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Spin Centers and Catalysis on Magnesia

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The rates of $pH_2 \rightarrow oH_2$, $oD_2 \rightarrow pD_2$ (77–273°K) and $H_2 + D_2 \rightarrow 2HD$ (195–273°K) have been studied on MgO (outgassed at 900°C). These rates are similar at 293°K, decreasing over the series $oD_2 > pH_2 > H_2 + D_2$ and all have positive temperature coefficients. The reaction orders are zero for pH_2 and oD_2, and 0.6 for $H_2 + D_2$, not much affected by temperature. No surface free electrons were detectable by ESR before irradiation. A 2 Mrad dose of γ-radiation from ^{60}Co enhanced the rate of all three reactions 3-fold, and raised the order of the pH_2 reaction to 0.3. The irradiated oxide showed an ESR signal indicative of three surface centers, designated F_s, V_s and X. Of these, the V_s center signal decreased on exposure to H_2 gas and is probably, therefore, the chemisorption center which catalyzes the hydrogen isomerization and equilibration reactions. It is concluded that all 3 reactions, both before and after irradiation, go by chemical mechanisms. The conversions probably involve 2 atom recombination and the $H_2 + D_2$ reaction molecule–atom exchange, on a small fraction of active sites. This may be compared with α and γ-Al_2O_3 in the previous paper, where before irradiation the oxides catalyze all three reactions by the chemical mechanism, and subsequent irradiation of the solid appears to promote a paramagnetic mechanism for the two conversion reactions.

INTRODUCTION

The bulk defect structure of MgO, a cubic lattice, has been studied by Wertz *et al.* (*1–7*). Charman and Dell (*8*) found fast neutron irradiation enhanced the chemisorption of hydrogen and oxygen by MgO, an observation followed up by ESR methods by Nelson, Tench *et al.* (*9–16*). Two active surface centers were identified, an S center being an anion vacancy with a trapped electron and an S_H center, which is an S center with a neighboring H nucleus. Lunsford (*17–19*) found both uv and neutron irradiation enhanced the catalysis of the $H_2 + D_2 \rightarrow 2HD$ by MgO to an extent which decreases the more stringently the solid is outgassed before irradiation (*18*). A correlation was found between V_I centers, holes trapped at anions adjacent to cation vacancies and the catalytic activity (*18*), three surface centers being identifiable by ESR (*19*), and those matters are discussed in a recent review (*20*). The present study follows up earlier work from this laboratory on α-Al_2O_3 (*21*) and γ-Al_2O_3 (*22*), by applying the same methods and arguments to MgO.

EXPERIMENTAL

All methods used were those described in the previous paper (*22*). Unless otherwise stated, the standard γ-irradiation dose was 2 Mrads to the MgO held at 77°K.

Materials

MgO (I) was prepared from $MgCO_3 \cdot 3H_2O$, a sample from a batch used in earlier UKAEA–Harwell studies (*9–16*). It was decomposed at a heating rate such that the pumps kept the pressure $< 10^{-3}$ Torr. When no further gas was evolved at 500°C, the temperature was raised to 900°C overnight. This careful procedure was recommended by Harwell to avoid sintering and specific areas were all in the range 40–200 m^2 g^{-1}. Samples were kept in vacuo in silica tubes under breakable seals, so as to exclude Hg vapor and tapgrease at all times. The UKAEA Analytical Group, Woolwich, gave the following impurities in ppm, Zn(70), Al(60), Sc (50), Ca(30), Fe(30), Mn(15), Cr(15), Pb(10), and Ni(7). Most of our work has been carried out with this specimen.

MgO (II), a Johnson-Matthey "Specpure" sample, No. 37775, after activating in 10^{-7} Torr for 30 hr at 760°C, had a specific area of 16.6 m^2 g^{-1}. The Johnson–Matthey analysis quotes impurities in ppm, as Fe(2), Si(2), Ca(1), and Al, Cu, and Na < 1. It was used in preliminary work only.

RESULTS

Catalytic Studies

All k_m, B_m, E, reaction order n, and other symbols are defined as in the previous paper (*22*).

