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Spin Centers and Catalysis on γ-Alumina

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The $pH_2 \rightarrow oH_2$ and $oD_2 \rightarrow pD_2$ (77–293°K) and $H_2 + D_2 \rightarrow 2HD$ (195–293°K) reactions have been studied over the temperature ranges indicated on γ-Al_2O_3 previously outgassed in vacuo at 550°C. The reaction rates are similar over the ranges indicated and at 293°K decrease in the order $pH_2 > oD_2 > H_2 + D_2$. In the outgassed state and before irradiation, the solid showed 4×10^{16} free spins g^{-1}, $g = 2.003$, line width 6 gauss, and it was concluded that surface free valencies were catalyzing all three reactions by chemical mechanisms. The conversions probably involve 2 atom recombination, and the $H_2 + D_2$ molecule–atom exchange, on a small fraction of active sites. A 2 Mrad dose of γ-irradiation gave a 100-fold increase in free spins in the γ-Al_2O_3, which now showed an anisotropic signal, g (average) $= 2.01$, line width 40 gauss and a 2–3-fold increase in catalyzed rate for the pH_2 conversion, but no change in HD equilibration rate. Presumably, therefore, the pH_2 increase arises from onset of a paramagnetic mechanism. Admission of oxygen to the irradiated γ-Al_2O_3 gave first an intensification of signal associated with a chemisorbed monolayer and at higher pressure a "pressure broadening" of part of the signal associated with an interaction with physically adsorbed oxygen. The broadening left a residual signal attributable to bulk spins, and by difference, a surface spin concentration was calculated and could be associated with a rate of pH_2 conversion. This rate checks to a factor 1.9 with that calculated using Wigner's equation, confirming the view that the conversion on the radiation-induced surface free spins of γ-Al_2O_3 occurs mainly by the paramagnetic mechanism. A close similarity exists with α-Al_2O_3, and we revise our earlier view about this catalyst, concluding now that low temperature conversion on the solid before irradiation involves the chemical mechanism, as for γ-Al_2O_3.

INTRODUCTION

Recent reviews (*1*, *2*) suggest the value of quantitative correlations in the effects of γ-radiation on solid catalysts. Kohn and Taylor (*3*) described the effects of γ-radiation on γ-Al_2O_3 as measured by the $H_2 + D_2 \rightarrow 2HD$ reaction, and Acres *et al.* (*4*) compared this reaction with $pH_2 \rightarrow oH_2$ on irradiated α-Al_2O_3. In neither paper were free spins detected on the heated and outgassed oxide before irradiation. The present paper, part of a general program (*5*), attempts to correlate catalytic activity for the three related reactions, $pH_2 \rightarrow oH_2$, $oD_2 \rightarrow pD_2$ and $H_2 + D_2 \rightarrow 2HD$ with surface free electrons on γ-Al_2O_3, (a) activated thermally in vacuo and (b) after subsequent γ-irradiation. Where necessary, some additional measurements on α-Al_2O_3 have been made to aid comparison with our earlier work (*4*).

EXPERIMENTAL

A conventional Pyrex-glass high vacuum (10^{-6} Torr) apparatus was used, with greased taps in the gas handling section, but a mercury cut-off for the catalyst section (*6*). The γ-Al_2O_3 was contained in a 150 cm^3 silica reaction vessel, connected via a graded seal, liquid nitrogen trap, and cut-off to the main gas handling section. The three hydrogen mixtures, pH_2–oH_2, oD_2–pD_2 and H_2–D_2–HD, were analyzed by a micro Pirani gauge (*7*), which limited

HD equilibration studies to catalyst temperatures > 195°K. ESR studies of the catalyst in a tube attached to a gas handling apparatus, were made with a Decca X-band instrument. After irradiation, the alumina could be tipped into an appendage while the tube walls were heated to remove the signal arising in the silica itself, before inserting in the ESR cavity. We estimate for a line width of 40 gauss a minimum detectable spin concentration of about 10^{16} free spins per gram (fs g^{-1}), an improvement over our earlier work (*4*). Spin concentrations were determined by comparison of signal peak areas with those from carbon standards calibrated against DPPH. ESR spectra were obtained for the solids at 77°K and various intermediate temperatures up to 293°K, and gas adsorption experiments, where reported, were carried out under the same conditions of temperature as the ESR spectra. Surface areas were determined by the BET method using Kr gas ($\sigma = 21.0\ \text{Å}^2$). The irradiation was carried out by a 500 Ci (nominal) ^{60}Co source, calibrated by a Fricke dosimeter, the solid being in every case at 77°K during irradiation.

MATERIALS

γ-Al_2O_3(I) Johnson–Matthey Specpure, Lab. No. 35352, specific area 21.4 $m^2\ g^{-1}$ (after a standard outgassing for 60 hr in 10^{-6} Torr at 550°C). Trace metal impurities in ppm, (analysis by Johnson–Matthey), are Na(3), Co(1), Si(1), Mg(1).

γ Al_2O_3(II) An I.C.I. Ltd. (Billingham) specimen, 101.5 $m^2\ g^{-1}$. Ca(3), Co(2), Fe(20), Na(200), Si(20).

