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NOTES

Studies of the Surface of Titanium Dioxide

IV. The Hydrogen–Deuterium Equilibration Reaction

The interaction of hydrogen with the surface of titanium dioxide has been studied in connection with the hydrogen-reduction mechanism of titanium dioxide, by means of such measurements as weight decrease, magnetic susceptibility, hydrogen uptake, and electrical conductance (*1–4*). It was postulated in the previous study (*1*) that the rate-determining step of the hydrogen-reduction reaction may be the formation of surface hydroxyl groups, followed by the rapid removal of water molecules from the surface.

In this study, the interactions between hydrogen and the surface of titanium dioxide were investigated by measuring the hydrogen–deuterium equilibration reaction, $H_2 + D_2 = 2HD$, at temperatures above 200°C on both surfaces before and after hydrogen reduction to compare the differences in the reactivities.

EXPERIMENTAL

Materials. Titanium dioxide was prepared by the hydrolysis of titanium isopropoxide dispersed in ethyl alcohol by the addition of water, followed by calcination at 550°C for 10 hr in a stream of oxygen. X-Ray analysis showed that the crystal structure was anatase. From nitrogen gas adsorption at 77 K the surface area of the sample was found to be 56 m^2/g. The gas mixture containing 50% hydrogen (99.995%) and 50% deuterium (99.5%) obtained from Takachiho Chemical Company was used without further purification.

Procedure. One gram of the anatase sample was put in the reaction cell shown in Fig. 1. The volume of the cell was about 25 ml. Two different pretreatments of the sample were as follows:

(A) Outgassing at 500°C and 1.3×10^{-3} Pa (10^{-5} Torr) for 3 hr (outgassed surface).

(B) Addition of 51 kPa (0.5 atm) of hydrogen at 500°C for 2 hr after treatment (A) followed by the evacuation at 500°C for 30 min (hydrogen-reduced surface).

A liquid-nitrogen trap was installed just before the sample to protect it from contamination due to organic substances and to condense the water vapor produced by the hydrogen reduction of the sample. After treatment (B) the color of the sample changed from white to gray and it was determined that 6% of the surface oxygen had been removed from the sample by the weight decrease measurements using a vacuum microbalance.

Hydrogen and deuterium gas mixtures at pressures between 5.1 and 68 kPa (0.05 and 0.67 atm) were added to the sample and the equilibration reactions were performed at temperatures between 200 and 500°C in a closed circulating system. The whole volume of the reaction system was 150–155 ml and 0.5 ml of the reacting gas was pipetted out for each gas analysis.

Hydrogen, hydrogen deuteride (HD), and deuterium in the gas mixture were analyzed by gas chromatography with alumina coated with ferric hydroxide as a column material cooled at 77 K (*5*); separated hydrogen gases were converted to water by passing through cupric oxide heated at 700°C (*6*). The flow rate of helium as a carrier gas, purified by passage through molecular sieve 5A in a liquid-nitrogen trap, was 150 ml/min. The retention time was 8 min.

Each run was performed on a fresh sam-

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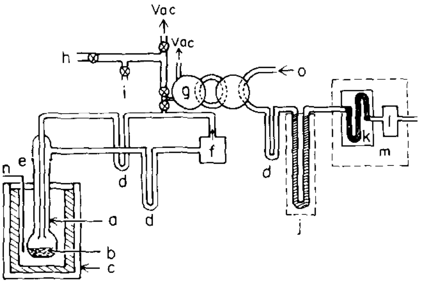

FIG. 1. Experimental apparatus for studying the hydrogen–deuterium equilibration. (a) Reaction cell, (b) sample, (c) electric furnace, (d) liquid-nitrogen trap, (e) O-rig, (f) glass fan (1000 ml/min), (g) circular gas pipet, (h) gas reservoirs, (i) Hg manometer, (j) alumina coated with ferric hydroxide, (k) cupric oxide, (l) detector, (m) electric furnace maintained at 120°C, (n) thermocouple, (o) purified He.

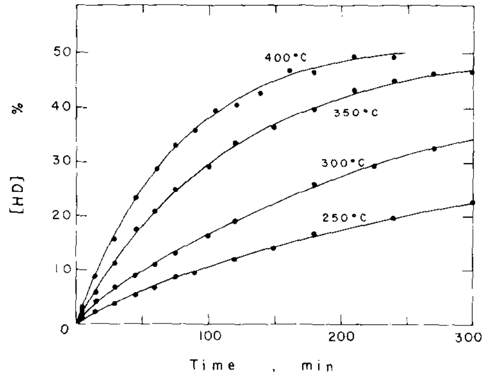

FIG. 3. HD formations on the hydrogen-reduced surface of titanium dioxide (after hydrogen reduction) at temperatures between 250 and 400°C and 51 kPa as a function of time.

ple. The isotope effects on the equilibration at the investigated temperature are negligible.