Preliminary work on MgO (II) is briefly summarized. At 77°K, 10^{-12} k_m for the pH_2 conversion was 3.27 molecules cm^{-2} sec^{-1} at 1.4 Torr and 4.02 at 7.6 Torr, with order 0.12, and at 273°K, it was 0.254 at 1.4 Torr and 0.586 at 9.6 Torr with order 0.4. From the observed orders, we infer average fractional coverages of the catalyst (*24*) at 77°K of 0.88 and 0.60 at 273°K for these pressure ranges, and the negative temperature coefficient corresponds to an apparent activation energy of —460 cal $mole^{-1}$. Irradiation of the solid at 77°K with 0.2 to 0.4 Mrad enhanced the pH_2 rate by a factor 1.5–2.0, the original lower activity being regained after standing 15 hr in hydrogen at 77°K.

The main work was carried out on MgO (I), specific area 185.4 m^2 g^{-1}. From Fig. 1, the order of the pH_2 conversion may be calculated as: before irradiation, $n = 0$ at 77, 90 and 273°K, and $n = 0.16$ at 195°K; after irradiation $n = 0.2$ to 0.3 at 77, 195 and 273°K. From Fig. 2, we may calculate apparent activation energies over the range 77–273°K; before irradiation, $E(pH_2) = 220$, $E(HD) = 685$, after ir radiation $E(pH_2) = 105$, $E(oD_2) = 123$ $E(HD) = 123$, all in cal $mole^{-1}$. From Fig 3, the order of the HD reaction is $n = 0.($ at 195 and 273°K, both before and after ir radiation. Similarly for oD_2 the order i;

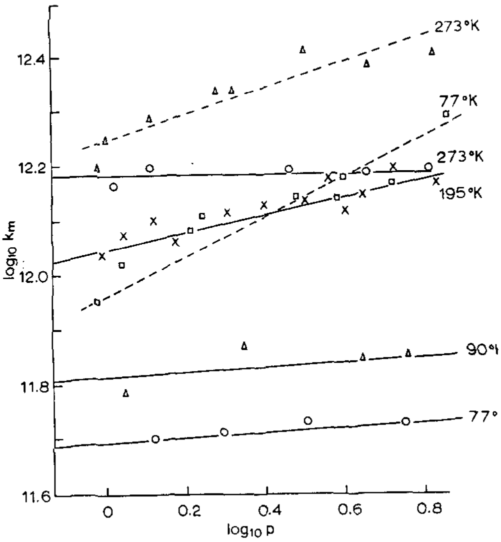


FIG. 1. The pressure dependency of the para hydrogen conversion at various temperatures; (a before represented by (————) and (b) afte irradiation represented by (– – – – – – –).

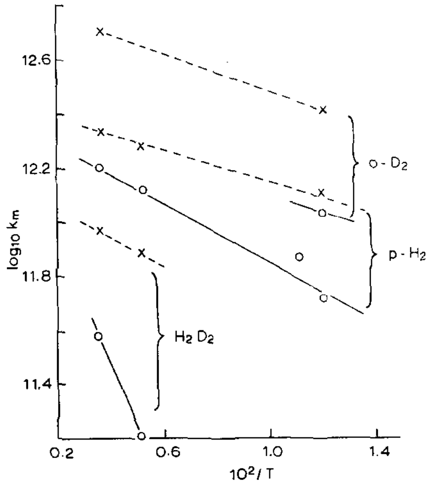


FIG. 2. The temperature coefficient of the para hydrogen and $H_2 + D_2$ reaction at $p = 2$ Torr be fore (————) and after (– – – – – – –) 3.6 Mra(^{60}Co γ-irradiation. One point is shown for ortho deuterium (before) and two points for after ir radiation.

