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Catalytic Activation of Vycor Glass for the H_2–D_2 Exchange Reaction by Beta Irradiation

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The catalytic activity of Vycor glass tubes for the H_2–D_2 exhange reaction was found to be considerably increased by irradiation of the glass with beta radiation. This result is in general agreement with that of Kohn and Taylor (*1*) who found a marked increase in the catalytic activity of other SiO_2-type materials as a result of gamma and neutron irradiation. However, the activation energy for the reaction on Vycor was not changed appreciably by beta irradiation. This is in contrast to the drastic reduction in activation energy observed by Kohn and Taylor (*1*) for gamma and neutron irradiated silica gel.

Discussion of the Experiment

In the present work, the H_2–D_2 exchange reaction was studied in small volume Vycor reaction vessels consisting of two concentric Vycor tubes, the outside tube having an inside diameter of 20 mm and the inside filler tube having an outside diameter of about 18 mm. A schematic representation of a reaction tube is shown in Fig. 1. The reaction gas volume was the annular space between the tubes plus the space in the side arm filler tube. The total reaction volume was less than 10 cc.

Because the reaction rates were very slow, the reaction was carried out as a batch process. For runs in the nonirradiated vessels, as long as 48 hr at 100°C was required to achieve a measurable reaction. First order kinetics were assumed and the following equation was used to analyze the results:

$$dP_{HD}/dt = k_f P_{H_2} - k_r P_{HD} \qquad (1)$$

where P_{H_2} and P_{HD} are the partial pressures of H_2 and HD, respectively, and k_f and k_r are the forward and reverse rate constants, respectively. For all the experiments a 50–50 mole % mixture of H_2 and D_2 was used. Therefore, by integrating Eq. (1), assuming that the gases obey the perfect gas law, the forward rate constant can be written as,

$$k_f = -\frac{2 \ln \{1 - [1 + (2/K)]X_{HD}\}}{t[1 + (2/K)]} \qquad (2)$$

The constant K was selected to give a constant value of k_f. It was found that this

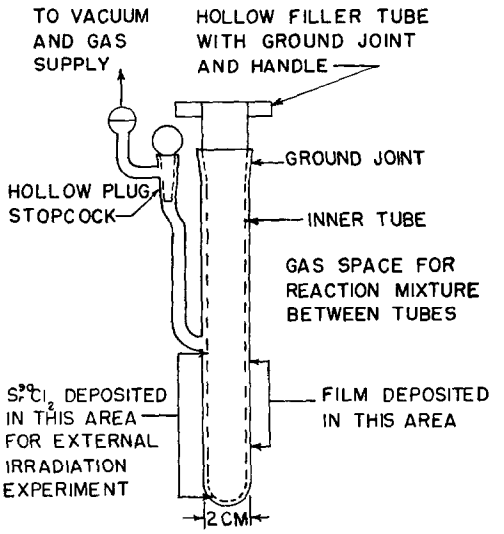

FIG. 1. Vycor small volume reaction tube.

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could be done by setting $K = K_{eq}^{1/2}$ where K_{eq} is the equilibrium constant for the reaction $H_2 + D_2 = 2HD$. The theoretical values for K_{eq} reported by Woolley (*2*) were used. The term X_{HD} is the mole fraction of reaction product HD produced in time t. It was determined by chromatographic analysis of the reaction mixture. Using Eq. (2), calculated values of k_f were found to be independent of the total system pressure (usually between 30 and 60 cm of Hg) and, within experimental error, gave the same value for various reaction times at the same pressure. For these reasons it is believed that k_f calculated from Eq. (2) adequately represents the catalytic activity of the Vycor.

