Activation of Hydrogen at 78°K on Paramagnetic Centers of Magnesium Oxide

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Abstract: The H_2–D_2 equilibration at 78°K has been studied in a flow system over three varieties of MgO powders with or without addition of impurities. The only impurity that affected the catalytic activity consisted of protons, the surface content of which could be regulated by pretreatment of the samples *in vacuo* at temperatures between 500 and 900°C. Thus, samples were prepared with catalytic activity differing by more than five orders of magnitude. The activity was correlated with the spin density of an electron-deficient paramagnetic center which was shown to be a surface center. The exchange-narrowed symmetrical epr line, corresponding to this new V-like center called V_1, was assigned to a triangular array of O^- ions situated on a (111) plane of MgO. The catalytic site then consists of an OH^- ion adjacent to the V_1 center which adsorbs the deuterium molecule to form a quasi-sorbed Rideal–Eley transition state bringing about exchange. The proposed ion–molecule type reaction explains its low activation energy (2 kcal mol^{-1}) and the possibility of carrying out the reaction at 78°K without the participation of transition metal ions. The apparent necessity of metastable (111) planes on MgO for obtaining catalytic sites and V_1 centers was suggested by the irreversible loss of activity and spin density upon heating MgO samples in the presence of H_2O vapor at temperatures at which recrystallization sets in with a change of crystal habit. Thus the catalytic site is associated with a proton impurity, an electronic defect, and a specified crystallographic plane.

Few chemical reactions take place at liquid nitrogen temperature (78°K). This is not surprising since extrapolation of the rate constant for the elementary process $H + D_2 \rightarrow HD + D$ shows that a hydrogen atom in molecular deuterium at 1 atm would have a half-life of several years at 78°K. It is, therefore, remarkable that the isotopic equilibration $H_2 + D_2 \rightleftarrows 2HD$ is known to proceed readily at 78°K over a number of solid catalysts. Among these are transition metals such as W, Ni, and Pt,[1] as well as transition metal oxides Cr_2O_3, NiO, and Co_3O_4.[2] The activity of all these catalysts is normally associated with the ability of transition metals to dissociate H_2 as a result of oxidative adsorption of the molecule on the metal or metallic ion with bonding involving d electrons of the latter, in analogy with the formation of hydride ligands by soluble transition metal complexes.[3]

Besides these solid catalysts with transition metal sites capable of bringing about H_2–D_2 equilibration at 78°K, two other catalytic systems have been reported to do the same on sites that do not contain elements with accessible electronic d levels. The first system consists of silica gel containing aluminum impurities. After prior irradiation with γ-rays, this material was capable, in the absence of radiation, of equilibrating H_2–D_2 mixtures at 78°K. This unusual discovery by Kohn and Taylor was later explained by Kazanskii, Boreskov, *et al.*, who assigned the catalytic sites to paramagnetic defect centers observable by epr spectroscopy.[4] These defects apparently consist of a positive hole trapped on an oxygen ion forming a V center: O^-. A second catalytic system which now appears closely related to the preceding one was reported by Lunsford and Leland.[5] Magnesium oxide powders after prior evacuation at 500°C were found by these

authors to catalyze the H_2–D_2 exchange at 78°K, without the need for any irradiation before or during the reaction. Much interesting work on MgO powders preevacuated at various temperatures and preirradiated with uv light was published subsequently by Lunsford[6] and by Harkins, *et al.*,[7] who studied the H_2–D_2 exchange at 195°K and room temperature (which will be abbreviated hereafter: 298°K), respectively. This later work, which also involved epr spectroscopy, led the authors to propose V–type centers as catalytic sites and in particular[7] to assign to O^- ions the role of sites responsible for the H_2–D_2 reaction at 78°K on MgO preevacuated at 300°C.

A similar conclusion was reached independently and by analogy with the system of Kohn and Taylor in a study by Benson, *et al.*, of the H_2–D_2 equilibration at 78°K on magnesium oxide powders containing various amounts of copper ions.[8] It was also assumed by Benson, *et al.*, that the catalytic sites consisted of O^- ions formed by electron capture: $O^{2-} + Cu^{2+} \rightarrow O^- + Cu^+$. The catalytic study, which was carried out in a flow system, reported no measurable exchange rates at 78°K on MgO samples without deliberate addition of copper ions. This result was not in agreement with the earlier finding of Lunsford and Leland but these authors did not report catalytic rates, and they used a static system so that a direct comparison between the results of both investigations could not be made on the basis of published data.

We undertook the present investigation as a result of this possible discrepancy but especially because of the great interest in establishing by more extensive work whether MgO powders do possess catalytic sites not directly associated with transition metal ions and capable of carrying out the H_2–D_2 reaction at 78°K. The present paper reports the catalytic results that have been ob-

(1) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, p 155.
(2) D. A. Dowden, N. MacKenzie, and B. M. W. Trapnell, *Advan. Catal. Relat. Subj.*, 9, 65 (1957).
(3) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).
(4) E. H. Taylor, *Advan. Catal. Relat. Subj.*, 18, 111 (1968).
(5) J. H. Lunsford and T. W. Leland, *J. Phys. Chem.*, 66, 2591 (1962).

(6) J. H. Lunsford, *ibid.*, 68, 2312 (1964).
(7) C. G. Harkins, W. W. Shang, and T. W. Leland, *ibid.*, 73, 130 (1969).
(8) J. E. Benson, A. B. Walters, and M. Boudart, *ibid.*, 72, 4587 (1968).

tained on a variety of MgO samples following various kinds of pretreatment over a wide temperature range. These samples were also examined by epr spectroscopy. The catalytic sites have been identified as surface electronic defects which consist of a new kind of V centers. After this work was terminated, there appeared a paper by Eley and Zammitt[9] dealing with the H_2-D_2 exchange at and above 195°K on MgO outgassed at 900°C before and after exposure to γ-rays. The results of these authors will be discussed briefly in the light of the data presented below.

Experimental Section

Catalysts. Three varieties of MgO were used to prepare the catalysts. They are designated as MgO-EP, MgO-JM, and MgO-M. The first one, MgO-EP, was prepared by temperature-programmed decomposition in vacuo up to a specified temperature of $3MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$ ($x \sim 3$), hereafter called basic carbonate of Mg, precipitated with K_2CO_3 from a HCl solution of triply distilled magnesium metal provided by Dow Chemical. To avoid contamination by impurities, doubly distilled water collected from a quartz condenser was used in the preparation and washing of the precipitate, polyethylene bottles were used exclusively, all operations were performed in a polyethylene box, and the product was ground in an agate mortar. A neutron activation analysis revealed only Sb (1 ppm) and K (0.2%). The results of a spectrographic analysis are (in ppm): Al (2), Cr (<0.2), Cu (<1), Fe (<6), Mo (<0.04), Ni (0.5), Sn (<0.2), Ti (0.3), V (<0.02), Zn (10), Zr (0.1), Mn (<0.02). Both before and after heating MgO-EP in air or in He at 1000°C, it was not possible to detect in it any epr signal from Cr^{3+}, Mn^{2+}, or Fe^{3+} under conditions which revealed these impurities in the other samples of MgO used in this work. A sample called 0.01% Li-MgO-EP was prepared by impregnation of our basic carbonate of Mg with a water solution of Li_2CO_3 (Baker and Adamson, reagent grade) so as to obtain a nominal concentration of 0.01% Li by weight after decomposition in vacuo. Two other samples, Cu-MgO-EP, were prepared as the Li sample from a copper acetate (Baker and Adamson, reagent grade) solution in ethanol. The nominal Cu contents were 0.5 and 5%.

