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On the Hydrogen–Deuterium Exchange Activity of Silica Gel: Aluminum Impurity and Radiation Effect

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The range of hydrogen–deuterium exchange on several silica gel samples was shown to increase with increasing alumina content. Chemisorption of hydrogen on gamma-irradiated gels and the increase of the exchange rate due to irradiation also increased with increasing alumina. Maximum obtainable exchange rates for silica samples which were extensively degassed are also reported.

The H_2–D_2 exchange activity of commercial silica gel can be increased a billionfold by gamma irradiation. The first experiments indicated a connection between impurity content and both catalytic activity and radiation enhancement (ref. *1* and ref. *6,* Table II), but results were not conclusive. In this paper we report the results of better experiments using gels specially prepared for intercomparison rather than the commercial ones used before.

We used the following procedure. Technical $SiCl_4$ was fractionally distilled in a quartz apparatus. Sixteen cc of this $SiCl_4$ was slowly added with constant stirring to 200 cc of conductivity water and ice, giving a clear solution which gradually gelled. Stepwise calcination gave a product with very low aluminum content (5 ppm†) and a surface area of 6×10^2 m^2/g.‡ Adding appropriate amounts of $Al(NO_3)_3$ to the water before gelling gave gels of 0.01, 0.1, and 0.5% aluminum impurity. An ultrapure gel (no impurities detectable by the spark spectrograph) was made from $SiCl_4$ from the reaction of Cl_2 with zone-refined silicon. All gels had similar surface areas.

The samples were degassed at high temperature and irradiated at ambient (~35°C) temperature in a 600 curie Co^{60} γ source. H_2–D_2 exchange activity was measured after each treatment. Representative rate constants are shown in Table 1.

Since higher temperatures of degassing up to 920° produced materials of higher catalytic activity, and since crystallization of the gel begins near this temperature (*2*) we thought it worthwhile to re-examine the H_2–D_2 exchange rate constants obtainable on gel, quartz, cristobalite, and vitreous silica (*3*). Contrary to popular belief, the exchange reaction will proceed at a lively rate on these materials even at −78°C if the catalyst is first degassed for a weekend at 920°C. So far, the maximum rate constants observed after this treatment have been (at −78°C): 10^{-3} min^{-1} $meter^{-2}$ on quartz, 10^{-4} min^{-1} $meter^{-2}$ on vitreous silica and cristobalite. (These materials were ground to a surface area of 6–8 m^2/g.) The rate constant of commercial gels can be brought to 5×10^{-7} min^{-1} $meter^{-2}$ at −78°C.

In a separate experiment, the very pure gel even after extensive (6×10^{20} ev/g)

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* Operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission.

† Spectrographic analysis by Cyrus Feldman, ORNL Analytical Division.

‡ Measured for nitrogen adsorption by Paul Dake, O.R.G.D.P.

TABLE 1

EFFECT OF DEGASSING AND OF Co^{60} γ IRRADIATION ON H_2–D_2 EXCHANGE ACTIVITY OF SILICA GELS OF DIFFERENT PURITIES

Treatment	Rate constant at 25°C, measured after each treatment (min^{-1} meters^{-2})			
	0.5% Al^{3+}	0.1% Al^{3+}	0.01% Al^{3+}	No Al^{3+}
Degas 500°C, 1 hr.	2.6×10^{-6}	1.2×10^{-6}	1.4×10^{-7}	$<6 \times 10^{-8}$
Degas 500°C, 16 hr	2.2×10^{-6}	2.1×10^{-6}	8.0×10^{-7}	2.7×10^{-8}
Irrad. 1 min.	$>1.6 \times 10^{-4}$	5.5×10^{-5}	3.5×10^{-5}	3.7×10^{-6}
Degas 625°C, 16 hr	2.5×10^{-6}	6.1×10^{-6}	6.9×10^{-6}	$<3.3 \times 10^{-7}$
Prepare new samples, 550°C, 16 hr	—	1.5×10^{-5}	1.7×10^{-6}	4.0×10^{-7}
Irrad. 20 sec	—	1.8×10^{-5}	4.3×10^{-6}	2.7×10^{-6}
Degas 920°C, 16 hr, rate constant at −78°C	10^{-6}	6×10^{-7}	2×10^{-7}	$\sim 10^{-7}$
Irrad. 1 hr		All gels extremely active at −195°		
Not irrad., degas at 900°C, rate constant at −196°C	—	—	$<3 \times 10^{-7}$	—
Irrad. 16 hr, rate constant at −196°C	—	—	$>3 \times 10^{-4}$	—

