1 atm total pressure. In order to determine the dependence of the rate upon the partial pressure of ammonia, experiments were performed in which the temperature, the hydrogen flow, and the total flow were held constant and ammonia flow was varied. Helium was used as diluent. In a similar manner, the dependence upon the hydrogen was studied. The rates thus obtained are shown in Figs. 1 and 2 as a function of partial pressure of ammonia and hydrogen at the inlet of the catalyst bed. Evidently the rate V can be approximately expressed as $V = k(P_{NH_3}/P_{H_2}{}^{0.5})^{0.44}$. According to Temkin-Pyzhev theory (*5*) the ratio of the exponents of hydrogen to ammonia should be -1.5, as observed in the previous experiments (*3*, *4*) around 420°C. However, the rate equation obtained in the present experiment is quite similar to that obtained previously above 479°C.

We, therefore, conclude that the rate-determining step of the decomposition changes with the content of the potassium oxide promoter. Furthermore, on the basis of results previously obtained on another catalyst with a high content of potassium oxide at higher temperature, we concluded that the slow step is probably the dehydrogenation of the adsorbed amino group, $NH_2(a)$.

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The Effect of Ionizing Radiation on the Chemical Activity of Alumina*

Kohn and Taylor (*1*) demonstrated that ionizing radiation enhances the activity of gamma-Al_2O_3 as a catalyst for H_2–D_2 exchange. More recent experiments have been conducted with both exchange reaction (*2*) and chemisorption (*3*, *4*) to learn more about the nature of the effect of radiation on alumina. In these previous studies the behavior of the alumina after irradiation was compared to preirradiated samples. To complement these results, a different approach, used in this work, utilized measurements of catalytic activity made during irradiation.

A 5-g sample of adsorption alumina (Fisher Scientific) was irradiated in a 5 megawatt swimming-pool type nuclear reactor. The quartz reaction vessel, sealed in a water-tight canister, was positioned 18 to 30 inches from the reactor core face, where the gamma dose rate drops from 10^7 to 10^6 rad/hr. At these distances the contribution by fast neutrons is less than 1% of the total dose.

Since catalyst activity was gradually poisoned by hydrogen, before each run the catalyst was heated overnight at 500°C in hydrogen or helium. Although poisoning did occur during a run, use of 20% H_2 in helium at 25 psia for the process carrier gas permitted activity measurements in the 50° to 150°C region. To conserve the expensive

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deuterium, slugs of 10% D_2-10%H_2-80% He were injected into the process carrier stream whenever an activity measurement was taken. After passing over the catalyst, the slug was trapped and analyzed by gas chromatography.

The ratio of HD to D_2, separated in a 3-m silica gel column at liquid nitrogen temperature with a hydrogen carrier, indicated the extent of conversion. Even though approach to equilibrium with an exchange reaction is first order (*5*, *6*), conversions were usually less than 20% of equilibrium, because the lower the conversion the lower the effect of dilution of the slug with process carrier.

A definite enhancement of the activity by radiation was observed. The advantage of *in situ* measurements was demonstrated since the activity decayed rapidly towards its initial value once it was removed from the radiation field. The effect of temperature on the radiation-induced activity was similar to that observed by Kohn and Taylor (*1*) in that it decreased with increasing temperature. At 150°C and 10^7 rad/hr, the change