A second variety of MgO, designated as MgO-JM, was obtained from Johnson and Mathey. It was a spectrographically standardized sample (No. S 7505) with impurities (in ppm) as reported by the manufacturer as follows: Fe (3), Na (2), Cr (1), Al (1), Si (1), Ca (<1), Cu (<1). A neutron activation analysis of MgO-JM revealed Ir (2), Na (2), and probably Cu (2). A spectrographic analysis gave the results: Al (5), Cr (0.8), Cu (<1), Fe (11), Mo (0.2), Ni (1.3), Sn (<0.2), Ti (0.3), V (0.03), Zn (<10), Zr (<0.1). Besides, the presence of Mn^{2+} in ppm quantity was ascertained by epr spectroscopy.

The third variety of MgO, designated as MgO-M, was obtained from Mallinckrodt (analytical reagent grade). It was used as such. A sample of MgO-M was hydrolyzed in water and then dehydrated in air for 24 hr at 400°C. The resulting product will be called MgO-M-HS (because of its high surface area). Another sample of MgO-M was treated with excess HNO_3 and the nitrate was decomposed in air at 400°C for 24 hr to give a product called MgO-M-N. Another catalyst, 0.05% Ni-MgO-M, was prepared by adding $Ni(NO_3)_2$ (Baker and Adamson reagent grade) to MgO-M during the hydrolysis. The product was treated in air for 24 hr at 400°C. The next catalyst, Cu-MgO-M, containing 0.5 and 5% Cu, was prepared by impregnating MgO-M with a $Cu(NO_3)_2$ solution obtained by dissolving ASARCO copper metal (99.999% Cu, less than 1 ppm of Ni) in Baker and Adamson reagent grade nitric acid. The product was also treated in air at 400°C for 24 hr. Finally a sample called Cu-MgO-M-EA, containing 5% Cu, was prepared by impregnating MgO-M with Baker and Adamson reagent grade cupric acetate in ethanol.

Besides the MgO catalysts listed above, three other powders were used in this work: CaO (Mallinckrodt analytical reagent) used as supplied, and α-Cr_2O_3 and α-Fe_2O_3 prepared by the method of Dowden, et al.[10]

Gases. Both H_2 (General Dynamics, 99.5%) and D_2 (Matheson Co., 99.5%) were purified by diffusion through a heated Pd-Ag

thimble. Oxygen (General Dynamics, 99.5%) was condensed at 78°K and pumped on briefly; the middle portion was vaporized into a Pyrex storage bulb preceded by a trap cooled at 195°K. Distilled H_2O was placed in a Pyrex bulb and purified by evacuation at 298°K followed by a freeze-pump-thaw method to remove dissolved gases.

Equipment and Procedures. The apparatus used for the H_2-D_2 exchange has been described previously.[8] It consisted of a flow reactor with gas chromatographic analysis of the effluent. The catalysts were placed in Pyrex or quartz reactors fused to 2-mm i.d. coiled Pyrex tubing traps upstream and downstream. The pretreatment and reaction temperatures were measured with a thermocouple inserted into a well in the reactor.

The flow reactor was connected to a conventional high-vacuum pumping system for in situ activation. Unless otherwise noted, the catalysts were cooled to reaction temperature in vacuo before exposure to the reactant H_2-D_2 mixture. Reaction temperatures of 79, 113, 195, and 273°K were provided by liquid thermostatic baths.

Approximately equimolar H_2-D_2 mixtures at 1 atm were allowed to flow over the catalysts for a time sufficient for at least three complete exchanges of gas contained in the reactor and downstream tubing before sampling the product gas mixture. This procedure gave results which agreed with samples taken after longer times on stream. Flowing gas mixtures in the range 3–180 cc/min (STP) were used. The volumetric flow rates were measured with a soap bubble flow meter located after a protective Hg bubbler at the end of the flow apparatus.

The upstream and downstream traps were cooled to liquid nitrogen temperature during exchange measurements. Water collecting in the traps during pretreatment was found to poison occasionally the catalyst during exchange measurements. The traps were left at room temperature during activation and were dried by heating in vacuo prior to cooling the catalyst to reaction temperature and the traps to liquid nitrogen temperature. This procedure was an improvement on that used in the previous investigation.[8]

The pretreatment with H_2-D_2 mixtures was performed by flowing the mixtures over the catalysts. The O_2 and H_2O was pumped over the catalysts by cooling the latter to ensure adequate contact.

An additional experiment was performed to test the role of surface hydrogen in the exchange reaction. A 3.0-g sample MgO-JM was placed in a Pyrex batch reactor and activated by evacuation for 2 hr at 500°C. D_2 was expanded into the catalyst chamber and the gas mixture was sampled by mass spectroscopy.

Calculation of Rate Constants. The maximum amount of HD that can be formed in the exchange reaction is limited by the equilibrium $H_2 + D_2 \rightleftarrows 2HD$ characterized by its equilibrium constant K. The extent of reaction can be conveniently expressed by the efficiency η defined as

$$\eta = \frac{\text{moles of HD formed}}{\text{moles of HD at equilibrium}} \quad (1)$$

The absolute first-order rate constant k in cm/sec, for a simple flow reactor is then

$$k = -\ln (1 - \eta) \cdot 2FK^{1/2}/A(2 + K^{1/2}) \quad (2)$$

where F is the volumetric flow rate at the reaction temperature and pressure in cm^3 sec^{-1}, and A is the total surface area of the catalyst in cm^2. Formula 2 gave consistent results over a fairly wide range of flow rates and was used to calculate the k values presented in this work. No attempt was made to determine the complete rate law for H_2-D_2 equilibration on our catalysts. The use of a first-order rate constant properly corrected for surface area is a convenient way to express the results. Since we are concerned in this work with very large variations in activity (five to six orders of magnitude), it is clear that none of our conclusions would be affected by departure of the rate from first-order behavior.

Catalyst Pretreatment. As a rule, all catalysts were activated in vacuo during 16 hr at 500°C. Additionally MgO-EP, MgO-JM, MgO-M, 0.01% Li-MgO-EP, γ-Cr_2O_3, α-Fe_2O_3, and CaO were activated by successive in situ evacuations at increasing temperatures between 400–500 and 900°C to increase gradually the degree of dehydration. Following the 900°C evacuation MgO-EP, MgO-JM, MgO-M, and 0.01% Li-MgO-EP were exposed to H_2O vapor at 20 Torr for 20 min and then evacuated at about 500°C for 16 hr. Further, three different samples of MgO-EP were decomposed in air respectively at 500, 770 and 950°C for 24 hr. The samples

(9) D. D. Eley and M. A. Zammitt, *J. Catal.*, 21, 377 (1971).