gamma irradiation adsorbed very little hydrogen. This amount corresponds to a concentration of hydrogen chemisorption sites of less than 5 ppm, whereas an impure or commercial gel so irradiated would easily adsorb one hundred times as much (*4*).

It is therefore apparent that hydrogen-deuterium exchange activity, the increase in this activity induced by irradiation (k irradiated minus k unirradiated), and radiation-induced H_2 adsorption in silica gel are all increased by the presence of aluminum impurity. Hence, there is a strong temptation to ascribe radiation-induced catalytic activity in silica gel to the complex consisting of adsorbed hydrogen plus a positive hole trapped at an aluminum atom. It is only fair, however, to warn the reader that this is probably an oversimplification, since it fails to account for the increased activity of UV-irradiated samples (*4*) of samples irradiated with γ rays and bleached with UV, (*4*) or for the poisoning of the catalytic activity of irradiated samples by dry oxygen (*5*).

We also believe that the radiation effects on the catalytic activity of silica gel noted here and elsewhere are not likely due to the removal of water by radiolysis of surface hydroxyl groups. For one thing, it is doubtful that the samples listed in Table 1 differ very much in hydroxyl content. If they did, it would have to be associated somehow with the aluminum content (a postulate for which there is some evidence, ref. *6*). Therefore, if the samples with higher aluminum content contained more water, they should be less active than those of lower aluminum content since removing water increases catalytic activity. This reasoning is invalid if the water is an active intermediate on the irradiated catalyst, or if the higher aluminum content is associated with lower water content. That the water does not participate in the reaction has been previously shown (*4*). A decrease in water content with increased alumina content would again be difficult to explain since removing water increases catalytic activity for all samples. Furthermore, pumping on an irradiated sample at an elevated temperature, which would be expected to remove the radiolysis products of water, decreases the catalytic activity (Table 1, lines 3 and 4).

Finally, in spite of the high catalytic activity (exchange at —78°) in silica which can be obtained by prolonged pumping these samples are still inactive at —195°. Although the picture is complicated by several activation energies (*7*) the irradiated samples, which are active at —195°C are probably a thousand times more active catalytically than our most active unirradiated samples.

REFERENCES

1. KOHN, H. W., personal communication to P. H. Emmett, cited in "New Approaches to the Study of Catalysis," p. 85. Pennsylvania State Univ., 1962.
2. WAHL, F. M., GRIM, R. E., AND GRAF, R. B., *Am. Mineralogist* **46,** 196 (1961).
3. HOLM, V. C. F., AND BLUE, R. W., *Ind. Eng. Chem.* **44,** 107 (1952).
4. KOHN, H. W., *Nature* **184,** 630 (1959); KOHN, H. W., AND TAYLOR, E. H., "Actes due Deuxieme Congres International de Catalyse," Paper 71. Editions Technip, Paris, 1961.
5. KOHN, H. W., *J. Phys. Chem.* **66,** 1017 (1962).
6. WEISS, H. C., KNIGHT, J. A., AND SHAPIRO, J., *J. Am. Chem. Soc.* **81,** 1823 (1959).
7. KOHN, H. W., AND TAYLOR, E. H., *J. Phys. Chem.* **63,** 967 (see Fig. 1), (1959).