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Influence of Radiation on Alumina as a Parahydrogen Catalyst

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The velocity of conversion of parahydrogen and of orthodeuterium is measured on θ-alumina at temperatures between room temperature and 230°C before and after irradiation with reactor neutrons. The temperature coefficient is negative (magnetic mechanism) and the isotope effect of 4.8 is independent of temperature. Previous irradiation diminishes the velocity, dependent on the dose, for both isotopes, the isotope effect after irradiation increasing up to 9 with temperature. The radiation damage can be healed out by heating in hydrogen at 450°C. The effects are discussed.

INTRODUCTION

In two preceding papers (*1*, *2*) the damage by energetic radiation of copper and nickel catalysts for the hydrogenation of ethylene has been investigated and explained by the removal of bound hydrogen from the metal lattice. In the present paper the investigation is expanded to oxidic contacts; as a reaction the conversion of parahydrogen and orthodeuterium was chosen. Instead of α, β, and X-radiation, the neutron radiation of the research reactor in Garching near Munich was used. In spite of these changes the effects to be described are surprisingly similar.

EXPERIMENTAL ARRANGEMENT

The symbols in Fig. 1 designate: VP, the forepump; QD, the mercury diffusion pump; QU, a gas circulating pump operated by mercury; $WL_{1,2}$ two Schleiermacher cells; Ma, manometer; V, gas storage vessels; KF, cooling traps with active charcoal for the preparation of parahydrogen and orthodeuterium; Pd, a heated palladium tower for the purification of hydrogen; ED_2, an electrolyzer for the preparation of deuterium, as described by Schwab and Wandinger (*3*). K is the reactor and furnace containing the catalyst, through which the gas is pumped by the route QU–trap–WL_2–K–trap–QU. SV is a mercury safety valve, VS, a "vakuscope" (Leybold).

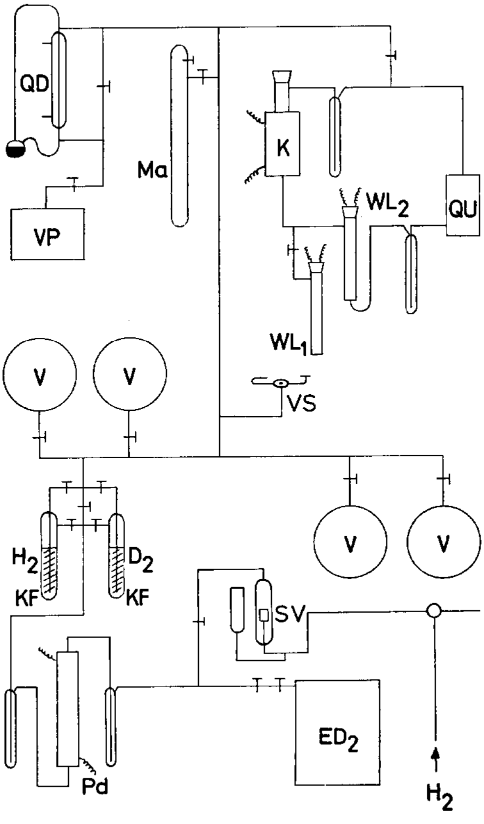

FIG. 1. The apparatus (see text).

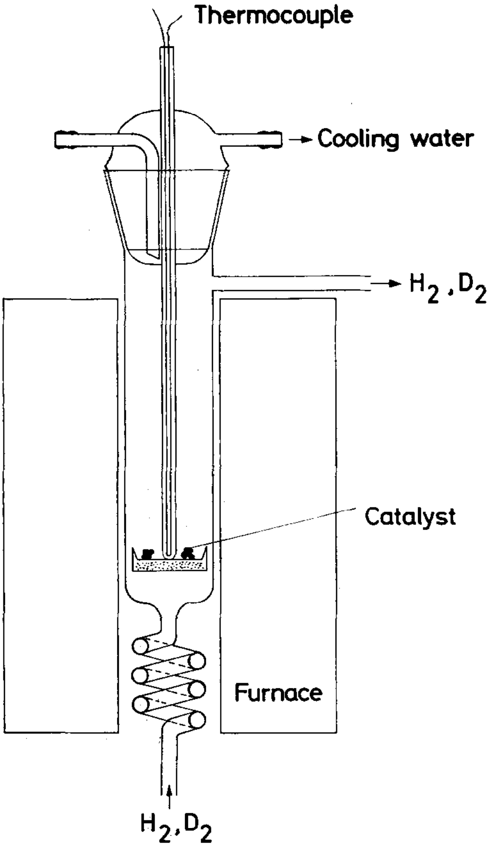

FIG. 2. The reactor.