α-Al_2O_3(I) Johnson–Matthey Specpure, Lab. No. 16371/B, 9.2 $m^2\ g^{-1}$ (used in (*4*)). Na(2), Ca(1).

α-Al_2O_3(II) L. Light & Co., 13.5 $m^2\ g^{-1}$. Ca(80), Cu(100), Fe(30), K(20), Mg(20), Na(60), Pb(20), Si(200).

RESULTS

γ-Al_2O_3 and α-Al_2O_3 Before Irradiation

After outgassing γ-Al_2O_3 (I) for 60 hr at 550°C, an ESR line was detected with $g = 2.003$, $\Delta H = 6$ gauss, 4×10^{16} fs g^{-1}. This was a very weak signal and a high modulation amplitude, ca. 10 gauss, was used to aid in display. The fact that the signal disappears on heating the solid in air at 500°C suggests that the free electrons are on, or at least readily accessible to, the surface, so we may calculate a surface concentration of 1.87×10^{11} fs cm^{-2}. By comparison, it was relatively easy to detect a thermally activated ESR signal from α-Al_2O_3. Our earlier difficulties in this direction (*4*) arose from the less sensitive spectrometer used. For both samples of α-Al_2O_3, at 77 and 293°K, the signal had $g = 2.003$, $\Delta H = 6$ gauss. In the case of α-Al_2O_3 (I), there were 3×10^{16} fs g^{-1}, instantly removed on admission of air, and therefore corresponding to a surface concentration of 3.3×10^{11} fs cm^{-2}. In the case of α-Al_2O_3 (II), there were 1.5×10^{17} fs g^{-1}, but raising the outgassing temperature from 550 to 900°C completely eliminated the signal. Admission of hydrogen at 77 or 300°K had no effect, but oxygen at 100°K reversibly changed the line width and intensity as shown in Fig. 1. Addition of oxygen at a higher temperature, 293°K, gave a new irreversible component in the signal,

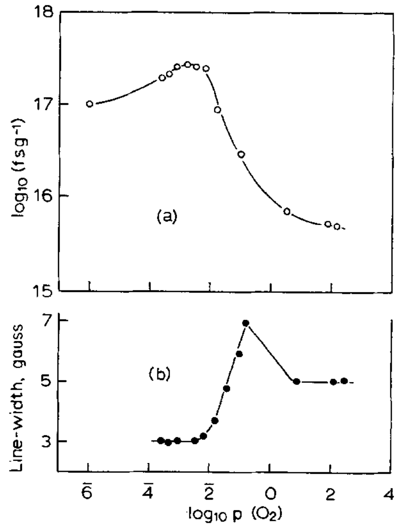


FIG. 1. Effect of oxygen pressure on (a) intensity and (b) linewidth of the ESR signal for α-alumina (II) at 100°K.

as shown in Fig. 2a, which we attribute to chemisorbed oxygen. The anisotropic character of this new signal, with $g_{\parallel} = 2.0167$ and $g_{\perp} = 2.0005$, points to the adsorbed oxygen being in an axially symmetric electric field. Further addition of oxygen gave a reversible broadening as in Fig. 2b.

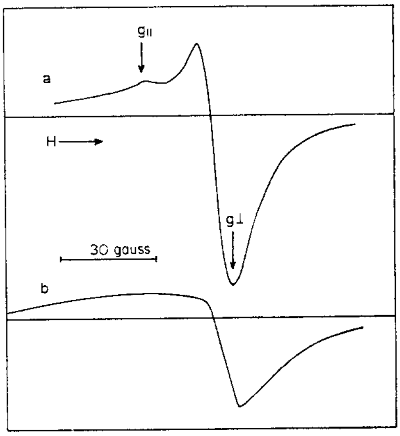


FIG. 2. (a) The effect of a low pressure of oxygen on thermally activated α-alumina at 253°K and (b) the effect of increasing the oxygen pressure to 12 Torr in broadening the signal, 295°K.

The catalytic activities of the thermally activated γ-Al_2O_3 (I) are defined in the usual fashion (*4*). If Ω_0, Ω_t are the resistance values for the hydrogen species (pH_2, oD_2 or HD) specifying the difference in concentration from the equilibrium value, then the results all fit the first order law (*8*);

$$k_e = \frac{2.303}{t} \log_{10} \frac{\Omega_0}{\Omega_t} \text{ min}^{-1}$$

and

$$k_m = \frac{k_e N}{60A} = \frac{k_e}{60A} \cdot \frac{pV}{kT} \text{ molecules cm}^{-2}\text{s}^{-1},$$

where N is the number of molecules in the reaction volume V, pressure p, temperature T°K, and A is the area of the catalyst.

Apparent activation energies E, frequency factors B_m, and reaction orders n are calculated by

$$k_m = B_m \exp \frac{-E}{RT}, \text{ and } k_m = k_m{}^0 p^n.$$

From Fig. 3 we see $n = 0$ for pH_2 at all temperatures except 800°K, where at low pressures $n = 0.6$ tending to zero at higher pressures. For oD_2, $n = 0$ at 800°K. For HD, at 195°K $n = 0.5$, and at 800°K, $n = 0.6$.