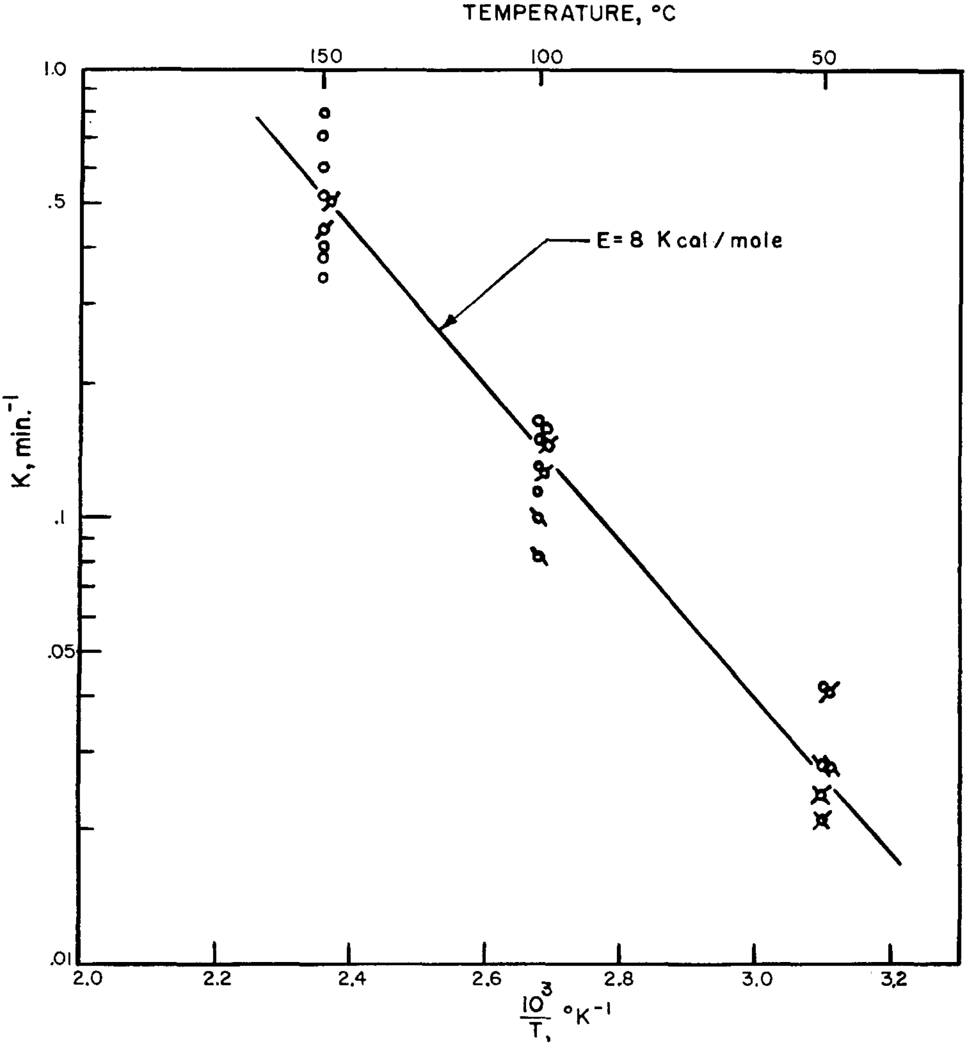


FIG. 1. Activity for hydrogen exchange versus reciprocal temperature for an activated alumina catalyst outside a radiation field. Each symbol at each temperature represents a different day's run.

was only a factor of 4 or 5, whereas at 50°C, the activity increased by almost three orders of magnitude.

In Fig. 1 are given data taken after activation of the alumina, but before any irradiation. Each symbol at each temperature represents a different day's run. The activation energy determined from these data is about 8 kcal/mole, in reasonable agreement with previous work for activation at 500°C (*7*, *8*).

The data taken during irradiation are shown in Fig. 2, in which the net increase in activity divided by dose rate is plotted versus reciprocal temperature. Since over an order of magnitude change in dose rate there is no definite trend at any one temperature, the change in activity appears