In Fig. 2 the reactor is shown. It contains some pellets of the catalyst on a sintered glass disk. One of the two heat conductivity cells is part of the circulation path and the other one is closed and contains for comparison hydrogen of the concentration produced in KF (50% p-H_2 or 70% o-D_2). They are both branches of a Wheatstone bridge, so that the deviation of the zero instrument is, at least with small changes of resistance, a direct measure for the resistance difference and hence after calibration for the amount of conversion (the total conversion goes up to 25% p-H_2 or 66.7% o-D_2). It amounts to 25% or only 3.3%. Therefore in the case of deuterium a more sensitive instrument had to be used. The power supply for the bridge and at the same time for the heating of the wires is continuously closed through a parallel resistance in order to keep it constant. The measurements were carried out at 50 Torr because at this pressure neither convection nor the pressure-dependence of heat conductivity are too disturbing.

PROCEDURE

The procedure is essentially self-evident from the description of the device. It must be mentioned that the catalyst (0.65 g) was heated every time before the measurements, for several hours in hydrogen *in situ* to 350–400°C, before a conversion was measurable. In the case of deuterium the same pretreatment was done in deuterium. After the first measurement the preparation was sealed in evacuated glass tubes and was irradiated 1–20 hr in the research reactor of Munich near Garching with a neutron flux of 10^{12} n/cm^2. The energy of the neutrons is not known, nor is the dose of the accompanying γ radiation. After some days, when the radiation of Mg^{27}, Na^{24}, Al^{26}, and Al^{28} was sufficiently decayed the substances were used. It may be mentioned here that between measurement and irradiation and between irradiation and measurement the catalysts were exposed to atmospheric air for a short time.

THE CATALYST

The starting material was a 97% gibbsite (No. RD 6820) which we owe to the kindness of Peter Spence (Widnes). After calcination it contained less than 0.13% impurities, half of which was iron and silicon. It was pressed to pellets and heated 1 hr to 820°C. Probably after this treatment it is in the θ-modification. The mean diameter of the pores, according to BET measurements, amounts to 25 Å, which indicates the absence of considerable diffusion inhibition. The active surface in the actual experiment was 260 m^2.

EVALUATION

Let A_0 be the position of the galvanometer after an infinite time (i.e., at 25% o-H_2 or at 66.7% o-D_2) and A be its position at time t. Provided the reaction is first order as for the distance from equilibrium, it follows that

$$\ln [(A_0 - A)/A_0] = -kt$$

A plot of log $(A_0 - A)$ over time gives straight lines with a slope of $0.43\,k$. We designate the distance from equilibrium (proportional to $A_0 - A$), measured in partial pressures of parahydrogen by p' or in partial pressures of orthodeuterium by o', and the corresponding absolute partial pressures by p or o and the equilibrium partial pressures by $\bar{p}$ or $\bar{o}$. Then it follows that

$$-dp'/dt = -dp/dt = k_p^{\mathrm{H}} \cdot p - k_o^{\mathrm{H}}(3\bar{p} - p')$$

and for deuterium

$$-do'/dt = -do/dt = k_o^{\mathrm{D}} \cdot o - k_p^{\mathrm{D}}(\tfrac{1}{2}\bar{o} - o')$$

With

$$k_o^{\mathrm{H}}/k_p^{\mathrm{H}} = \tfrac{1}{3} \quad \text{and} \quad k_p^{\mathrm{D}}/k_o^{\mathrm{D}} = 2$$

we get:

$$-dp'/dt \equiv k^{\mathrm{H}} \cdot p' = \tfrac{4}{3}k_p^{\mathrm{H}} \cdot p' \quad \text{and} \quad -do'/dt \equiv k^{\mathrm{D}} \cdot o' = 3k_o^{\mathrm{D}} \cdot o'$$

and for the isotope effect:

$$k_p^{\mathrm{H}}/k_o^{\mathrm{D}} \equiv \alpha = (9/4)(k^{\mathrm{H}}/k^{\mathrm{D}})$$