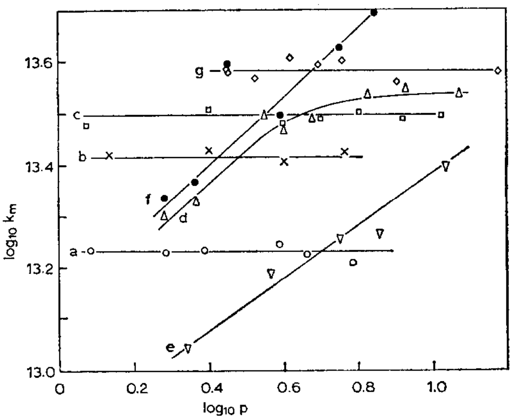


FIG. 3. Pressure dependencies, for reactions and temperatures indicated, on γ-alumina (I) previously outgassed 60 hr at 550°C. (a) pH_2, 77°K, (b) pH_2 195°K, (c) pH_2 273°K, (d) pH_2 800°K, (e) $H_2 + D_2$ 195°K, (f) $H_2 + D_2$ 800°K, (g) oD_2 800°K.

From Fig. 4 we calculate for HD, $E = 360$

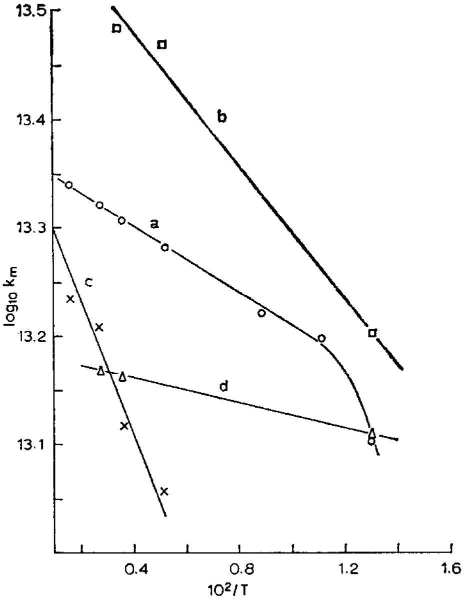


FIG. 4. Temperature coefficients on γ-alumina (I) previously outgassed at 550°C (a) pH_2, 4.4 Torr, E = 68 cal/mole, (b) a later expt, pH_2 3 Torr E = 180 cal mole^{-1}, (c) $H_2 + D_2 \rightarrow 2HD$ 3.4 Torr E = 360 cal mole^{-1}, and (d) oD_2 c.3 Torr E = 27 cal mole^{-1}.

cal mole^{-1}, pH_2 $E = 68$ cal mole^{-1} and (in a later series 180 cal mole^{-1}), and for oD_2 $E = 27$ cal mole^{-1}. These values are all small but definitely positive and depend on the thermal history of the solid to some extent.

γ-Al_2O_3 *After Irradiation*

After outgassing γ-Al_2O_3 (I) for 60 hr at 550°C, it was then irradiated for 20 hr at 77°K with a standard total dose of 2 Mrads. The effect was to give an ESR signal at 77°K, g (average) $= 2.01$, $\Delta H = 40$ gauss as in Fig. 5a. The number of free spins reaches a maximum with a γ-ray dose of 1.5 Mrad, in Fig. 5b, as does also the rate of pH_2 conversion in Fig. 5c. This signal is mainly due to bulk rather than surface free electrons, since admission of air at 77°K had no measurable effect. On heating the solid to 293°K, the signal showed a small increase in anisotropy and a relatively slow decay, with a 20-fold decrease over 24 hr, as in Fig. 5d. Irradiation of outgassed γ-Al_2O_3, at 77°K, when measured gave a broader signal at 1.6 or 4.2°K, $g = 2$, $\Delta H = 300$ gauss, probably saturated to some extent even at minimum rf power.

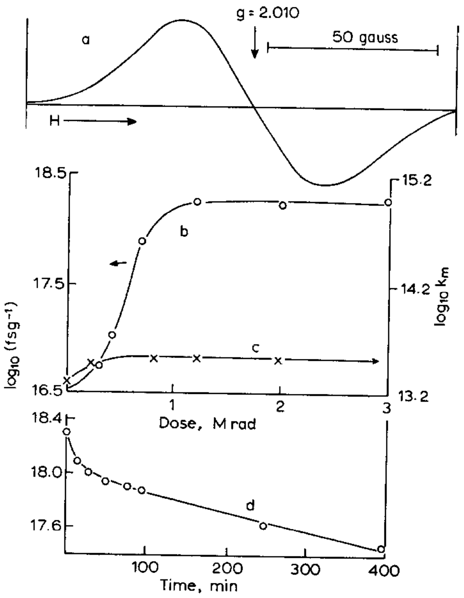


FIG. 5. (a) The (mainly bulk) signal resulting from γ-irradiation of γ-alumina at 77°K. (b) The concentration of free spins against γ-ray dose 77°K. (c) The parahydrogen conversion rate, 77°K against γ-ray dose. (d) The decay rate of free spins at 295°K.