To irradiate the Vycor tubes, two different types of beta sources were used. One source contained Sr^{90} and its Y^{90} decay product and the other source contained S^{35}. In using the Sr^{90} source, a portion of the inside wall of the filler tube of one vessel was coated with 10 mc of $Sr^{90}Cl_2$. For this arrangement only the more energetic Y^{90} betas [maximum energy, 2.26 Mev (*3*)] can penetrate the wall of the filler tube to irradiate the surfaces in contact with the reaction gas mixture. The weaker (0.54 Mev maximum) betas from Sr^{90} are largely stopped by the tube wall. Yittrium-90 decays with a half-life of 64 hr (*3*) which is so short compared to that of Sr^{90} [27.7 years (*3*)] that the two can be assumed to be in secular equilibrium. Effectively, for each Sr^{90} decay there is a corresponding Y^{90} decay. Two other Vycor vessels with similar dimensions were irradiated by S^{35} betas which have a maximum energy of 0.167 Mev (*3*). These betas, however, did not have to pass through a glass tube wall before reaching the surface in contact with the reactants. A film of radioactive CdS was deposited on a portion of the inside wall of the outer tube of each of these reaction vessels (see Fig. 1). One film had an initial activity of 12 mc of S^{35} and the other, 8 mc. The betas from these radioactive films were directed primarily at the portion of the filler tube surface which was adjacent to the film.

Since bulk CdS powder had some catalytic activity for the hydrogen–deuterium exchange, it was desired to determine whether the CdS films were catalytic. To do this, numerous experiments were performed with another reaction vessel of the same design containing a nonradioactive CdS film and it was found that the catalytic activity of the nonradioactive film was negligible compared to that of the unirradiated Vycor glass. Actually, the activity of the Vycor tube was decreased slightly by the deposition of the nonradioactive film and this decrease was attributed to the fact that the film covered some of the active glass surface. It was assumed that the same was true for the radioactive films.

Each tube studied was given approximately the same pretreatment before any reactions were run. This consisted of the following operations:

(a) Each tube was cleaned with hot dichromate cleaning solution and then thoroughly rinsed with distilled water and dried.

(b) The tubes were evacuated at 10^{-6} mm of Hg and at 180°C for several hours, cooled to room temperature and exposed to the air for a few minutes, and then re-evacuated at 120°C for several hours.

(c) The tubes were then exposed to 2–3 cm Hg pressure of H_2S gas. In the presence of the H_2S, the temperature was raised slowly to between 390° and 420°C and was kept in this final range for 12 to 24 hours.

(d) After being cooled back to room temperature and after the H_2S had been evacuated from them, the tubes were once more heated to 390–430°C for several hours in a vacuum of 10^{-6} mm of Hg.

(e) The tubes were then cooled to reaction temperature and filled with the 50–50 mixture of H_2–D_2 without exposure to the atmosphere. Between runs the tubes were either evacuated or kept full of the H_2–D_2 mixture.

This pretreatment with H_2S was carried out because the radioactive and nonradioactive films of CdS were produced by sulfiding thin vacuum-evaporated Cd films with H_2S in accordance with the above. In order to have a consistent basis on which

to make intercomparisons, all the tubes were treated the same way regardless of whether they contained films. However, it should be pointed out that preliminary experiments with unirradiated tubes indicated that the catalytic activity was rather insensitive to the pretreatment.

Results

The catalytic activity of the Vycor vessels was measured before and during irradiation. The activity of all vessels before irradiation was the same within a factor of about 2. No increase in activity with time was observed for any of the tubes prior to irradiation. The activation energy for the vessels ranged from 8.3 to 9.4 kcal/mole, which compares closely to Kohn and Taylor's value of 9 kcal/mole reported for unirradiated silica gel (*1*).

At 98°C the catalytic activity of the vessel irradiated by Y^{90} betas from the Sr^{90} source increased gradually in 9 days to a steady state value which was greater than the pre-irradiated activity by a factor of about 7. The activation energy measured after reaching this steady value was 8.3 kcal/mole, which was not appreciably different from that of the unirradiated glass. These results are shown in Fig. 2. Several values of k_f for this tube before irradiation are shown as well as values for another similar unirradiated tube.