RESULTS

1. The Nonirradiated Catalyst

Figure 3 gives the measured velocity constants k_p^{H} and k_o^{D} in the above notation and in min^{-1}. It can be seen that the temperature coefficient is negative. Hence we have not to do with a thermal conversion by a proton exchange with atomic adsorbed hydrogen, but with the magnetic mechanism.* This has already been found in our laboratory previously by J. Reisberg (*4*). According to the formula of Wigner (*5*) the impact efficiency must be inversely proportional to the square of the mean molecular velocity and hence inversely proportional to absolute temperature. This is approximately the case. Calculating the impact efficiency from this formula by plausible assumptions for the magnitudes entering, we get an order of magnitude of 10^{-12}. Calculating the pre-exponential of the velocity constant from the number of impacts according to Schwab and Drikos (*6*) and multiplying both numbers, we get for the velocity constant an order of magnitude of 0.1 min^{-1}, which corresponds closely to the measured results. This correspondence is surprising since certainly not the total surface of the alumina can be paramagnetic, and even if it were, no inhomogeneous field would result. Obviously in reality isolated paramagnetic centers (see below) are present, and their small number is compensated by a time of residence (time of collision according to Wigner) enhanced by adsorption.

The isotope effect α is shown in Fig. 4 as a function of temperature. Its average is 4.8, whereas from the formula of Wigner a maximum effect equal to the square of the ratio of magnetic moments $[(2.79/0.86)^2 = 10.5]$ is to be expected. The fact that it is not attained is probably due to a higher adsorption of deuterium which results in a longer average residence time within the inhomogeneous field.

2. The Irradiated Catalyst

Figure 5 shows how the constants k_p^H and k_o^{D} are diminished after irradiation times of 1, 5, 10, and 20 hr. At the same time the isotope effect which before irradiation was nearly independent of temperature, now increases with increasing temperature. After an irradiation of 20 hr it reaches at 490°K (220°C) nearly the theoretical limit (Fig. 6). After 7 hr heating in hydrogen at 450°C the damage is nearly completely healed out, as is indicated by the jumps at the right end of Fig. 5. This re-creation is nearly complete with catalysts irradiated 1 hr, whereas after 20 hr of irradiation, as shown in the figure, an irreversible damage remains of the order of

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* Endothermal dissociative chemisorption (de Boer) would, for that matter, also lead to a negative temperature coefficient. However, in this case, the isotope effect could hardly exceed a factor of $\sqrt{2} = 1.4$.

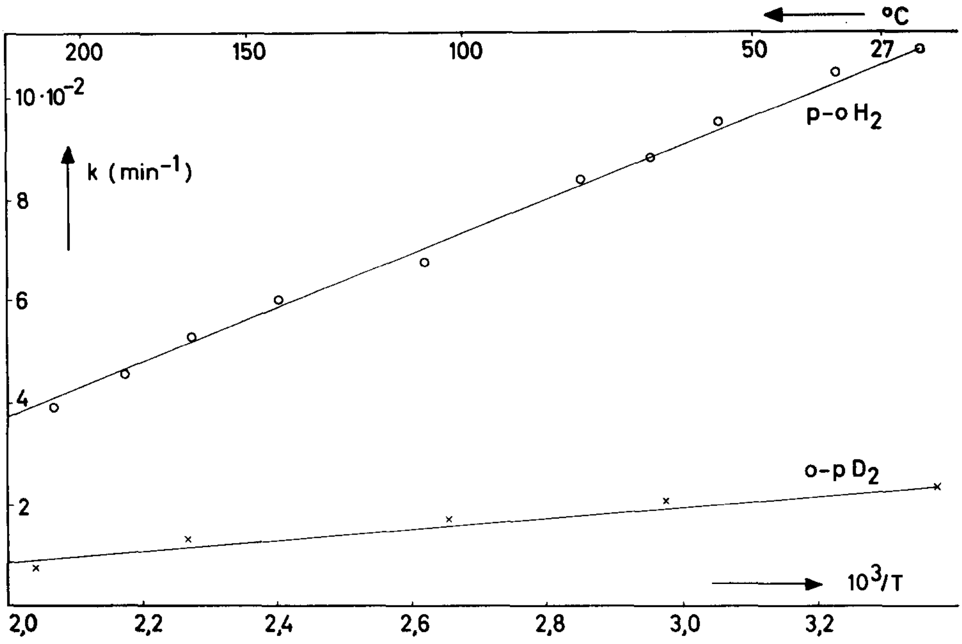

FIG. 3. Conversion constants at different temperatures.