On exposure of the irradiated γ-Al_2O_3 (I) to hydrogen at 100°K, there was only a small decrease in ESR signal. On the other hand, admission of oxygen at this temperature first irreversibly increased the signal 2.5-fold, presumably due to a chemisorbed layer, and on increasing the oxygen pressure there followed reversible broadening. Nitric oxide gave a similar broadening effect. The residual signal left at high oxygen pressures may presumably be attributed to the free electrons in bulk, so that subtraction of the residual signal from the original total signal (which resulted from irradiation followed by oxygen) should give the surface component of the signal. The resulting surface signal is shown in Fig. 6, and, as discussed later, probably corresponds to a chemisorbed O_2^-, the two g values, $g_{\parallel} = 2.038$ and $g_{\perp} = 2.006$ denoting axial electric symmetry. Attention is drawn

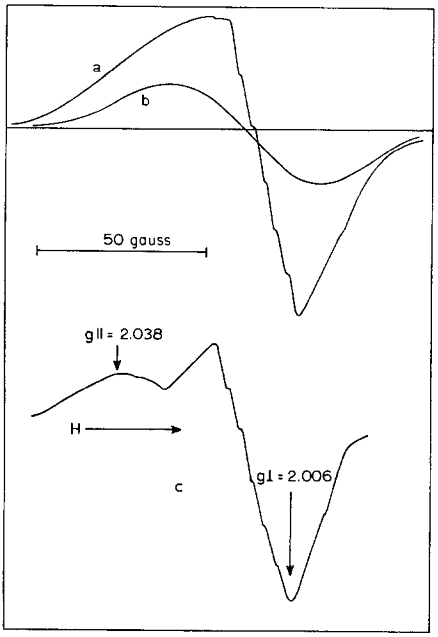


FIG. 6. (a) The ESR signal resulting from adding 10^{-3} Torr oxygen to γ-irradiated γ-alumina (I) at 100°K. (b) The effect of a high pressure of oxygen in quenching this signal, leaving the signal due to bulk spins. (c) The signal due to surface spins, formed by substracting (b) from (a).

to the hyperfine splittings of 3.6 gauss on the $g_\perp$ side of the signal. This is indicative of a slight overlap of the wave function of the O_2^- radical with a neighboring ^{27}Al nucleus, which with a spin of 5/2 is expected to give rise to a sextet of equally spaced lines, as found. This surface signal showed some stability loss on warming the alumina to 423°K. Since total spins were 4.8×10^{18} fs g^{-1}, bulk spins 2.0×10^{18} fs g^{-1}, then the surface spins were 2.8×10^{18} fs g^{-1}, equivalent to 1.36×10^{13} fs cm^{-2}. Rather similar results were found with other samples of γ-Al_2O_3, although the hyperfine splitting of 3.6 gauss was not always clearly resolved.

The effect of oxygen and irradiation together was to give a very intense signal. Thus our outgassed sample of γ-Al_2O_3 (I) exposed at 77°K to 4 Torr oxygen and γ-irradiated, gave the signal in Fig. 7. Here, besides the ordinary signal found with vacuum-irradiated γ-Al_2O_3, there is a second, very intense component, with $g = 2.003$, total concentration 2.74×10^{19} fs g^{-1}. Reversible oxygen treatment left a residual signal of 9.6×10^{18} fs g^{-1}, giving a surface signal of 1.78×10^{19} fs g^{-1} equivalent to 8.3×10^{13} fs cm^{-2}. A comparable result was found with α-Al_2O_3 (II).

Experiments were made to reveal possible effects of surface OH groups, which infrared studies (*9*) have shown to be largely removed at 900°C. After outgassing at this temperature, no ESR signal was detectable, but subsequent γ-irradiation gave the usual broad line with $g = 2.01$. Oxygen quenching as before established an anisotropic surface signal with $g_\parallel = 2.040$ and $g_\perp = 2.001$.

The effect of preirradiation of γ-Al_2O_3 (I) (previously outgassed at the usual temperature of 550°C) on the catalyzed rate of conversion of pH_2 at 77°K was to increase $10^{-13}\ k_m$ from 1.7 to 3.4 (cf. Fig. 5) and for γ-Al_2O_3 (II) from 0.19 to 0.34, a factor of approximately 2 in each case. There was no change in HD rate. In Fig. 8, we show the effect of outgassing temperature on k_m for pH_2 on the solid at 77°K, and the results tend to run parallel both before and after irradiation. Pumping a specimen at 20°C (off the graph) gave no catalytic activity, although subsequent irradiation gave a k_m (77°K) of 10^{11} molecules cm^{-2} s^{-1}. These results suggest that

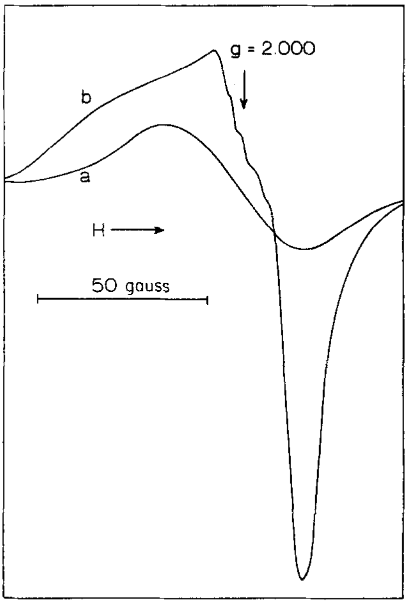


FIG. 7. (a) The ESR signal resulting from γ-irradiating γ-alumina (I) while exposed to 4 Torr oxygen. (b) The effect of pumping out the gas-phase oxygen.