(10) D. A. Dowden, N. MacKenzie, and B. M. W. Trapnell, *Proc. Roy. Soc., Ser. A*, 237, 245 (1956).

Table I. Surface Areas

Catalysts	Surface area, $m^2 g^{-1}$	Catalysts	Surface area, $m^2 g^{-1}$
MgO–EP (500)	171	MgO–M (500)	21
MgO–EP (750)	93	MgO–M (900)	29
MgO–EP (900)	77	0.5% Cu–MgO–M (500)	27
MgO–EP (900–H₂O–500)	69	5% Cu–MgO–M (500)	27
MgO–EP–A	8.3	5% Cu–MgO–M–EA (500)	17
MgO–EP–He	25	0.05% Ni–MgO–M (500)	118
0.01% Li–MgO–EP (500)	170	MgO–M–N (500)	7.8
0.5% Cu–MgO–EP (500)	140	MgO–M–HS (500)	138
5% Cu–MgO–EP (500)	152	α-Cr₂O₃ (500)	39
MgO–JM (500)	41	α-Fe₂O₃ (500)	51
MgO–JM (900)	24	CaO (900)	2.8
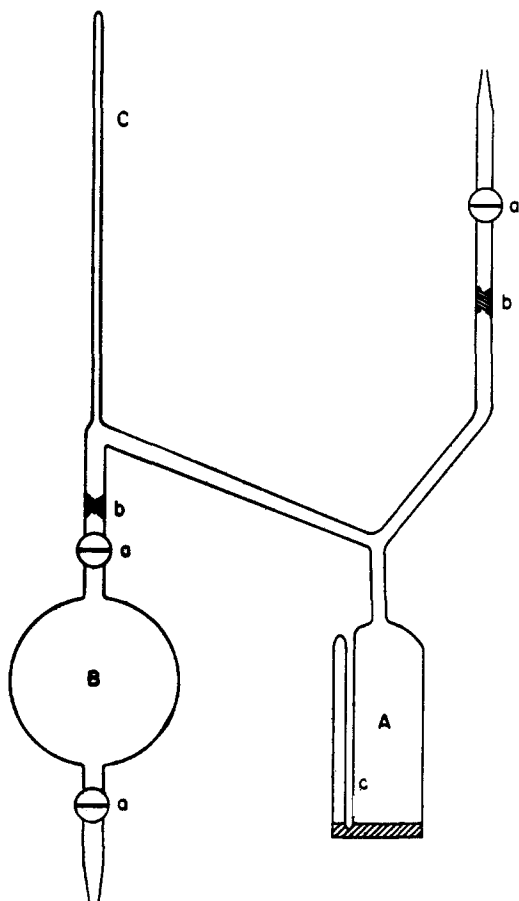
Figure 1. Apparatus for the treatment of epr samples: (a) stopcock to vacuum line, (b) quartz plug, (c) thermocouple well, (A) quartz reactor, (B) gas storage bulb, (C) epr sample probe.

were then left in air at room temperature for 12 hr and then evacuated at 500 °C for 16 hr.

Additionally, a sample of MgO–EP was heated at 1000 °C for 24 hr in flowing helium (0.8 cm³ sec⁻¹) containing 2.5% of H₂O vapor. After this treatment in the catalytic reactor, the sample was then heated *in vacuo* at 500 °C for 16 hr without exposing it to the air. We will refer to MgO–EP heated in air at MgO–EP–A and to MgO–EP heated in wet helium as MgO–EP–He. Occasionally, the catalysts were exposed to O₂ or H₂O vapor at room temperature. Further details on these particular pretreatments are given below in the section on results.

Physical Examination of the Catalysts. The N₂ BET surface areas of all the catalyst samples are listed in Table I. They were determined on samples treated in the same way as in the kinetic runs, *i.e.*, *in vacuo* at the temperature (in °C) specified in parentheses, except for the samples heated in air or helium. The notation —H₂O–500 behind the name of a sample means that the sample has been exposed to water vapor at 298 °K, then evacuated again at 500 °C as described above.

Samples of MgO–JM, MgO–EP, and MgO–M–N were examined by scanning electron microscopy with a JSM-U3 apparatus of Jeolco Inc. and by transmission electron microscopy with a Philips machine and a JEM 120 of Jeolco. Some electron diffraction studies were also carried out during the latter studies.

Catalyst samples were examined by epr spectroscopy. Most measurements were carried out with a Varian E-3 spectrometer (X-band, 100-kHz field modulation, TE₁₀₂ mode rectangular cavity). Spectra were taken at room temperature and 78 °K. For g-value calibration, DPPH was taped to the sample tube, or for MgO–JM, use was made of the Cr³⁺ impurity line. A few spectra at 9 to 20 °K were recorded on a Varian E-9 spectrometer (X-band, 6- and 100 kHz field modulation and a cylindrical cavity). For determination of spin density, a sample of Varian weak pitch on KCl (10^{13} spins cm⁻¹ ± 15%) was used. The derivative spectra were doubly integrated numerically following the method described by Poole.[11]

Samples were pretreated according to a schedule identical with that used in the kinetic runs in a standard quartz epr sample tube (2.7-mm i.d.) or in a special quartz reactor (Figure 1) which could be connected to the vacuum line and from which powder could be introduced *in vacuo* into the epr tube. No difference in spectra was observed between samples pretreated in the standard tube or in the reactor. Gases of similar origin and pretreatment as described above for the kinetic studies could be stored in a bulb at 1 atm for H₂, 200 Torr for O₂, and 4 to 200 Torr for H₂O and then be introduced into the epr tube while spectra were being taken.

Results

Electron Microscopy. Fresh samples of MgO–JM showed particles with (111), (211), and (210) orientations in order of decreasing importance. After a heat treatment *in vacuo* at 1000 °C, the dominant orientation became (110) with (111), (211), and (100) orientations of secondary importance. With MgO–EP powders evacuated at 500 °C, the surface reactivity was so large that the samples examined in the electron microscope were completely rehydrated and showed nice platelets of Mg(OH)₂. At lower magnification, the scanning electron microscope revealed a chiplike texture (platelets) which was stable after treatments *in vacuo* between 500 and 1000 °C but collapsed after treatment in air at 1000 °C to be replaced by a globular texture with a smaller surface area. Particularly clear results were obtained with a sample of MgO–M–N, which exhibited very large particles (about 5000 Å) with (111) orientations corresponding to the almost perfect octahedra which were seen on scanning electron micrographs.