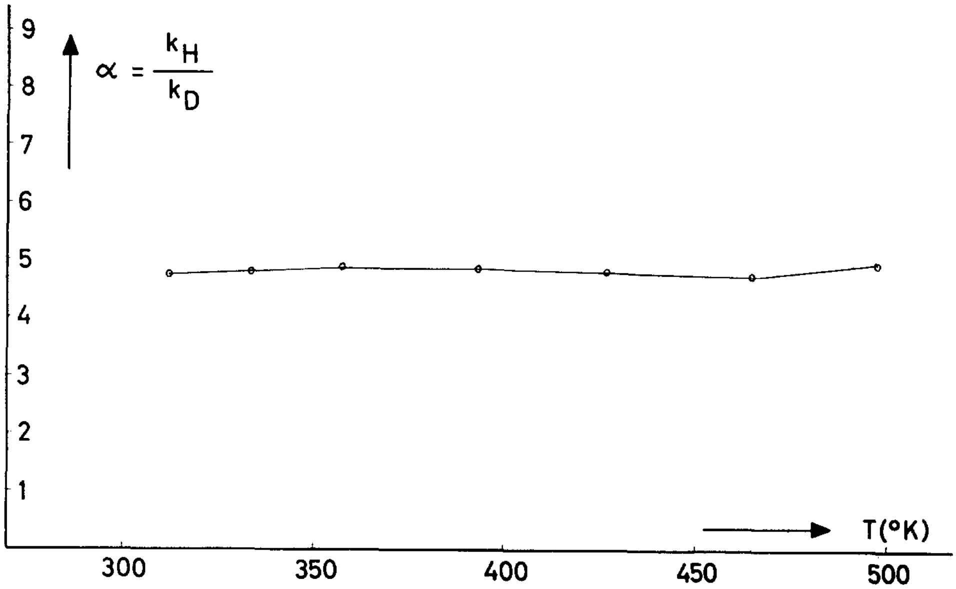

FIG. 4. Isotope effect before irradiation.

magnitude of 0.4×10^{-2} min^{-1} in k_p^H and 0.2×10^{-2} min^{-1} in k_o^D.

DISCUSSION

As already mentioned, the observed conversion shows all the characteristics of the magnetic mechanism, i.e. allowance for forbidden transitions in the inhomogeneous magnetic field of surface elements. The isotope effect also corresponds to this model if a strong adsorption of deuterium is assumed, as it has often been found. A sur-

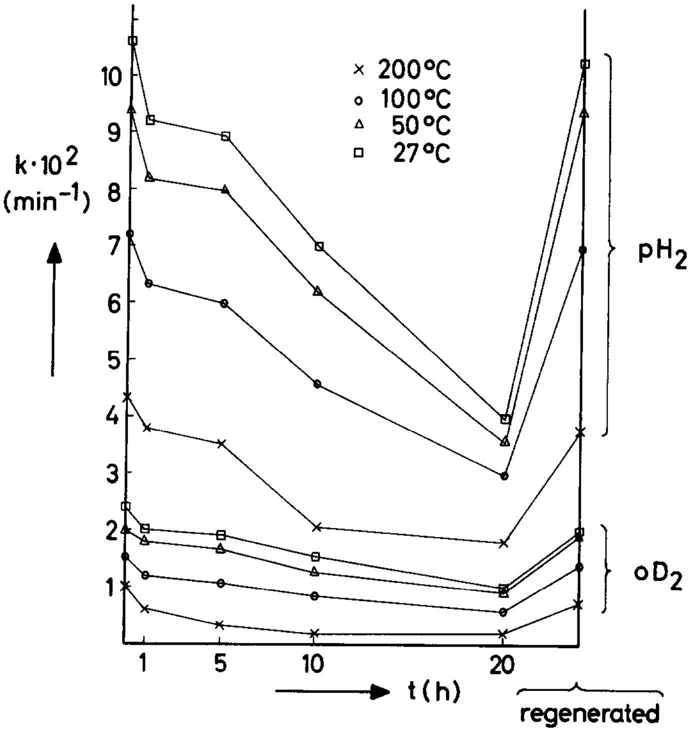

FIG. 5. Influence of radiation time on conversion constant (the increase at the right edge designates reactivation by heating).