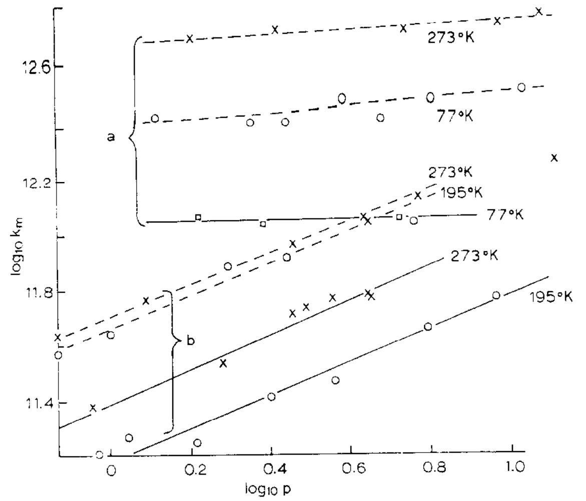


FIG. 3. (a) The pressure dependency of the orthodeuterium conversion, at 77 and 273°K after 2 Mrad irradiation (– – – – – – –), and at 77°K after annealing at 900°C the catalyst from the previous 2 experiments (————). (b) The pressure dependency of the $H_2 + D_2$ reaction at 195°K and 273°K before (————) and after (– – – – – – –) irradiation.

$n = 0$ (we may take the rate after annealing at 700°C as equivalent to that before irradiation). The actual radiation enhancement factor for all three reactions, pH_2, oD_2 *and* HD, is 2–3, and it is interesting that the oD_2 rates, both before and after irradiation, are *faster* than the pH_2 rates (Fig. 1). A study of the hydrogen adsorption at 77°K, showed a tendency to approach a saturation value of 6×10^{12} molecules cm^{-2} at 7 Torr corresponding to only 0.05% of surface sites.

In Fig. 4, the effect of exposing the irradiated catalyst to 2×10^{-3} Torr oxygen at 77°K is to somewhat lower the reaction rate and to change the pressure dependency. Outgassing at 900°C for approximately 18 hr restored the original preirradiation activity.

Later it is shown that γ-irradiation of

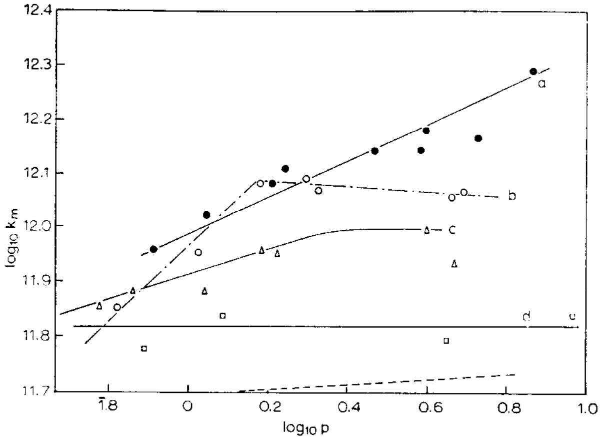


FIG. 4. *Parahydrogen conversion on magnesia,* (a) after γ-irradiation in vacuo; (b) after exposure to 2.4×10^{-3} Torr oxygen at 77°K, followed by pumping and flushing with hydrogen (———·———·———); (c) after exposure to 3 Torr oxygen, at 77 and 296°K, and (d) after outgassing 18 hr at 900°C. The dashed line (– – – – – – –) denotes the preirradiation level of activity.

MgO in oxygen causes marked differences in ESR spectra. However, the enhancement factors obtained for the three reactions after oxygen treatment were closely similar to those found for irradiation in vacuo, i.e., factors 1.5–3. In the case of the HD equilibration, no enhancement was observed until the catalyst after irradiation in oxygen had been thoroughly outgassed at 273°C.

ESR Spectra

A study of MgO (I) outgassed in vacuo at 900°C, *before* irradiation, in one case revealed a signal characteristic of two extrinsic centers (a) $g = 1.98$, probably Cr^{3+} in a cubic field, and (b) $g = 2.007$, the Mn^{2+} sextet, with the 2 center lines separated by 87 gauss. It was not possible to estimate what fraction of these centers was on the surface of the MgO, or to reproduce these signals. Our discussion, therefore, refers to MgO (I) *after* irradiation, and we first refer to the three surface centers described in the earlier work of Wertz, Tench, Lunsford, *et al.* These are as follows:

(a) The F_s or surface F center, an electron in an anion vacancy;
(b) The V_s or surface V center, a positive hole on a cation vacancy, possibly equivalent to an O^-, and
(c) The X center, nature not defined.