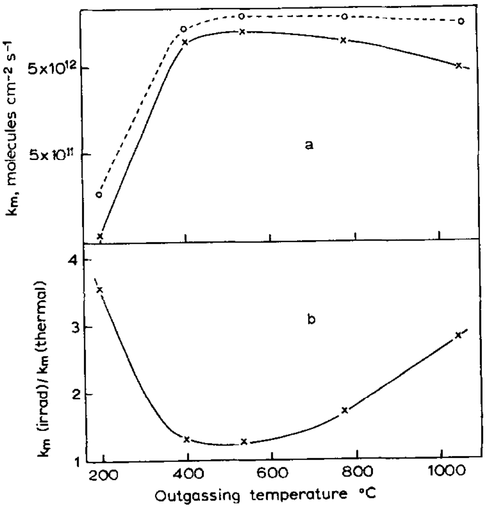


FIG. 8. (a) The effect of outgassing temperature on the pH_2 rate at 77°K γ-alumina (I) before (*x*) and after (*o*) γ-irradiation (2 Mrads). (b) The enhancement factor due to irradiation k_m(irradiated)/k_m(thermal).

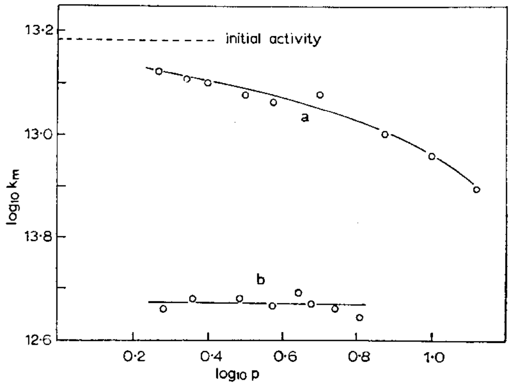


FIG. 9. The effect of γ-irradiation on the order of the parahydrogen conversion rate at 77°K on γ-alumina (I), (a) pretreated with 14 Torr oxygen at 500°C after outgassing, then irradiated with 4 Mrads and (b) the activity of catalyst from (a) after annealing for 2 hr at 295°C.

outgassing below 400°K leaves a surface covered with adsorbed gas, probably water, which poisons the catalyst, but which on irradiation decomposes to give free radicals which convert pH_2.

Although irradiation of γ-Al_2O_3 in vacuo raised k_m at 77°K by a factor 2, the order of the reaction, over the pressure range 1–6 Torr, remained zero. Figure 9 shows a very interesting effect of 14 Torr oxygen, which lowers the reaction velocity from the initial activity line to line (b), both rates being independent of pressure. A 4 Mrad dose in the presence of oxygen raised the activity to line (a), now with a negative order, while annealing some hours at 295°K returned the activity to line (b). The effect of a 2 Mrad dose on γ-Al_2O_3 (I) in vacuo was to change the activation energy from 240 cal mole^{-1} (cf. earlier values, 180 and 68 cal mole^{-1}) to zero, and this is a very significant result, as shown in Fig. 10.

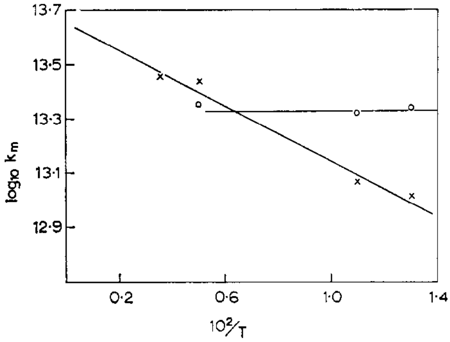


FIG. 10. The effect of γ-irradiation on the activation energy E for the parahydrogen conversion activity of γ-alumina (I) (77–273°K), (o) irradiated (2 Mrads) $E = 0$ (x) annealed, $E = 240$ cal mole^{-1}.

In Fig. 11 (b) γ-irradiation of γ-Al_2O_3 (I) at 77°K appeared to increase the amount of hydrogen adsorbed, whether the previous outgassing was carried out at 550 or 900°C. The isotherms of Fig. 10 (a) give a heat adsorption of hydrogen on γ-Al_2O_3 (I), outgassed at 550°C and before irradiation, of about 900 cal mole^{-1}.