Kinetic Data on H₂–D₂ Equilibration. The rate of H₂–D₂ exchange was measured on a variety of samples as a function of the temperature of pretreatment *in vacuo* (Figures 2–5) or in a gas containing water vapor (Figure 6). Rates were also measured on MgO samples containing deliberately introduced impurities: copper (Figure 7) or lithium (Figure 8). For many samples, the

(11) C. P. Poole, Jr., "Electron Spin Resonance," Interscience, New York, N. Y., 1967.
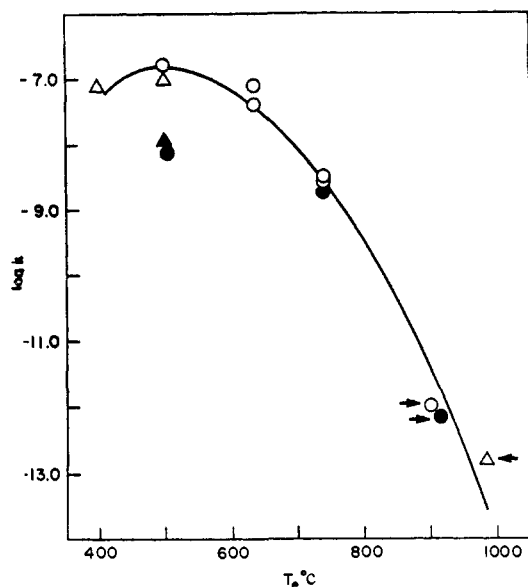
Figure 2. Variation of k (cm sec^{-1}) at 78°K with temperature of evacuation T_e (°C) for MgO–EP (arrows refer to k measured at 195°K and extrapolated 78°K): O, MgO–EP, sample A; $\triangle$, MgO–EP, sample B; ●, MgO–EP (900–H$_2$O–T_e), sample A; ▲, MgO–EP (900–H$_2$O–500), sample B.

Figure 4. Variation of k (cm sec^{-1}) at 113°K with temperature of evacuation T_e (°C) for MgO–M. The time of evacuation in hours is indicated next to each point: ●, measured at 113°K; O, extrapolated to 113°K; ■, MgO–JM (920–H$_2$O–550) extrapolated to 113°K.
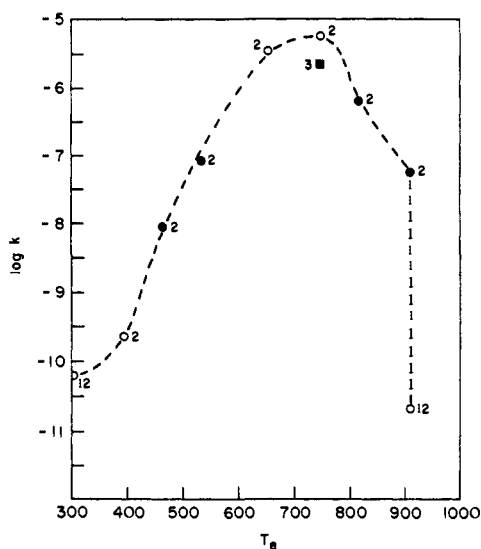
Figure 3. Variation of k (cm sec^{-1}) at 113°K with temperature of evacuation T_e (°C) for MgO–JM. The time of evacuation in hours is indicated next to each point: ●, measured at 113°K; O, extrapolated to 113°K; ■, MgO–JM (920–H$_2$O–750) measured at 113°K.
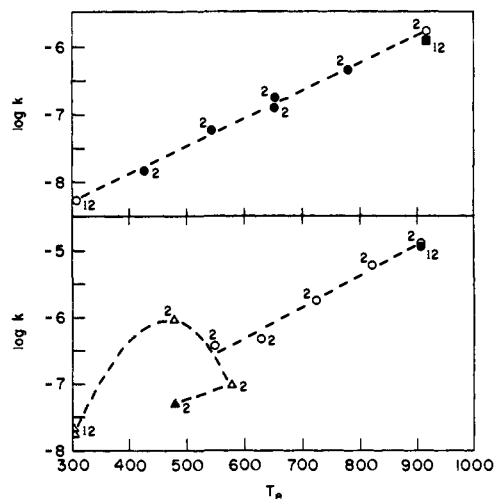
Figure 5. (Upper) Variation of k (cm sec^{-1}) at 113°K with temperature of evacuation T_e (°C) for α-Cr$_2$O$_3$. The time of evacuation in hours is indicated next to each point: ●, measured at 113°K; ■, extrapolated to 113°K. (Lower) Variation of k (cm sec^{-1}) at 273°K with temperature of evacuation T_e (°C) for α-Fe$_2$O$_3$ and CaO. The time of evacuation in hours is indicated next to each point: $\triangle$, α-Fe$_2$O$_3$ (T_e); ▲, α-Fe$_2$O$_3$ (846–H$_2$O–500); O,● CaO.

Arrhenius temperature dependence of the rate was obtained[12] and the corresponding activation energies are listed in Table II. These were used, as indicated, to extrapolate the rate constants to a common temperature in Figures 2–8. For all samples except CaO, the activation energy is practically the same within experimental error: 2.2 ± 0.1 kcal mol^{-1}.

All MgO samples exhibit the same behavior with respect to variation of rate with temperature of evacuation T_e (Figures 2–4, 8). The rate goes up with T_e, reaches a maximum for values of T_e around 500–750°C, and declines precipitously by five to six orders of magnitude for values of T_e around 950°C. However,

(12) A. B. Walters, Ph.D. Dissertation, Stanford, 1970.

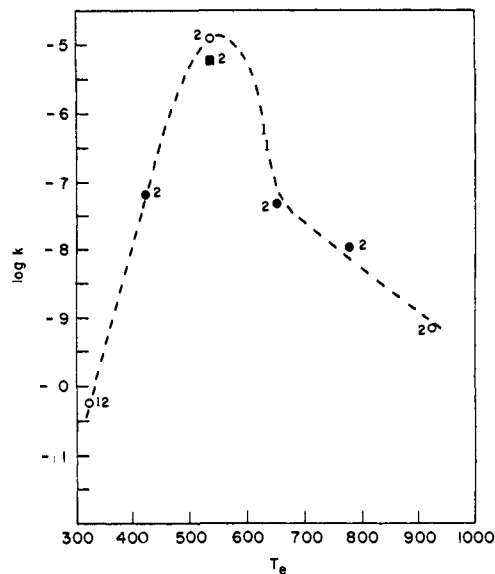Table II. Activation Energies

Catalysts	E, kcal mol^{-1}	Temp range, °K
MgO–EP (500)	2.2	78–113
MgO–EP (895)	2.3	195–273
MgO–EP (740–H$_2$O–500)	2.1	78–113
MgO–EP (900–H$_2$O–500)	2.3	195–273
MgO–JM (500)	2.2	113–273
MgO–M–HS (500)	2.2	78–273
α-Cr$_2$O$_3$ (500)	2.1	78–113
α-Fe$_2$O$_3$ (500)	2.3	195–273
CaO (500)	3.7	195–273

