The Effect of Ionizing Radiations on the Adsorption Rate of Hydrogen on Manganese Dioxide

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Kolarov and Kirilov[1] determined the temperature at which the reduction of differently-treated samples of manganese dioxide in a stream of hydrogen started; they found that this temperature was 234°C for the original manganese dioxide, whereas it was 217°C after the oxide had been ground for half an hour and 239°C after the irradiation of the oxide with ultraviolet light for half an hour. From these experimental results, they concluded that the grinding caused an activation, whereas the ultraviolet light caused an aging, of the oxide. We found a similar inactivation of manganese dioxide caused by the irradiation of ionizing radiations; the rate of hydrogen adsorption decreased for the oxide previously irradiated with radiations from a reactor or with ^{60}Co γ-rays.

The manganese dioxide was prepared by the thermal decomposition of manganous nitrate, and the surface area of the oxide was measured by the B. E. T. method and found to be 10 m^2/g. The pile-irradiation of the oxide was carried out in the experimental hole of a swimming pool reactor of the Tokyo Atomic Industrial Research Laboratory. The flux of thermal and fast neutrons in the experimental hole was 1.7×10^{12}n/cm^2 sec. and 0.7×10^{12}n/cm^2 sec. respectively, and the dose rate of γ-rays was 1.1×10^6 r./hr. The oxide was irradiated in the hole for 15 hr. in the presence of air. The irradiation of the oxide by ^{60}Co γ-rays was carried out in the hot cell of the Tokyo Metropolitan Isotope Research Center, under conditions similar to those of the pile-irradiation; the oxide was irradiated for 15 hr. in the presence of air, and the dose rate of γ-rays was 1.0×10^6 r./hr.

The oxide (400 mg.) was placed in the adsorption apparatus; after it had been evacuated at 100°C for 1 hr. the temperature of the apparatus was raised and kept costant at 175, 200, or 250°C respectively, and 1.6 ml. (N. T. P.) of the hydrogen gas was introduced. Then the pressure of the hydrogen in the apparatus was measured from time to time by a mercury manometer attached to the apparatus through a liquid nitrogen trap.

An example of the experimental results is graphically shown in Fig. 1, where the ordinate represents the logarithm of the manometric reading of the hydrogen pressure. As will be seen from Fig. 1, a rapid stage in the decrease of hydrogen pressure, shown by dotted lines, is followed by a slow stage of pressure decrease, shown by full lines in the figure. The slow stage proceeds as a first-order reaction rather than as a Zeldowitch[2] form. From the slope of the straight line, the rate

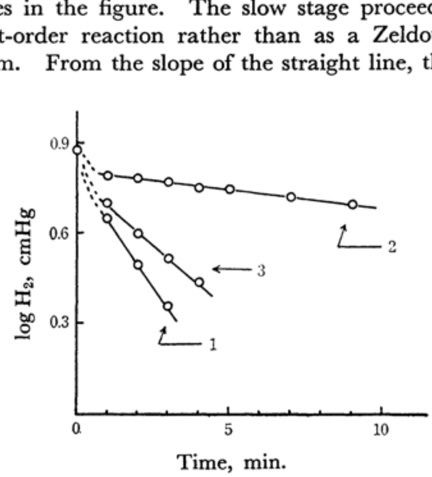

Fig. 1. The decrease of the pressure of hydrogen with time at 200°C.

1 Original
2 Irradiated in a reactor
3 Irradiated by ^{60}Co γ-rays

1) N. Kolarov and M. Kirilov, *Bulgar. Akad. Nauk. Geol.-Geograf. i Khim. Nauk. Izvest. Inst.*, **1**, 205 (1951).

2) J. Zeldowitch, *Acta Physicochim. U. S. S. R.*, **1**, 449, 554, 559 (1934).

TABLE I. ADSORPTION RATE CONSTANTS UNDER VARIOUS CONDITIONS

Samples of MnO_2	Adsorption temp., °C Rate const., min^{-1}			
	175	200	250	Activation energy, kcal./mol.
Original	0.16	0.34		12.5 ± 0.5
Irradiated in a reactor		0.033	0.12	12.8 ± 0.5
Irradiated by ^{60}Co γ-rays	0.092	0.19		12.0 ± 0.5

constant can be obtained. The adsorption rate constants thus obtained under various conditions are tabulated in Table I, where the activation energy in the last column was calculated from the rate constants obtained at two different temperatures.

From Fig. 1 and Table I we can see that the adsorption rate of hydrogen on manganese dioxide is decreased by the preirradiation of the oxide with ionizing radiations. The decrease is especially significant in the case of the pile-irradiation, where the rate constant for the adsorption decreases to about one-tenth of the original one. If this decrease in the activity of the oxide is wholly due to the increase in the activation energy, the activation energy of the irradiated oxide must be about 2 kcal./mol. higher than that of the original one. However, as will be seen from Table I, the activation energy of the original and the irradiated oxide agree with each other within the limits of experimental error ($\pm$0.5 kcal./mol.). Therefore, it must be concluded that the decrease in the adsorption rate on the pile-irradiated manganese dioxide is solely due to the decrease in the number of active sites on the surface of the oxide. A part of the active sites on the surface of the manganese dioxide may be sintered by the irradiation with ionizing radiations. This sintering effect of the ionizing radiations from a reactor, if any, must be mainly due to the neutrons, because the decrease in the adsorption rate on the oxide irradiated with ^{60}Co γ-rays is far smaller than that on the oxide irradiated in a reactor, as may be seen from Fig. 1 and Table I, in spite of the fact that the dose rate of γ-rays was almost the same in both cases.

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