DISCUSSION

There is a general similarity between these results on γ-Al_2O_3 and the earlier

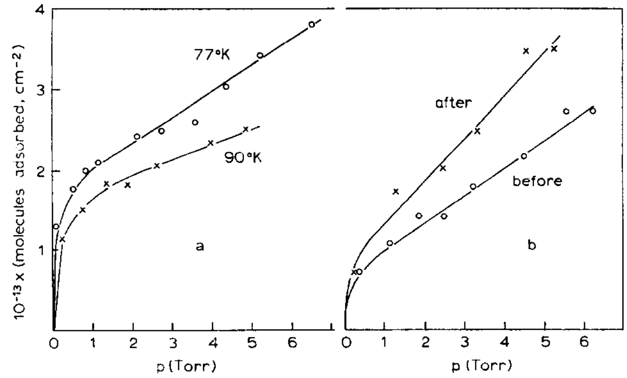


FIG. 11. (a) Adsorption isotherms for hydrogen at 77 and 90°K on γ-alumina (I) outgassed at 550°C, (b) before (o) and after (x) a 6 Mrad dose of γ-radiation, on γ-alumina (I) outgassed at 900°C.

work on α-Al_2O_3 (*4*), with some quantitative differences. Thus, on γ-Al_2O_3 (before irradiation) the pH_2, oD_2, and HD reactions from 195°K upwards have closely similar rates, with $k_m(pH_2)/k_m(HD) = 1.7$ at 195°K, compared with 17 on α-Al_2O_3. So it seems that the low temperature pH_2 reaction on γ-Al_2O_3 involves a chemical mechanism (similar to that for HD equilibration), while the case of α-Al_2O_3 we reconsider later. The small positive activation energy for pH_2 on γ-Al_2O_3 (also found on α-Al_2O_3 (*4*)) fits a chemical mechanism.

A possible mechanism involves a small number of isolated double sites which can chemisorb hydrogen and give the pH_2 and oD_2 conversion reactions by a Bonhoeffer–Farkas mechanism,

$$pH_2(oD_2) + 2M \rightleftarrows 2M - H(D) \rightleftarrows 2M + oH_2(pD_2),$$

and $H_2 + D_2$ by an Eley–Rideal mechanism involving D_2 and H_2 in a physically adsorbed layer.

$$D_2 + MHMH \rightleftarrows MHMHD_2 \rightleftarrows MHMD + HD \text{ etc.}$$

If the chemisorbed sites are saturated and the molecular adsorbed "layer" only partly covered (as evidenced by the isotherms in Fig. 10) this would explain the zero order for the two conversion reactions and the fractional order for the HD equilibration.

A saturation dose of radiation administered under our standard conditions increases the free spin concentration by a factor 100 and pH_2 velocity at 77°K by 2 for γ-Al_2O_3, compared with 30 and 3, respectively, for α-Al_2O_3, with the activity for HD at 195°K remaining unchanged on both solids. It must be realized that ESR does not necessarily detect all free electron spins, because of factors such as relaxation time and anisotropy. Also there is not *necessarily* a linear relationship between catalytic activity and the number of surface free spins. However, the catalytic centers produced by irradiation in each case are active only in the spin isomerization reactions, and it seems possible that the much smaller enhancement factor for activity compared with free spins will reflect the ratio of surface to bulk free spins. This agrees with the fact that admission of air showed no measurable effect on the ESR signal; we should only expect a 2% decrease, which would go undetected. There is a secondary effect of the radiation dose in raising the concentration of adsorbed hydrogen at 77°K and 1 Torr by about 30% (Fig. 10), but this effect is too small to account for all the observed increase in rate of conversion at 77°K.

The distinction between the role of the thermally-activated centers as chemical, (pH_2, oD_2 and HD active) and the radiation enhanced as paramagnetic (pH_2, oD_2 active, inactive for HD) is maintained by the effects of added oxygen gas, which in small amounts poisons the thermal centers and enhances the activity of the paramagnetic centers, probably by forming chemisorbed O_2^- groups. At higher pressures of oxygen, the reversibly (i.e., physically) adsorbed oxygen quenches out part of the enhanced ESR signal, presumably the surface contribution, which effect we have used to estimate the concentration of surface spins. This allows us later to give a more accurate calculation than heretofore of the contribution to the conversion of the Wigner paramagnetic mechanism.

As earlier in the rare-earth oxides (*10*, *11*), while the amount of adsorbed hydrogen at 77°K continues to increase with pressure, the pH_2 conversion itself is zero order, and one concludes the pH_2 and oD_2 conversion centers are strongly adsorbing and only make up a fraction of the total surface. This would agree with our ESR surface spin calculations (Table 1, later) in the range 10^{11}–10^{14}/cm^2 compared with an expected 10^{15} sites/cm^2. This corresponds to 0.1 to 10% of active paramagnetic sites, the figures increasing over the series, thermal activation only, radiation activated, and radiation plus oxygen activated. The latter, most active surface showed a slightly negative pressure dependency for pH_2 at 77°K, previously found for rare-earth oxides (*11*) and transition metals (*12*). These oxygen activated centers were

TABLE 1

PARAHYDROGEN CONVERSION AT 77°K

Al_2O_3	A, m^2 g^{-1}	Treatment	fs g^{-1} (total)	fs cm^{-2} (surface)	k_m(obsd)	k_m(calcd)	k_m(obsd)/k_m(calcd)
α (I)	9.2	T[a]	3.1×10^{16}	3.3×10^{11}	5×10^{13}	2.3×10^{10}	2200
"	"	T, Irradiated	3.0×10^{17}	3.3×10^{12}	6.5×10^{13}	2.3×10^{11}	290
α (II)	13.4	T[a]	ca. 1×10^{17}	7×10^{11}			
		T, 150 Torr O_2 at 100°K	5.0×10^{15}				
γ (I)	21.4	T	4×10^{16}	1.9×10^{11}	1.3×10^{13}	1.3×10^{10}	1000+[c]
		T, 10^{-3} Torr O_2 Irradiated	4.8×10^{18}	1.4×10^{13}	2.1×10^{13}*[b]	9.2×10^{11}	23
		Quench O_2	2×10^{18}		1.7×10^{13}		
"	"	Irradiated in O_2	2.7×10^{19}	8.3×10^{13}	1.1×10^{13}	5.6×10^{12}	1.9

[a] T denotes outgassing at 550°C for 60 hr.