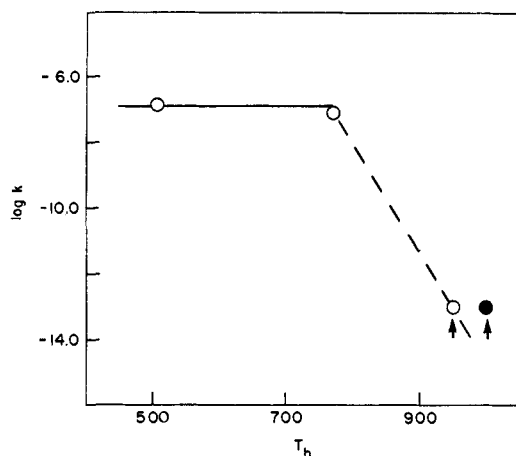most of the peak activity lost during evacuation at these high temperatures can be regained by exposing the

Figure 6. Variation of k (cm sec^{-1}) at 78°K with temperature T_h (°C) of heating in air (A) or He (containing H_2O vapor) for MgO–EP (arrows refer to k measured at 298°K and extrapolated to 78°K): O, MgO–EP–A; ●, MgO–EP–He.
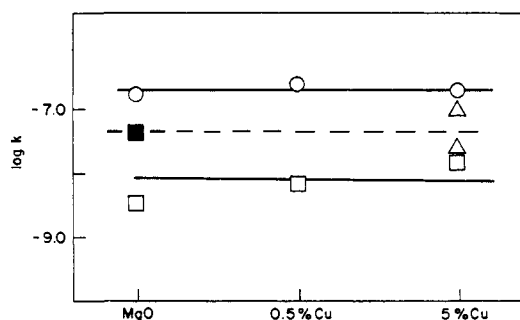
Figure 7. Variation of k (cm sec^{-1}) with copper content: O, MgO–EP (500); □, MgO–M (500), evacuation (12 hr) preceded by heating (8 hr) in flowing H_2 at 500°C; ▲, 5% Cu–MgO–M–EA evacuated for 12 hr at 500°C; △, as above, followed by reduction in flowing H_2 for 8 hr and again by evacuation for 12 hr at 500°C; ■, MgO–M peak activity (see Table III).

Figure 8. Variation of k (cm sec^{-1}) at 78°K with temperature o evacuation T_e (°C) for 0.01% Li–MgO–EP (arrow refers to k measured at 195°K and extrapolated to 78°K): O, 0.01% Li–MgO–EP (T_e); ●, 0.01% Li–MgO–EP (850–H_2O–550).

Table III. Comparison of H_2–D_2 Equilibration Activities (Peak Activities), at 78°K

Catalysts	Log 10^9 k, cm sec^{-1}	Catalysts	Log 10^9 k, cm sec^{-1}
MgO–EP	2.15	0.05% Ni–MgO–M	0.30
0.01% Li–MgO–EP	2.20	0.5% Cu–MgO–M	0.80
0.5% Cu–MgO–EP	2.30	5% Cu–MgO–M	1.20
5% Cu–MgO–EP	2.25	MgO–M–N	2.00
MgO–JM	1.35	α-Cr_2O_3	1.18
MgO–M	1.66		

sample to water vapor at room temperature and reevacuating at values of T_e near the optimum. By contrast, the loss in activity with α-Fe_2O_3 (Figure 6), when T_e exceeds 500°C, cannot be regained by a similar treatment. With α-Cr_2O_3 (Figure 5, upper part) and CaO (Figure 5, lower part), the activity increases steadily with T_e up to the highest temperatures.

When MgO is heated at increasing temperatures T_h not *in vacuo* but in air or helium containing water vapor, the activity stays the same for T_h up to near 800°C, then falls dramatically as before, but now the loss in activity appears irreversible; it cannot be regained by the treatment with water vapor as before.

As a result of the considerable variation of rate of H_2–D_2 exchange with T_e, a good way to compare various samples is to list peak values of the activity (Table III). When this is done, it can be seen that variations between individual MgO samples are very minor, in spite of the different history and impurity content. Besides, deliberate introduction of transition metal impurities (Cu, Ni) up to very high levels (5%) or of Li does not affect activity in a significant way (Figures 7–8, Table III). A deactivated sample of 5% Cu–MgO–EP (900) could be restored to its peak activity by treatment with H_2 instead of H_2O. By and large the peak activity of MgO samples varied much less than specific surface

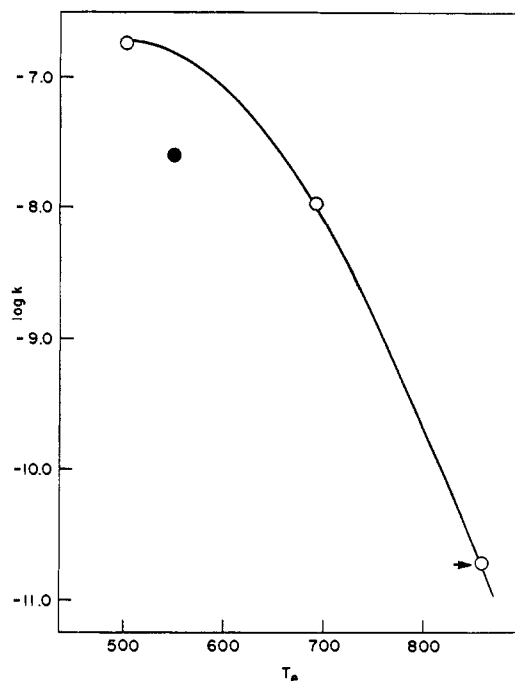areas. Note in particular the almost identical activity of MgO–EP and MgO–M–N (Table III) although these two samples have the highest (171 m² g^{-1}) and the lowest (7.8 m² g^{-1}) specific surface areas of all MgO samples listed in Table I. Also note that these two samples also have vastly different impurity contents.

During a 2-hr run at 78°K on MgO–EP (500), no difference in activity was detectable at the beginning or at the end so that the catalyst is not affected by H_2–D_2 mixtures at 78°K. The effect of H_2, O_2, and H_2O vapor at 298°K on k at 78°K was also studied on the three varieties of MgO samples. Results were the same on all three as follows. Flowing the H_2–D_2 mixture on an activated catalyst for 2 hr at 298°K has no effect on k at 78°K. Exposure of an activated catalyst to O_2 for 3 min followed by pumping (30 min), both at 298°K, yielded a catalyst with no measurable activity at 78°K. This catalyst was active at 273°K. Its 78°K activity could be completely restored after evacuation for 3 hr at 200°C. Similarly, exposure of an activated catalyst to H_2O vapor followed by pumping (2 hr), both at 298°K, also yielded a catalyst with no measurable activity at 78°K. This catalyst was active at 273°K. Its 78°K activity could be fully restored following evacuation for 3 hr at 500°C.

In an effort to determine whether surface hydrogen was part of the active site on MgO, a sample of MgO–JM (500) was contacted with D_2 at 78°K. No detectable HD was formed after 1.5 hr although a H_2–D_2 mixture would come to equilibrium over this catalyst in 10 min. At 300°K, exchange of surface hydrogen with D_2 took place and the amount of HD formed in 2 hr indicated that at least about 0.3% of the surface of MgO–JM (500) was covered with hydrogen.