All the spectra illustrated were obtained from MgO which had received a 2 Mrad dose of γ-radiation. In Fig. 5 the line labelled F_s, with $g = 2.0008$, slightly asymmetric with a line width of 1.3 gauss, was obtained at low rf power (< 3 microwatts), since it was found to saturate easily. The V_s center, $g = 2.038$, line width 4 gauss, on the other hand was only displayed at higher rf power (20 microwatts). The g-value and saturation characteristics of the first line are responsible for the assignment of the present signal as due to an F_s center (*9–25*). In this center, the free electron is surrounded by 5 Mg^{2+} ions, with the missing sixth ion above the surface giving rise to the anisotropic line shape. The effective isolation of the electron from the lattice vibrations gives it a long relaxation time and easy microwave saturation. In a sample of specific area

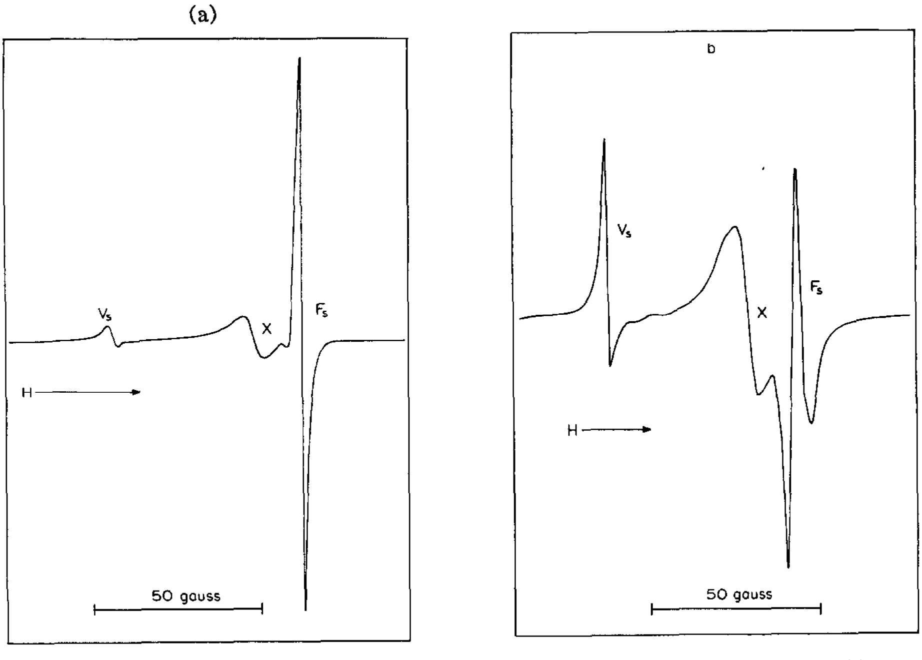


FIG. 5. ESR spectra for γ-irradiated MgO (I) in vacuum at 100°K, at low (a) and high (b) rf power.

100.1 $m^2 g^{-1}$, the F_s center concentration of 2.2×10^{17} fs g^{-1} corresponds to 2.2×10^{11} fs cm^{-2}.

Assuming the anisotropy of the V_s center corresponds to axial symmetry, the values $g_\perp = 2.038$, $g_\| = 2.003$ may be ascribed. Careful study of the whole spectrum of MgO, γ-irradiated at 77°K, before and after admission of H_2, showed that a diminution in the line of $g = 2.003$ paralleled the disappearance of the line at 2.038 ascribed to the V_s center. The difficulty of saturation is analogous to that of the bulk V_I center described by Wertz (*1*, *6*). The corresponding short relaxation time is attributed to a strong interaction between the $O^=$ ion (on which the positive hole is located) and the lattice. At room temperature the line width of the V_s center increases to 10 gauss, suggesting a reduction in the trapping time of the positive hole on the $O^=$ ion.