[b] * This value is k_m(irradiated) $-$ k_m(thermal) $= 3.4 \times 10^{13} - 1.3 \times 10^{13}$.

[c] + Corrected version of earlier values calculated for same data 4030 (*4*), 520 (*13*).

easily annealed out at 295°K when a lower activity and zero order was restored. The effect is, therefore, reversible. A negative temperature coefficient is characteristic of the paramagnetic conversion and a positive one for the chemical mechanism. The fact that γ-irradiation changes the temperature coefficient of the conversion from a positive value to a zero value, therefore, agrees with our suggestion that the chemical mechanism on the outgassed catalyst is supplemented by a paramagnetic conversion after irradiation.

The Calculated Paramagnetic Conversion

For the reasons advanced earlier for the rare-earth oxides (*10, 11*), it would appear that mechanism (1b) in the previous classification (*12*), in which a hydrogen molecule vibrates with frequency ν over strongly adsorbing paramagnetic sites, of moment μ_a, surface concentration n_0/cm^2 (*13, 14*), and fractional coverage $\theta = 1$, is the one to consider here.

Hence

$$k_m = n_0 \theta \phi \nu,$$

and with the usual assumption of $\nu = 4.5 \times 10^{11}$ sec^{-1}, $\theta = 1.0$, ϕ given as below, we can then take n_0 from the ESR estimate of the paramagnetic *surface* sites, as provided by the oxygen broadening data. The transition probability is $\phi = W_{01}G(T)$, where at 77°K (our standard temperature for this comparison), the sum-over-states are

$$G_{H_2}(T) = 0.22, \quad G_{D_2}(T) = 0.59,$$

and for hydrogen,

$$W_{01} = 1.152 \times 10^{-9} \mu_a^2 / T r_s^6 \text{cgs units.}$$

With our usual assumption for the collision radius, hydrogen-paramagnetic site, of $r_s = 2A$ and taking $\mu_a = 1.73$ BM (one unpaired electron) so that $\phi = 1.54 \times 10^{-13}$, we have

$$k_m(pH_2, 77°K) = n_0 \times 1.54 \times 10^{-13} \times 4.5 \times 10^{11} = 0.0693 n_0,$$

leading to the results in Table 1, which includes results for both α-Al_2O_3 (obtained earlier (*4*) and recalculated) and γ-Al_2O_3. On thermally activated surfaces, the large ratio of observed rate to calculated paramagnetic rate confirms the importance of chemical activation on these surfaces, supporting the $k_m(pH_2)/k_m(HD)$ ratio at 195°K of 1.7 for γ-Al_2O_3. In the earlier paper (*4*), the ratio of 17 for α-Al_2O_3 was explained as due to a predominant paramagnetic conversion in this case. It was noted at that time that a chemical mechanism for both pH_2 and HD reactions, with an activation energy difference due to zero point energy of only 108 cal $mole^{-1}$, could also explain the observed result. On reconsideration, the positive activation energy of the pH_2 conversion, 240 cal mole^{-1} at 77°K for α-Al_2O_3 (*4*) is similar to that observed here for γ-Al_2O_3, and therefore, unlikely to be associated with a paramagnetic mechanism. So it seems more likely that chemical activation is involved in each case, and we withdraw our earlier suggested mechanism for the pH_2 conversion on α-Al_2O_3 at 77°K.

The most striking result in these comparisons is that when one promotes the paramagnetic character of the surface by radiation, or even more so radiation plus oxygen, the k_m(obsd)/k_m(calcd) ratio decreases, until for the most highly paramagnetic surface, a ratio of 1.9 only is obtained. Bearing in mind the sweeping character of some of the assumed values for the parameters such as r_s, this seems a satisfactory result. It may be compared with the ratio of 10 for the rare-earth oxides, (Ref. (*11*) as corrected in Ref. (*13*)).

Isotopic ratios at 77°K, as calculated earlier for gadolinium (*15*) and zeolites (*16*), are given by

$$\frac{k_m(pH_2)}{k_m(oD_2)} = \frac{\mu_H^2}{\mu_D^2} \times \frac{G_{H_2}(T)}{G_{D_2}(T)} \times \frac{I_{H_2}}{I_{D_2}} \times \frac{\nu_{H_2}}{\nu_{D_2}} \times \frac{\theta_{H_2}}{\theta_{D_2}}.$$

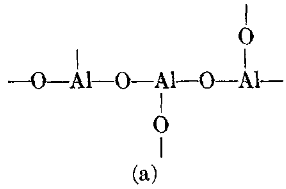
In the gadolinium paper (*15*), we assumed the ν ratio to be 1.0, but here we calculate it from the inverse square root of the molecular mass, as for the zeolites (*16*).