Epr Study of Catalysts. Observations *in vacuo* of a sample of MgO–EP (500) revealed an epr signal characterized by a *g* value equal to 2.0030, independent of temperature between 9 and 298°K. The line had a symmetrical Lorentzian shape and was homogeneously broadened as seen from a progressive saturation plot. Saturation could be achieved at microwave fields of about 0.15 Oe amplitude at 78 and 298°K. Line width was almost temperature independent: 0.7 and 0.4 Oe at 9 and 298°K, respectively. The signal followed Curie's law between 77 and 298°K. Apparent relaxation times at 298°K, $T_1^* = 10^{-6}$ sec and $T_2^* = 2 \times 10^{-7}$ sec, were determined by the progressive saturation method. The paramagnetic center corresponding to this signal will be called V_I because its *g* value, higher than that of the free electron, indicates that we deal with a V-like or positive hole center. The density of V_I centers did not vary appreciably after 5 hr of evacuation of the sample at 500°C and reached a steady value of about 10^{15} spins g^{-1} after 16 hr of evacuation. A similar signal was observed on activated MgO–JM samples.

Addition of H_2 at 1 atm did not affect the intensity or shape of the V_I signal after 24 hr at 78 or 298°K. By contrast, when an evacuated sample was exposed to O_2 at 200 Torr and 298°K, the V_I signal disappeared in 10 sec and was replaced *quantitatively* by a new signal V_b, a symmetrical line with $g = 2.0039$ and a line width equal to 4.4 Oe at 298°K. The characteristics of V_b did not depend on the pressure of O_2 and, in particular, V_I did not reappear upon pumping at 298°K but was fully recovered after 2 hr evacuation at 300°C.

Similarly, addition of H_2O vapor at 2 Torr and 298°K to an evacuated sample wiped out the V_I signal which was *quantitatively* replaced in 10 sec by another new signal V_w with an average *g* value of 2.0047 ($g_{\parallel} = 2.0028$ and $g_{\perp} = 2.0057$) and a line width of 5 Oe at 298°K. Pumping at 298°K did not affect V_w, but V_I was restored completely by evacuation for 3 hr at 500°C.

The very fast and quantitative response of V_I to O_2 and H_2O indicates that all V_I centers are surface centers, and their density will be expressed in spins cm^{-2} by using the specific surface area of the sample. The surface density of these centers changes in parallel with the catalytic activity of the samples as the temperature of evacuation is increased from 500 to 900°C. The V_I signal is progressively replaced by another one, V_I^*, in such a way that the sum of the concentrations of V_I and V_I^* remains approximately constant. The V_I^* symmetrical line has a *g* value of 2.0036 and a line width of 3.2 Oe at 298°K. For MgO–EP (900), the concentration of V_I is too small to be measured, and this is indicated by an arrow on one of the data points in Figure 9, the position of the point being that corresponding to the limit of detection in our spectrometer.

The full line on Figure 9 was drawn through the data of catalytic activity reported on Figure 2, and the open
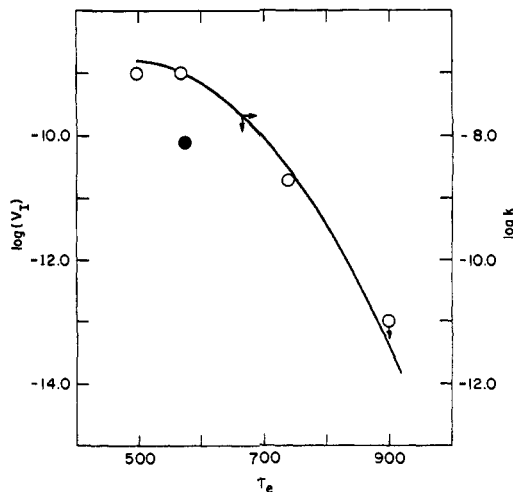

Figure 9. Variation of *k* (cm sec^{-1}) at 78°K (right ordinate axis) and of the concentration (left ordinate axis) of paramagnetic centers [V] in spins cm^{-2} (circles) with temperature of evacuation T_e (°C): O, MgO–EP (T_e); ●, MgO–EP (900–H_2O–T_e).

circles represent measured spin concentrations of V_I. After evacuation at 900°C, most of the intensity of the V_I signal can be restored by the treatment that also restored most of the catalytic activity, namely a treatment with H_2O vapor at 298°K followed by evacuation at 500°C. The concentration of V_I after such a treatment is shown by a full circle on Figure 9. By comparison with Figure 2, it is seen that the restoration of the V_I center parallels almost quantitatively that of the catalytic activity.

Finally, a MgO–EP sample heated in air or wet helium above 900°C exhibited no detectable signal of any sort, V_I, V_I^*, or impurity. This loss paralleled the irreversible loss of catalytic activity at 78°K suffered by MgO samples treated in this way.

Discussion

The earlier report of Lunsford and Leland[5] concerning the activity of MgO for the H_2–D_2 equilibration at 78°K is confirmed and amplified in the present study. Indeed, the activity of very pure MgO is higher than that of Cr_2O_3 and does not appear to rely on the presence of transition metal impurities present in vastly different quantities in samples exhibiting almost the same peak activity (Table III).

Our work indicates rather that the impurity associated with the active site is a proton. The presence of residual protons at the surface of MgO evacuated at 500°C was directly shown by exchange with deuterium, although failure to observe this exchange at 78°K suggests that the proton-containing active sites responsible for the H_2–D_2 equilibration must be present in very small concentration (certainly less than 0.3% of the surface). That the active sites contain protons is indicated by the deactivation of samples by evacuation at high temperatures followed by reactivation after exposure to water vapor.

Another interpretation of the reversible deactivation might be related to the micropores destroyed at high temperatures and restored by rehydration and subsequent dehydration of MgO samples. The existence of these micropores has been shown by Lecloux,[13] and it

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Table IV. Comparison between the Behavior of Active Sites (Characterized by k at 78°K) and V_I Paramagnetic Centers of Concentration [V_I], for MgO–EP

Treatment	Active sites	V_I centers
Heating in air or wet He above 900°C	Irreversibly lost	Irreversibly lost
Evacuation at 500°C	Highest value of $k \equiv k_{max}$	Highest value of [V_I] $\equiv$ [V_I]$_{max}$
Evacuation at 750°C	$k \cong 10^{-2}k_{max}$	[V_I] $\cong 10^{-2}$[V_I]$_{max}$
Evacuation at 900°C	$k \cong 10^{-5}k_{max}$	[V_I] $< 10^{-4}$[V_I]$_{max}$
As above, followed by exposure to H_2O and evacuation at 500°C	$k \cong 10^{-1}k_{max}$	[V_I] $\cong 10^{-1}$[V_I]$_{max}$
Fresh sample evacuated at 500°C then exposed to H_2 at 78 or 298°K	$k = k_{max}$	[V_I] $=$ [V_I]$_{max}$
Evacuated at 500°C followed by exposure to O_2 at 298°K	$k = 0$, activity restored by evacuation above 200°C	[V_I] $= 0$, signal restored by evacuation at 300°C
Evacuation at 500°C followed by exposure to H_2O at 298°K	$k = 0$, activity restored by evacuation at 500°C	[V_I] $= 0$, signal restored by evacuation at 500°C

might be said that our active sites are somehow associated with them. But this is unlikely as the sample with the smallest specific surface area, MgO–M–N, exhibiting beautiful octahedral large crystals, has the same activity per unit surface area as that of a sample of the same variety MgO–M–HS with a much higher surface area normally associated with micropores. Besides, a sample containing enough Cu was successfully reactivated with H_2; in that case hydrogen adsorbed on the copper impurities was apparently able to provide the protons required by the active site without the need for water. It must also be noted that the activation energy of the H_2–D_2 exchange is the same on a pure MgO sample at its peak activity or after its activity has been decreased by five powers of ten (Table II). Besides, the activation energy is also the same on all MgO samples no matter what their content might be in controllable or residual transition metal impurities.

