic, *i.e.*, ion–dipole forces.[1]

Complexing in solution can be detected in many different ways, such as spectral changes, altered solubilities, and electrochemically. Complexing equilibrium

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