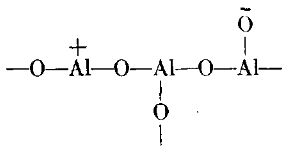
$$\frac{k_m(pH_2)}{k_m(oD_2)_m} = 10.61 \times 0.37 \times \frac{1}{2} \times (2)^{\frac{1}{2}} \times \frac{\theta_{H_2}}{\theta_{D_2}} = 2.8\,\frac{\theta_{H_2}}{\theta_{D_2}}.$$

Since both reactions are zero order, we take $\theta_{H_2} = \theta_{D_2} = 1$, giving a ratio of 2.8 to compare with our observed value here of ca. 1.0–2.0 and some relevant literature values for isotopic ratios at 77°K, 0.5 for metallic gadolinium (*15*), 1.44 for metallic nickel (*13*), and 1.7 for Nd^{3+} ions in 5A zeolite (*16*), together with a 193°K value of 2.0 for neodymium oxalate (*14*).

The Active Centers

The narrow ESR line of the thermally activated surface of α-Al_2O_3 and γ-Al_2O_3 may well arise from the postulated surface free valencies arising from dehydration of the hydroxylated surface, referred to earlier (*4*) and indicated below as (a) rather than (b). The signal is more marked in α-Al_2O_3 than in γ-Al_2O_3, which suggests its presence is associated more with impurity content (greater for α) than nonstoichiometry (smaller for α).


(a)


(b)

The signal with g (average) = 2.01, line width 40 gauss observed after irradiation of γ-Al_2O_3 is similar to that observed earlier on polycrystalline α-Al_2O_3 (*4*) and to that observed after irradiation of a single crystal of α-Al_2O_3 (*17*). In the last case, Gamble explained a line with $g_{\parallel} = 2.012$, $g_{\perp} = 2.008$, line width 50 gauss, in terms of three overlapping lines arising from 2 hole centers and an F center, the spectrum being broadened by an unresolved hyperfine interaction with the Al atom. The following facts support the view that the signal is mainly due to bulk rather than surface defects: (a) There is no effect of adsorbed air; and (b) the fact that a 100-fold increase in spins occasions only a 2-fold increase in the pH_2 conversion rate at 77°K.

The line-broadening effect of oxygen has allowed us to detect free spins otherwise unobservable. The idea that the signal which forms on exposure of preirradiated γ-Al_2O_3, to oxygen is due to a chemisorbed surface species O_2^- is based on earlier studies on ZnO, where the signals observed with two (*18, 19*) (or even three (*20*)) g values are closely analogous to that found for γ-Al_2O_3 and assigned to O_2^- in an axially symmetric electric field. It seems possible that there are at least two O_2^- centers, only one of which will exchange with $^{17}O_2$ according to experiments we hope to publish later. This would help to explain the complex nature of the signals described here. The effect of higher pressures of oxygen in causing an apparent intensity reduction in this signal may be associated with a dipolar broadening due to the paramagnetic oxygen molecule, as was the case for carbon (*21*).

It remains to correlate our findings with the classical studies of Kohn and Taylor (*3*). Using the HD equilibration as test reaction, they found that for γ-Al_2O_3 (a) there was no radiation enhancement for a sample outgassed at 520°C, as we find here. Our optimum temperatures of outgassing of 540°C (cf. Fig. 8b) agree with those of Weller and Hindin (*22*), (b) radiation enhancement of catalytic activity of the parahydrogen conversion of γ-Al_2O_3 increased when the outgassing temperature was lowered below 520°C, giving an enhancement factor of 200 for outgassing at 200°C. Weller and Hindin concluded that radiation enhancement of $H_2 + D_2$ was due to photolytic removal of catalyst poisons such as water. With pH_2 as test reaction, our corresponding enhancement factor for 200°C outgassing was only 3.5. The difference here may possibly be due to the difference in test reactions.

After this paper had been originally submitted, a paper appeared by van Cauwelert and Hall (*23*), who suggested that the pH_2 conversion at 77°K on a mixture of η and γ-aluminas outgassed at 500°C went by the paramagnetic mechanism on the nuclear moments of ^{27}Al surface atoms, estimated as 10^{19} g^{-1} from CO_2 poisoning. The k_m values were in reasonable agreement with those observed here, and the temperature coefficients were positive and similar in value to those found here. A clear distinction may therefore be drawn with the results of Schwab and Konrad (*24*) on θ-alumina containing 600 ppm Fe, which gave negative temperature coefficients for pH_2 and oD_2 conversion strongly suggestive of paramagnetic conversions. van Cauwelert and Hall suggested that the normally low Wigner transition probability on a nuclear moment is enhanced by several orders of magnitude by a strong electric field emanating from the ^{27}Al ions. They refer to the presence of Al^{3+} ions, but in terms of our usual ideas, their mechanism would necessitate model (b) above for the thermally activated surface, which would not be in accord with our ESR evidence for a free radical surface, i. e., model (a), with a chemical mechanism operating thereon. Nevertheless, this new suggestion may find an application to other solids, where there is more reason to believe that Al^{3+} sites are the only active centers present, and where the presence of a negative temperature coefficient for k_m suggests the paramagnetic mechanism as the most likely one.

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