It is concluded that the impurity responsible for the activity at 78°K is a proton, but there must be another requirement for obtaining an active site. Indeed the activity may be lost irreversibly by heating MgO in a gas containing water vapor, a treatment which is known to recrystallize and sinter MgO samples.[14] However, sintering associated with 20-fold reduction in specific area cannot explain a 10^5 change in k, a rate constant which already takes into account any change in surface area. Thus there must be an irreversible loss of a metastable crystal habit associated with freshly dehydrated MgO.[15] The desirable crystal orientation appears to be that corresponding to (111) planes which, according to our electron diffraction data and those of others,[13] tend to disappear upon dehydration of MgO in vacuo at increasingly higher temperatures but are probably wiped out by recrystallization in air as shown by the drastic change in texture observed after such a treatment by scanning electron microscopy. On the other hand, the partial irreversible loss of activity of samples heated in vacuo at 900°C and reactivated by exposure to water vapor might be explained by the partial loss of (111) planes during the high temperature evacuation, as observed by electron diffraction during transmission electron microscopy.

Thus the active site appears to require a proton and a (111) orientation. Further specifications rely on the results of the epr work. Now, the fast response of the V_I center to adsorbed gases, indicating that it is a sur-

face center, the quantitative correlation between the concentration of V_I centers and the rate constant over many orders of magnitude (Figure 7), and finally the analogy of behavior between the behavior of the paramagnetic center and of the active sites in the presence of various gases (Table IV) give us many compelling reasons to associate the V_I center with the active site and to suggest a one-to-one correspondence between the two. We consider this correspondence, especially over five orders of magnitude of concentration, as the main novel result of this work, and its validity does not depend on that of the model proposed for the V_I center and for the active site.

Before discussing a possible model for the V_I center, let us first note that although many V-like centers have been reported in and on irradiated MgO (for a partial list, see ref 9), none has been previously found on thermally treated MgO. Second, we must stress that the assignment of the V_I signal to a carbon impurity can be safely ruled out in spite of the fact that carbonaceous impurities on oxide surfaces give rise to a similar symmetrical and relatively sharp (5–10 Oe) line with the same g value (2.0025–2.0035).[16–19] First, it is known that heating an oxide sample exhibiting surface carbon impurities in oxygen or air at 500°C is sufficient to remove them by oxidation. By contrast, heating MgO–EP in air for 24 hr at 780°C did not affect in any measurable way the catalytic activity at 78°K of the sample after customary evacuation at 500°C prior to the run. The activity was the same as that of a sample evacuated at 500°C without prior oxidation (Figure 6). Since catalytic activity and V_I signal intensity go hand in hand, the latter cannot be a carbon impurity. Another argument against V_I being carbon is that V_I is transformed quantitatively into another signal V_I^* by evacuation of MgO–EP at 900°C. After this, V_I can be restored quantitatively by treatment of the sample with water vapor at 298°K followed by evacuation at 500°C. There is no chemical argument that can be advanced to explain the reversible transformation $V_I \rightleftarrows V_I^*$ due to loss or regain of protons, if V_I is a carbon impurity. Finally, the behavior of V_I in the presence of oxygen is totally different from that reported for carbon impurities. With the latter, oxygen is reversibly adsorbed at

(14) P. J. Anderson and O. L. Morgan, Trans. Faraday Soc., 60, 930 (1964).

(15) P. J. Anderson and R. F. Horlock, ibid., 58, 1993 (1962).

(16) C. P. Poole, E. N. Di Carlo, C. S. Nobel, J. F. Itzel, Jr., and H. H. Tobin, J. Catal., 4, 518 (1965).

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(19) W. S. Brey, R. B. Gammage, and Y. P. Virmani, J. Phys. Chem., 75, 895 (1971).

$298°K$ and the observed epr signal varies with the oxygen pressure.

Similarly, it does not seem reasonable to identify V_I centers with other types of impurities since the arguments used to rule out impurities as active centers can be repeated here, in view of the analogy of behavior between active sites and V_I centers (Table IV). Rather, the fact that V_I centers disappear irreversibly by heating MgO in air at temperatures at which metastable (111) planes disappear to be replaced by planes of lower free energy makes us suspect that (111) surface planes contain the V_I centers. Normally, (111) surface planes of MgO would be expected to consist of close-packed OH^- ions. At high temperatures *in vacuo*, O^{2-} ions and vacancies would be formed by dehydration. We shall assume that, near crystal corners where an excess of negative charge could build up if the crystal were terminated by O^{2-} ions, there is a possibility of formation of three O^- radical ions with three equivalent p^5 orbitals overlapping toward the exterior of the crystal in the region of a missing Mg^{2+} ion. This situation is depicted schematically on Figure 10, showing a small MgO particle with black balls symbolizing Mg^{2+} ions and white balls representing O^{2-}, OH^-, or O^- ions. A V_I center is represented by the three O^- ions numbered 1, 2, and 3, situated on a (111) plane of small area.

The characteristics of the V_I signal and its interaction with O_2 and H_2O can be explained by this model. A single symmetrical narrow homogeneous line with temperature insensitive width is expected because of effective exchange narrowing due to favorable overlap between p orbitals. Thus V_I is suggested to be an analog though not an antimorph of an R-like center consisting of three exchange-coupled F centers arranged in an equilateral triangle about the (111) direction and recently studied in irradiated MgO.[20] Both O_2 and H_2O can be adsorbed relatively strongly through their lone pairs of electrons on the electron-deficient center and disturb the overlap, thus broadening the line as observed. By contrast interaction between V_I and H_2 should be weak and, indeed, it is not observable by epr.