The surface nature of these centers is demonstrated by the effects of adsorbed gases. Admission of 10^{-3} Torr hydrogen almost completely removed the V_s center, its concentration in vacuo at 100°K being estimated as 6×10^{10} fs cm^{-2}, (Fig. 6) from the diminution in intensity using DPPH as calibration for numbers of spins. Due to effects of anisotropy, this estimate may be on the low side. Admission of 10^{-3} Torr oxygen to irradiated MgO at 100°K reduced the intensity of F_s and V_s centers, and a new anisotropic signal appeared at $g_\| = 2.017$, $g_\perp = 2.008$ (Fig. 7). Further oxygen removed completely the F_s and V_s centers and also the $g_\| = 2.017$, $g_\perp = 2.008$ center, and caused an increase in the X center signal. If hydrogen was admitted *before* oxygen, it removed the V_s signal, and now oxygen at pressures greater than 10^{-3} Torr developed the intensity of the X center *without* giving rise to the anisotropic signal at $g = 2.017$, which is formed only when oxygen is introduced prior to hydrogen. These experiments with hydrogen and oxygen were carried out on a number of identically prepared samples and were reproducible.

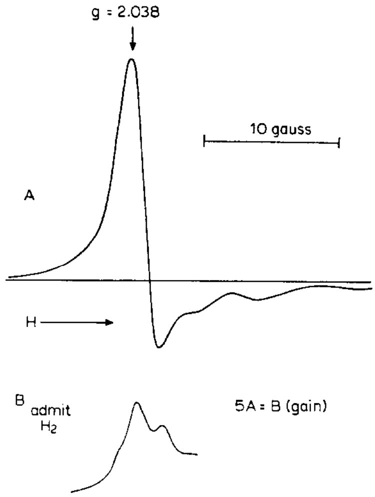


FIG. 6. Effect of hydrogen on the V_s center of MgO at 100°K. Spectrum B was taken at 5 times the gain of spectrum A.

Irradiation of MgO at 77°K *in the presence* of 10 Torr oxygen resulted (Fig. 8) in an ESR signal composed solely of

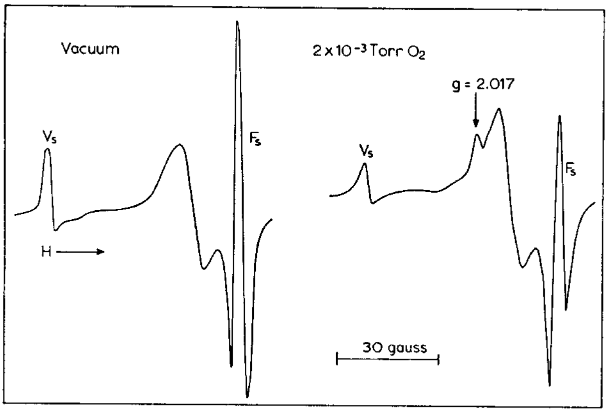


FIG. 7. Effect of admitting 10^{-3} Torr oxygen to irradiated MgO at 100°K.

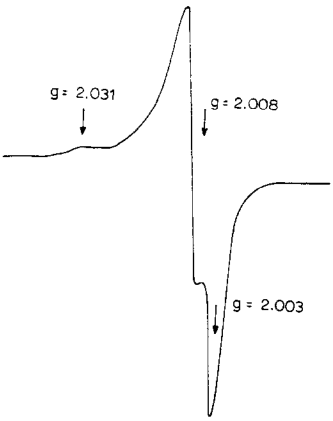


FIG. 8. Signal resulting from γ-irradiation of MgO at 77°K in 10 Torr oxygen, measured at 100°K.

the X center, with an intensity 15 times that resulting from irradiation in vacuo. On pumping out the oxygen and raising the temperature to 240°K, the X signal started to decay with the simultaneous reappearance of the V_s center signal at $g = 2.038$. The X center showed no pressure broadening with oxygen, and it was also found with MgO (II).

DISCUSSION

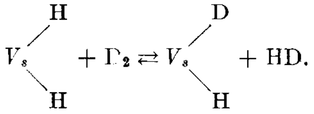
We shall base our discussion on the nature of the F_s and V_s centers as previously outlined. In recent work Tench and Nelson have observed the X center and have found that ^{17}O enriched adsorbed oxygen gave an X signal identical to that for normal oxygen. The center itself cannot, therefore, be associated with the adsorbed oxygen, but it may be centered on a lattice oxygen or impurity ion, which has transferred an electron to the adsorbed oxygen. However, we shall not need to consider the X center further, since although it is a surface center, its 15-fold enhancement on γ-irradiation in MgO in oxygen does *not* correlate with the 2–3-fold increase in the conversion reactions.