The catalytic activity of the vessels containing radioactive CdS films measured at 98°C also increased gradually with time

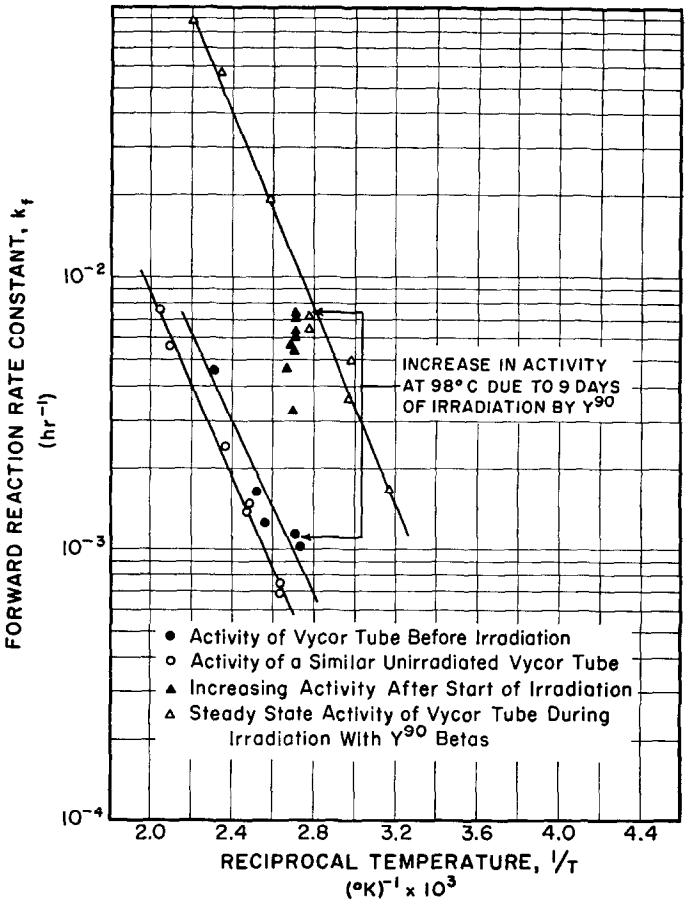

FIG. 2. Catalytic activity of a Vycor tube before and during irradiation with Y^{90} betas compared with the activity of another similar unirradiated Vycor tube.

to a steady value. The increase was measured for the tube containing the 8 mc film. The catalytic activity of this vessel increased by a factor of about 9 in 6 days from the date of sulfiding of the radioactive film. The activation energy measured after achieving this steady value was 8.4 kcal/mole compared to a value of 8.3 kcal/mole for the blank unirradiated tube shown in Fig. 2. A value of 9.4 kcal/mole was obtained for the tube containing a nonradioactive CdS film. The increase in activity at 98°C is shown in Fig. 3 as well as several points at different temperatures taken after reaching a steady activity at 98°C. Also shown in the figure for comparison are some data for the tube containing the nonradioactive film and values of k_f for the blank Vycor tube before deposition of the radioactive film.

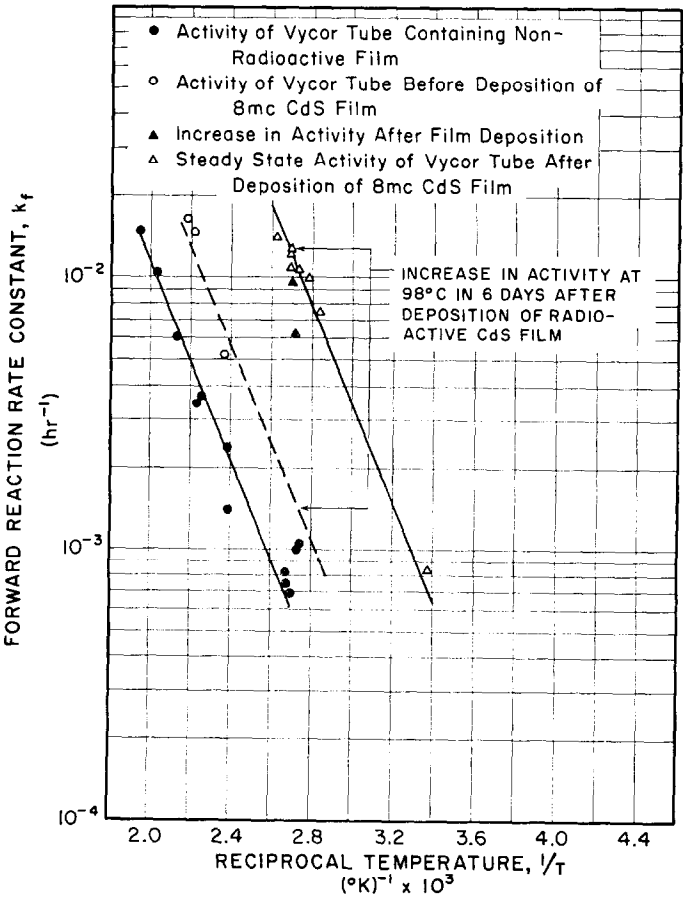

FIG. 3. Catalytic activity of a Vycor tube containing an 8 mc cadmium sulfide film as compared with that of a similar Vycor tube containing a nonradioactive cadmium sulfide film.