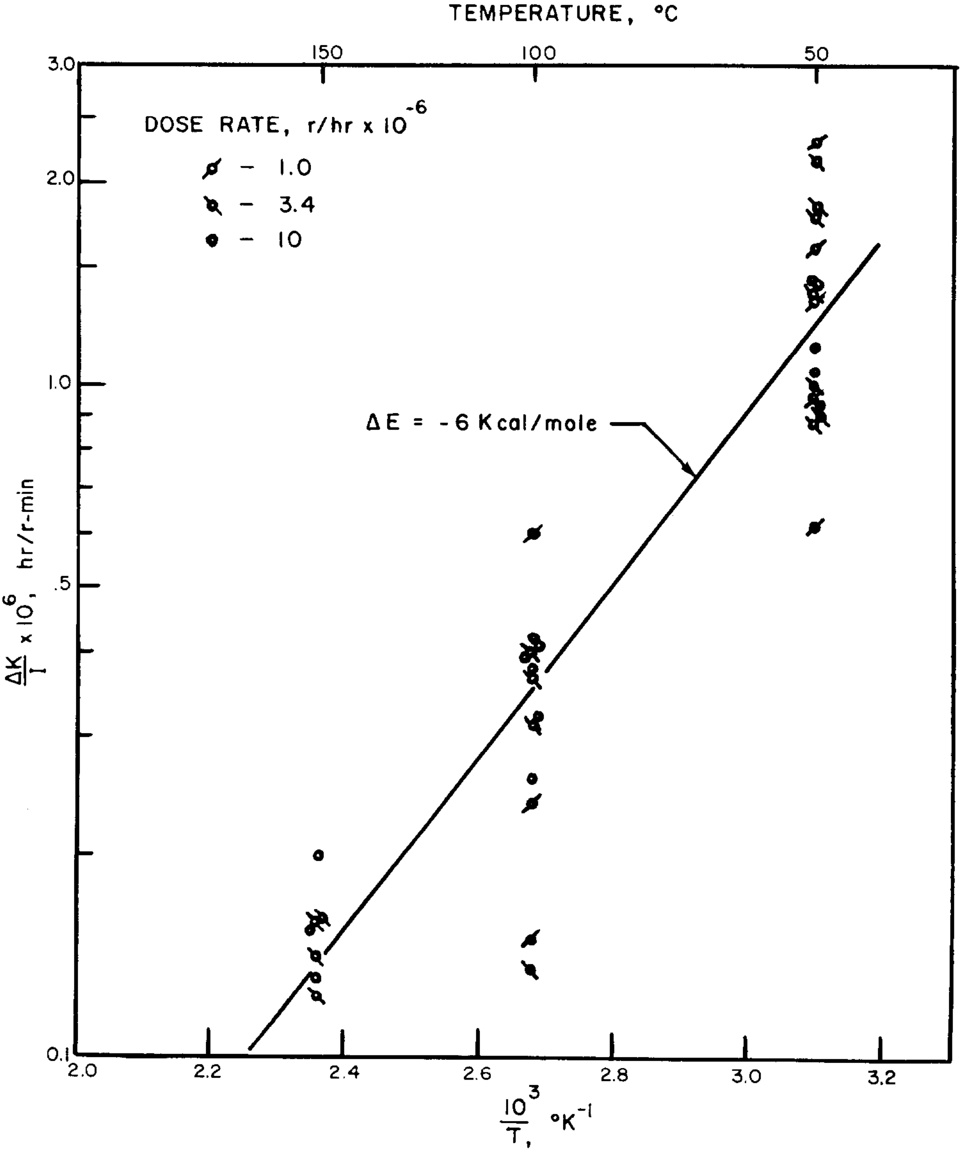


Fig. 2. Activity for hydrogen exchange divided by dose rate versus reciprocal temperature for an activated alumina catalyst.

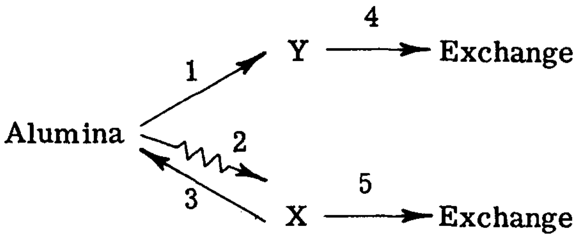
to be at least roughly linear with respect to dose rate. A least-square fit of the data gives a negative activation energy of 6 ± 1 kcal/mole (99% confidence limit).

An illustration of the drop in activity that occurs after irradiation is stopped is given in Fig. 3 in which log of the radiation-induced activity, Δk, is plotted versus time after irradiation at 10^7 rad/hr and 50°C. The only way found to correlate these rate data at 50°C and at 100°C was by means of an Elovich (*9*) plot—log Δk versus log time. In an integrated form of the Elovich equation

$$\ln\frac{\Delta k}{\Delta k_{(t=0)}} = \frac{RT}{\alpha}\ln\frac{(t+t_0)}{(t_0)}$$

the slope is RT/α' where α is independent of temperature, and t_0 is $RT/\alpha a$. The variation of a with temperature is approximately $e^{-E_0/RT}$, so that a value for the activation energy can be estimated from a's at two temperatures. The activation energy determined from data at 50° and 100°C was within 3 to 6 kcal/mole.

The following discussion may explain the results obtained with alumina. Assume that irradiation produces an excited species, X, active for H_2–D_2 exchange, but unstable. Thermal activation of alumina produces a relatively stable species, Y, also active for H_2–D_2 exchange. The reactions may be written



(1)