The close parallel in rates of oD_2, pH_2 and HD, *before* and *after* irradiation, points to a chemical mechanism in all cases, in distinction to α-Al_2O_3 (*20*) and γ-Al_2O_3 (*22*) where the radiation-enhanced spin isomerizations were not accompanied by an increased HD rate and were, therefore, assigned a paramagnetic mechanism.

The problem is now to decide the nature of the chemisorption sites. The present ESR evidence suggests that these are V_s centers, of estimated concentration 10^{11} sites cm^{-2}, since these disappear on exposure of irradiated MgO to oxygen. In agreement with Lunsford we write $H_2 + 2V_s \rightleftarrows 2V_sH$ and $D_2 + 2V_s \rightleftarrows 2V_sD$. For the HD reaction, there is the possibility that H atoms may show activated diffusion over the surface, total sites about 10^{15} cm^{-2}, between the V_s centers to allow for this reaction to occur in the necessary 2 steps (since only 1 in 10^4 sites is a V_s center), viz.,

$$H_2 + V_s \rightleftarrows H_2V_s \rightleftarrows HV_s + H \rightleftarrows 2HV_s.$$

However, this would imply a similar zero order for all these reactions. As in the case of alumina, the fractional order for the HD reaction is best explained by invoking an Eley–Rideal exchange involving hydrogen molecules adsorbed on these sites


$$V_s(H)(H) + D_2 \rightleftarrows V_s(D)(H) + HD.$$

The observed order of 0.6 would qualitatively agree with expectation from the adsorption isotherm in the region of 2 Torr at 77°K. Other features besides the order which suggest the different mechanism for $H_2 + D_2$ are the slightly higher activation energy (still very low at 685 cal $mole^{-1}$) and the inhibiting effect of adsorbed oxygen on the HD rate after irradiation. There is also some parallel between the way pumping thereafter increases the intensity of the V_s signal and raises the rate of the HD reaction. It does not seem possible to take this discussion any further at present.

The radiation enhancement of the pH_2 conversion rate at 77°K is $(11.5–5.0)$ $10^{11} = 6.5 \times 10^{11}$ molecules cm^{-2} s^{-1}. We may easily calculate the paramagnetic conversion rate, from

$$k_m(\text{calcd}) = n_0 \phi \nu \theta,$$

using $\theta = 1$, ϕ and ν as in the previous paper, and the following n_0 values:

V_s centers

$$n_0 = 6 \times 10^{11} \text{ fs cm}^{-2}$$
$$k_m(\text{calcd}) = 0.402 \times 10^9 \text{ molecules cm}^{-2}\text{ s}^{-1},$$
$$k_m(\text{obsd})/k_m(\text{calcd}) = 1600;$$

F_s centers

$$n_0 = 2 \times 10^{11}$$
$$k_m(\text{calcd}) = 1.35 \times 10^9$$
$$k_m(\text{obsd})/k_m(\text{calcd}) = 481.$$

In general, where in earlier papers we have supported a paramagnetic mechanism for the radiation enhanced rate on a particular solid, a much smaller ratio has been obtained for $k_m(\text{obsd})/k_m(\text{calcd})$. This confirms our view that the present radiation enhanced rate is primarily chemical in mechanism.

It is of interest that over the range 77–273°K, the reaction rates *decrease* over $oD_2 > pH_2 > H_2 + D_2$, both *before* and *after* irradiation (Fig. 2). Usually the chemical mechanism considered to hold here results in the order of rates $pH_2 > H_2 + D_2 > oD_2$ as for the case of Ni (*26*, *27*) at 293°K, which receives a simple explanation in terms of the differences in zero-point energy of the molecules in the initial state. In the case of Gd metal (*28*) at 77°K where $oD_2 > pH_2\ H_2 + D_2 \simeq\gg 0$, it was possible to infer that a paramagnetic mechanism was at work and to invoke an electrical quadrupole conversion (*29*) as giving rise to the faster conversion for oD_2. Such a possibility does not enter for the chemical mechanism, and we need to consider (since for both hydrogen and deuterium the sites are saturated) the energy and entropy effects in the transition state of the reaction.

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