DISCUSSION

Since there is little change in activation energy, the gradual increase in activity to a steady value after a few days of irradiation may be explained by assuming that the enhanced activity is due to the production of new active sites on the Vycor surface accompanied by the annealing of these sites at some rate which is proportional to the number of sites. We may then write,

$$dN/dt = k_1F - k_2N \qquad (3)$$

where N is the surface concentration of

sites, F is the flux of incident radiation, and k_1 and k_2 are constants. Therefore, steady state is reached when k_1F equals k_2N for which condition,

$$N_{\text{steady state}} = (k_1/k_2)F \qquad (4)$$

Of course, the attainment of a steady state does not require the assumption of a first order annealing process, but if it is first order then Eq. (4) indicates that the number of sites is proportional to the irradiating flux. If it is also assumed that the increase in the forward rate constant for the catalytic reaction is directly proportional to N, then k_f at steady state minus k_f for the unirradiated Vycor should also be proportional to the flux. Because of the similarity in the behavior of the Vycor tube irradiated by Sr^{90}–Y^{90} source and the tubes containing radioactive CdS films it is likely that in both cases the same type of active site is responsible for the enhanced activity. Consequently, the annealing process (or k_2) should be the same in both cases while k_1 should depend on the nature of the irradiation and might be different for the two different beta sources. However, the ratio of the beta flux from the Sr^{90}–Y^{90} source to the beta flux from the 8 mc radioactive film was surprisingly close to the ratio of the radiation-induced change in k_f for the Sr^{90}–Y^{90} irradiated Vycor to the change in k_f for the S^{35} irradiated Vycor at 98°C. These ratios were computed to be:

$$\left(\frac{F_{Y^{90}}}{F_{S^{35}}}\right) = \frac{0.14 \times 10^7 \text{ betas/cm}^2\text{/sec}}{0.65 \times 10^7 \text{ betas/cm}^2\text{/sec}} = 0.22 \qquad (5)$$

and

$$\left(\frac{\Delta k_{fY^{90}}}{\Delta k_{fS^{35}}}\right) = \frac{1.0 \times 10^{-4} \text{ hr}^{-1} \text{ cm}^{-2}}{5.5 \times 10^{-4} \text{ hr}^{-1} \text{ cm}^{-2}} = 0.18 \qquad (6)$$

The F's are the estimated average beta fluxes at the irradiated surfaces in contact with the reaction gases and the Δk's are the radiation-induced changes in the forward reaction rate constants divided by the estimated superficial Vycor surface area which was irradiated. The indication is that the Sr^{90}–Y^{90} radiation was no more effective in producing active sites than the S^{35} radiation which is surprising considering the large difference in energy between the two types of radiation. However, the calculation of these ratios, which is outlined in the following section, is very approximate and requires a large number of assumptions.

Finally, it should be noted that Vycor was colored magenta by the Y^{90} radiation, whereas, no coloration resulted from S^{35} irradiation. Therefore, the enhanced catalytic activity cannot be attributed to color centers.

Furthermore, exposure of the tubes for long periods of time to air or water vapor at the temperature of reaction prior to a reaction run had very little effect on the catalytic activity. This was true for both irradiated and nonirradiated tubes. These exposure experiments were performed on the irradiated tubes only after the enhancement of activity by irradiation had already been observed on the clean surface. This result indicates that the irradiation activation of the Vycor is not due to the action of the radiation on adsorbed water on the surface.