We can now propose a model for the active site, closely associated to, though not identical with, the V_I center. The catalytic data suggest that a proton is required for the equilibration of H_2 and D_2. Thus, on Figure 10, an OH^- group is shown next to the V_I center, perhaps at a crystal corner or at some other surface site characterized by a large binding energy of OH^- groups on MgO.[21] The exchange reaction is then believed to take place *via* a Rideal–Eley mechanism; a deuterium molecule (D–D distance equal to 0.746 Å) approaches the surface and inserts itself between two O^- ions (numbered 1 and 2, normal distance equal to 2.97 Å). As the D_2 molecule binds weakly to the surface, attracted by the low electron density of the V_I center, it forms a triangular transition state with the neighboring proton; this transition state decomposes at random and exchange takes place by a quasi-molecule-ion type reaction. This reaction takes place with a low activation energy as compared to the corresponding H + D_2 reaction involving a free hydrogen atom as a result of the lower electron density of the ionic transition state.
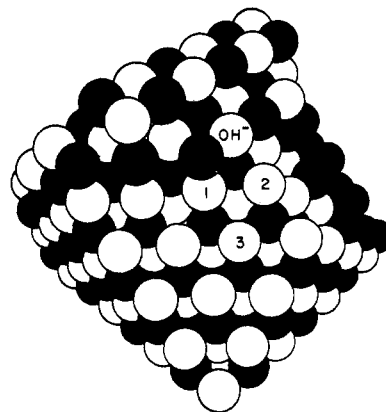

Figure 10. Schematic representation of an active site and V_I center.

This possibility was first clearly perceived by Temkin[22] and explains why the surface exchange reaction can take place with an activation barrier considerably smaller than that required between neutral partners in the gas phase.

Conclusion

In the present study the catalytic activity of unirradiated MgO for the H_2–D_2 equilibration at $78°K$ has been confirmed. The active sites have been shown to be closely associated with positive paramagnetic centers. The only impurity involved in the postulated Rideal–Eley mechanism of the exchange consists of protons. It does not seem that other impurities are required for the formation of the active sites or V_I centers although the question concerning the formation of the latter is left open at the present. The maximum surface concentration of V_I centers (Figure 9) is very small, about 10^9 cm^{-2}, or about one site in a million. It is interesting that the same value is obtained in order of magnitude from the preexponential factor A of the rate constant $k = A \exp(\sim E/RT)$ if it is assumed that $A = pZ$, where Z is the gas-kinetic collision frequency and p is the fraction of surface covered with active sites. The calculated turnover number of these sites at $78°K$ is extremely high, 10^3 sec^{-1}, which is comparable to that claimed for efficient enzymes operating at an absolute temperature more than three times higher.

While the active sites as well as the paramagnetic centers are blocked by water adsorption, a surface proton which is adjacent to the V_I center appears essential to the catalytic mechanism. This proton is removed by high temperature evacuation, and the V_I center is replaced quantitatively by another related center called V_I^*. The latter by adsorption of H_2 followed by uptake of H_2O goes over quantitatively to yet another paramagnetic center V_{OH}^* which contains three surface protons and can be transformed readily at $300°K$ into its deuterated analog V_{OD}^* in the presence of D_2. All these observations, which will be presented in detail elsewhere, confirm the role of surface protons in the behavior of the paramagnetic center and catalytic site.[23]

Finally, the results reported here complement the earlier data on the H_2–D_2 equilibration at $78°K$ on MgO

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(21) T. H. Nielsen and M. R. Liepold, *J. Amer. Ceram. Soc.*, 49, 627 (1966).

(22) M. I. Temkin, "Khimicheskaya Kinetika i Reaktsionnaya Sposobnosm," Moscow, 1955, p 492.
(23) E. G. Derouane, V. Indovina, A. B. Walters, and M. Boudart, paper presented at the 7th International Symposium on the Reactivity of Solids, University of Bristol, England, July 1972.

samples containing copper.[8] It is now believed that copper exerts no measurable effect on the activity of MgO itself and that earlier indications to the contrary[8] as well as evidence concerning the poisoning of the H_2–D_2 reaction at 78°K hydrogen adsorption at higher temperatures[8] must be ascribed to artifacts due to the extraordinary sensitivity of the system to traces of water vapor. This can be understood quite readily if the peak concentration of active sites (1 surface site in 10^6) determined by epr is kept in mind. Future work must establish the mode of formation of the active sites and V_I centers as this question was not considered in this investigation.

Besides establishing for the first time a correlation between active sites for a catalytic reaction and epr centers over at least five orders of magnitude of surface concentrations, we have suggested a molecule–ion surface exchange mechanism which is compatible with the low activation energy of the process and relies on protons as surface impurities but not on transition metal ions. An attempt was made to find another related H_2–D_2 equilibration catalyst active at 78°K. The

choice was CaO because of its resemblance to MgO and with same rock salt structure. However, this attempt failed indicating that geometric and energetic parameters for the exchange at 78°K are quite demanding. On the other hand, the mechanism of the reaction on Cr_2O_3 appears to be different from that proposed for MgO, since in the case of Cr_2O_3 the activity at 78°K keeps increasing as the sample is pretreated *in vacuo* to higher temperatures; the active site on Cr_2O_3 probably involves a transition metal ion and not a proton.

Proton Affinities of Benzene, Toluene, and the Xylenes

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Abstract: By operating the ion source of a mass spectrometer at pressures above 0.14 Torr, equilibrium constants have been obtained for the proton transfer reaction of formic acid with benzene, and of both methanethiol and dimethyl ether with toluene and the three xylenes. The resulting free energies when combined with the known proton affinities of the reference compounds (and assuming zero intrinsic entropy of reaction) give the following values for the proton affinities: benzene, 178.0 ± 2.23; toluene, 187.4 ± 1.14; p-xylene, 188.0 ± 1.11; o-xylene, 188.0 ± 1.09; m-xylene, 188.1 ± 1.11, all in kcal/mol. The value for benzene is referred to $\Delta H_f(sec\text{-}C_3H_7^+)$ of 191.7 and all others are referred to PA[$(CH_3)_2O$] of 187 kcal/mol.

Proton affinity plays an important role in solution chemistry, and values have been obtained by several means for a number of inorganic and aliphatic organic compounds.[1-8] However, the literature gives no information about proton affinities of aromatic compounds except benzene.[3,6,7] We have initiated such an investigation and have started with benzene, toluene, and the xylenes. The results of this first investigation are presented herein.

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(8) J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

Experimental Section

The method employed in this study was that of determining the equilibrium constant for a proton transfer reaction of the type

$$MH^+ + R \rightleftarrows RH^+ + M \qquad (1)$$
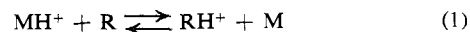
For this purpose the donor molecule, M, was introduced into the ion source of a quadrupole mass spectrometer at sufficiently high pressure to permit the formation of a large intensity of the protonated donor, MH^+. The donors employed were methanol, formic acid, dimethyl ether and methanethiol. The aromatic, R, was then introduced through a separate heated inlet line into the source at a series of known pressures and the intensities of MH^+ and RH^+ measured. In all cases, the source pressure was sufficiently high to ensure that the ions would undergo a large number of deactivating collisions and thus be as near as possible to the ground vibrational state. In most of the experiments, this was accomplished by using high pressures of the reactants. In one, a high pressure of inert gas (argon) was employed.

All of the gases in these experiments were purchased from Matheson Co. and were used without further purification. Methyl mercaptan and dimethyl ether were research grades of 99.8% purity. Formic acid and toluene were reagent grades of 99.97%.