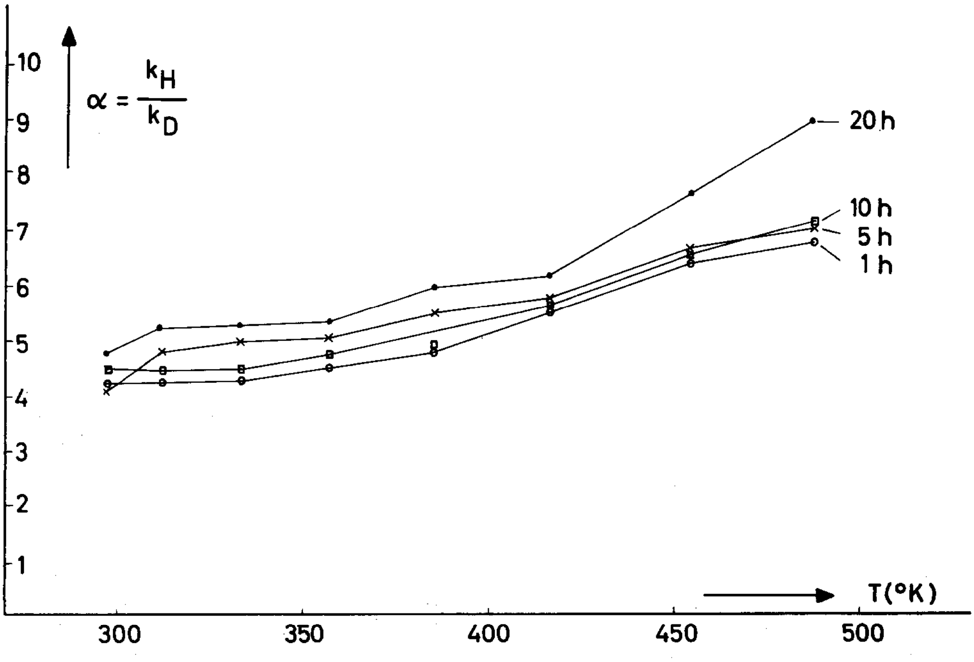

FIG. 6. Isotope effect after irradiation.

prising point is the temperature-dependence of the isotope effect after neutron irradiation. In the frame of our model, it means that after irradiation the adsorption of deuterium decreases to a higher degree with temperature (can be baked out) than hydrogen adsorption, so that the residence times become more or less equal. We may imagine that in the irradiated state all the centers adsorb hydrogen less than deuterium, that, however, both adsorptions depend on temperature equally or not at all. Irradiation eliminates to an increasing degree all those centers which have strong adsorption and to an increasing degree only those remain, which at elevated temperature loose deuterium more than hydrogen because of its higher adsorption energy.

What may be the nature of paramagnetic centers which can be eliminated by neutron impact and can be restored by heating in hydrogen? The primary effect of neutron irradiation can be one Frenkel defect (lattice vacancy + interlattice ion) or a whole cascade of Frenkel defects, a foreign atom produced by a nuclear reaction, ionization by the accompanying γ radiation, and finally thermally disturbed regions (spikes). Now, as mentioned in the introduction, the behavior of copper and nickel catalysts for ethylene hydrogenation is strikingly similar to that of alumina for parahydrogen conversion in the present investigation: In both cases irradiation eliminates the activity and hydrogen treatment of the heated catalyst restores it. For the metals the conclusion reached was that the active centers are bound hydrogen. It is only logical, even in view of the different systems, to apply the same conclusion to the present case. This would mean that alumina becomes paramagnetic at points where hydrogen is adsorbed. Neutron impacts would then remove these hydrogen atoms and hydrogen treatment at elevated temperature would introduce them once more. Another model which could explain the same facts would be a partial reduction of alumina during the hydrogen treatment, producing free, isolated, and, because of their electron configuration $3s^2 3p^1$, paramagnetic aluminum atoms in the surface. This state would approximately correspond to the "black alumina" of Teichner (*7*). The removal of these atoms by neutron impacts could occur by a mechanism similar to that of Frenkel defect production.

With both hypotheses, however, it must be kept in mind that in our experimental technique the catalyst has been brought into air before and after irradiation. Probably both kinds of active centers discussed above will be removed by air and must be restored by the hydrogen treatment mentioned. During the neutron irradiation, hence, they are not present or at least not in their catalytically active state. The influence of neutron irradiation is then essentially that it eliminates the re-reducibility by hydrogen or the ability to readsorb hydrogen quickly, e.g. by stabilization in thermal spikes or by production of sterically hindered interlattice ions. It would of course be sheer speculation to develop more specified models.

The irreversible damage remaining after regeneration of the catalyst can most probably be explained by a partial transition into the stable α-corundum modification at the high temperature of the thermal spikes.

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