Calculations

The calculations of the ratios in Eqs. (5) and (6) above were carried out as follows:

Only about the lower 5 cm of the reaction vessels were heated to the reaction temperature while the upper portion of the tubes was kept at approximately room temperature. The activation energy for the reaction was large enough so that for the lower portion of the tube at 98°C only the glass in this heated zone need be considered active. Since the $Sr^{90}Cl_2$ was deposited on the inside wall of the lower 5 cm of the filler tube (see Fig. 1), it is assumed that all of the glass area in the hot region was uniformly irradiated by this source. The superficial surface area in this region was calculated as the inside of the outside tube plus the outside of the filler tube and was measured as 59.6 cm^2. The inside coated diameter and the outside diameter of the

filler were, respectively, 2.0 and 1.8 cm. It was assumed that any radiation penetrating the filler tube irradiated not only the filler tube outside surface but also the adjacent outside tube inner surface. The magnitude of this penetrating flux was calculated from the relation given by Evans (4) for the attenuation of a beta flux in aluminum assuming that beta absorption coefficients are proportional to density:

$$F/F_0 = \exp(-\mu x) \tag{7}$$

where

$$\mu = (17/E_m^{1.14})\rho_{Al} \text{ in cm}^{-1} \tag{8}$$

and μ is the absorption coefficient, ρ_{Al} is the density of aluminum, E_m is the maximum energy of the beta spectrum in Mev, and x is the thickness of the absorbing aluminum in cm. Since SiO_2 has about the same number of electrons per atom as aluminum it was assumed that μ for Vycor could be written:

$$\mu_{Vycor} = (\mu_{Al})\left(\frac{\rho_{Vycor}}{\rho_{Al}}\right) = \frac{17}{(2.26)^{1.14}}(2.18 \text{ g/cc}) = 14.6 \text{ cm}^{-1} \tag{9}$$

The thickness of the Vycor filler tube was 1 mm, so using Eqs. (9) and (7):

$$F \text{ (penetrating the filler tube)} = F_0 \exp(-\mu x) = (0.23)\,F_0 \tag{10}$$

Since the activity of the total $Sr^{90}Cl_2$ deposit was 10 mc, F_0 was taken to be

$$F_0 = \frac{1}{2}\left[\frac{(10 \text{ mc})(3.7 \times 10^7 \text{ betas/mc})}{\text{Inside area of the filler tube}}\right] = \frac{18.5 \times 10^7}{(\pi)(1.6)(5)} = 0.73 \times 10^7 \text{ betas/cm}^2\text{/sec} \tag{11}$$

The factor of ½ is introduced because only about ½ of the emitted radiation was assumed to be directed toward the filler tube substrate. Thus the average flux irradiating the Vycor surfaces in the hot region was estimated to be:

$$F_{Y^{90}} = (0.73 \times 10^7)(0.23)\left(\frac{\text{Area of the inside of the filler}}{\text{Average area of the two coaxial reaction surfaces}}\right) = (0.73 \times 10^7)(0.23)\left(\frac{(\pi)(1.6)(5)}{(\pi)(1.9)(5)}\right) = 0.14 \times 10^7 \text{ betas/cm}^2\text{/sec} \tag{12}$$

$\Delta k_{fY^{90}}$ was calculated as the difference between the total rate constant at steady state (0.74×10^{-2} hr^{-1}) divided by the superficial glass surface in the hot region (59.6 cm^2).

In the case of the radioactive film it was assumed that the area covered by the film did not participate in the reaction and that the area activated by the irradiation was the area of the outside surface of the filler tube adjacent to the film and extending ½ cm above and below the length of the film. This area was approximately equal to $(\pi)(1.8)(4)$ or 22.6 cm^2 and was assumed to be uniformly irradiated. The total radiation striking this surface was considered to be ½ the total beta emission from the film so that

$$F_{S^{35}} = \frac{1}{2}\left[\frac{(8 \text{ mc})(3.7 \times 10^7 \text{ betas/mc/sec})}{2.26 \text{ cm}^2}\right] = 0.65 \times 10^7 \text{ betas/cm}^2\text{/sec} \tag{13}$$

$\Delta k_{fS^{35}}$ was calculated as the difference between the total rate constant at steady state (1.4×10^{-2} hr^{-1}) and the total rate constant before irradiation (1.6×10^{-3} hr^{-1}) divided by the superficial glass surface irradiated (22.6 cm^2).

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