The rate of exchange is then

$$r = k_4[\mathrm{Y}] + k_5[\mathrm{X}] \qquad (2)$$

so that the net rate of reaction due to radiation is

$$\Delta r = r - k_4[\mathrm{Y}] = k_5[\mathrm{X}]. \qquad (3)$$

Let the rate of generation of X be given by

$$d[\mathrm{X}]/dt = a_2 I, \qquad (4)$$

where I is the dose rate. Since the concentration of X reaches a steady-state value during irradiation

$$d[\mathrm{X}]/dt = 0 = a_2 I - k_3[X] \qquad (5)$$

$$[\mathrm{X}] = a_2 I/k_3. \qquad (6)$$

Therefore,

$$\Delta r = k_5 a_2 I/k_3. \qquad (7)$$

Assuming that a_2 is independent of temperature, the relationship for Δr can be written

$$\Delta r = (a_2 a_5 I/a_3) \exp -[(E_5 - E_3)/RT]. \qquad (8)$$

The activation energy measured during steady state irradiation, −6 ± 1 kcal/mole, is $(E_5 - E_3)$, that is,

$$E_5 = E_3 - 6 \text{ kcal/mole}. \qquad (9)$$

After irradiation, the following equation applies:

$$d[\mathrm{X}]/dt = -k_3[\mathrm{X}]. \qquad (10)$$

Substituting for [X] from Eq. (3),

$$d(\Delta r)/dt = -k_3(\Delta r) \qquad (11)$$

or

$$d \ln(\Delta r)/dt = -k_3 = -a_3 \exp(-E_3/RT). \qquad (12)$$

If E_3 were constant, one should have been able to correlate the data with a ln Δr versus t plot. If E_3 is assumed to vary with coverage θ according to the relationship

$$E - E_0 + \alpha\theta, \qquad (13)$$

the Elovich equation applies (*9*). The value for activation energy obtained from these correlations, 3–6 kcal/mole, is the initial value of E_3. The value for E_5 is obtained from Eq. (9)

$$E_5 = (4.5 \pm 1.5) - (6 \pm 1) = -1.5 \pm 2.5 \text{ kcal/mole}. \qquad (14)$$

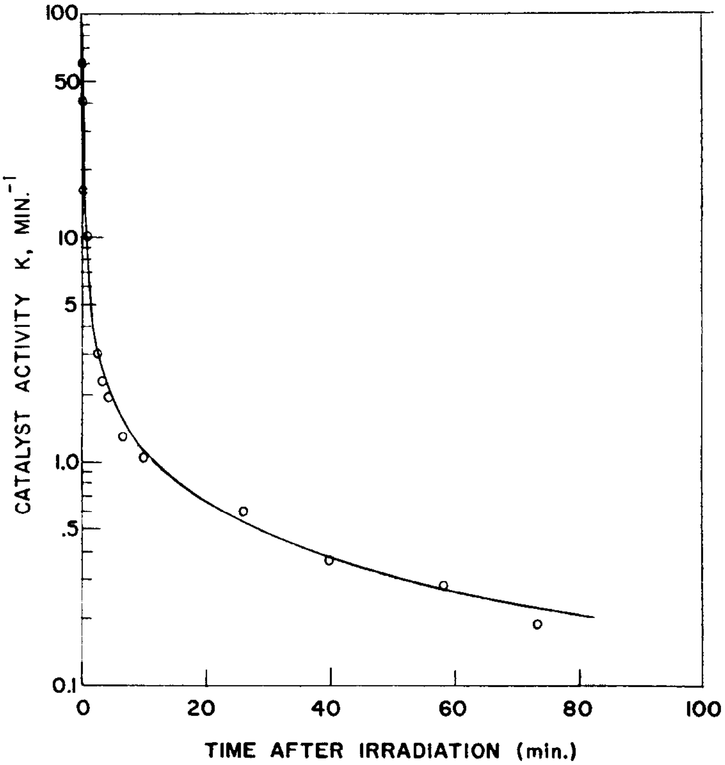


FIG. 3. Decrease in activity of an alumina catalyst for the hydrogen-deuterium exchange reaction at 50°C after irradiation at 10^7 rad/hr.

Hydrogen exchange therefore appears to occur without any significant activation energy on the sites produced during irradiation. If exchange takes place on X with zero or a small positive activation energy, $E_5 \geq 0$, then from Eq. (9)

$$E_3 \geq 6 \pm 1 \text{ kcal/mole.} \tag{15}$$

Kohn and Taylor (*1*) irradiated alumina at various temperatures up to 25°C, but made all activity measurements at −78°C after irradiation. The activation energy they reported for E_3 was 3 kcal/mole. Although there is some difference between these two values for E_3, the general interpretation appears to be the same. The active site X is definitely different from Y, for which the exchange has an activation energy of 8 kcal/mole. It is reasonable that X involves trapped electrons or holes, which recombine slowly in an insulator-like alumina.

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