RESULTS AND DISCUSSION

Figures 2 and 3 show the formation of HD on the surfaces before and after the hydrogen reduction at temperatures between 200 and 500°C and 51 kPa, respectively. The HD concentration, $[\mathrm{HD}]_t$, expressed by the fraction of HD present at time *t*, was plotted as a function of time. Over the period of the reaction, experiments with no sample showed no appreciable equilibration reaction. The HD amounts at equilibrium, $[\mathrm{HD}]_{\mathrm{eq}}$, were in good agreement with the theoretical values obtained from Urey and Rittenberg (*7*). The rates of HD formation increase with an increase in the temperature, having the same tendency as the weight decrease and hydrogen uptake (*1*, *2*). It should be noted that the HD formation shown in Fig. 2 exhibits the sigmoidal curves which have often been observed in autocatalyzed reactions.

The equilibration curves in Fig. 3 are in

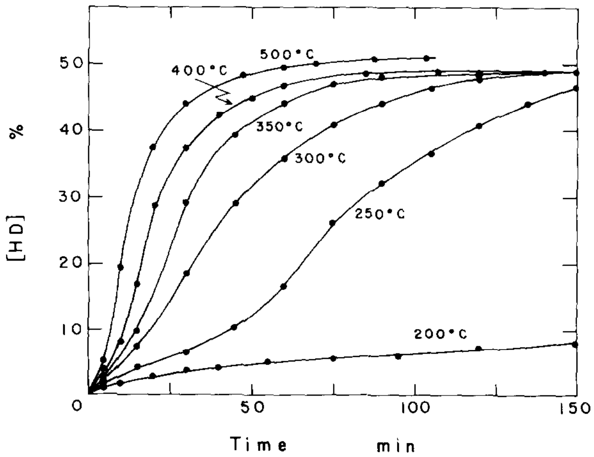

FIG. 2. HD formations on the outgassed surface of titanium dioxide (before hydrogen reduction) at temperatures between 200 and 500°C and 51 kPa (0.5 atm) as a function of time.

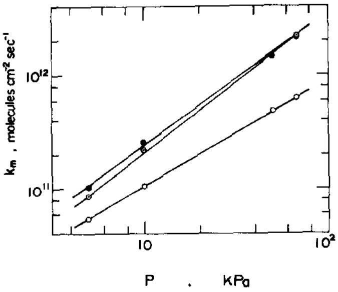

FIG. 4. Pressure dependence of k_m on the outgassed surface at 300°C. (○) $0 < \alpha < 0.22$, (●) $0.22 < \alpha < 0.63$, (⊙) $0.63 < \alpha < 1$.

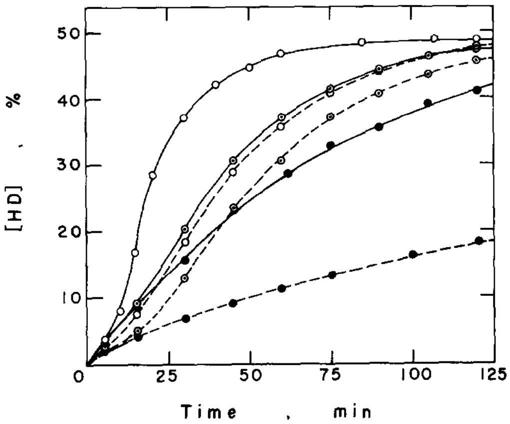

FIG. 5. HD formation curves on the surface of outgassed (○), hydrogen-reduced (●), and reoxidized (⊙) samples at 300°C (broken lines) and 400°C (solid lines) and 51 kPa.

good accord with the usual first-order reaction kinetics given by

$$\ln(1 - \alpha)^{-1} = k_e t, \qquad (1)$$

where α is the reaction degree given by $[\mathrm{HD}]_t/[\mathrm{HD}]_{\mathrm{eq}}$ and k_e is the first-order reaction rate constant. The temperature dependence of k_e gives the activation energy, 37.8 kJ/mol, of the equilibration on the hydrogen-reduced surface. This value is rather small compared with the results of Harris and Rossington (*8*); in the latter case 42–84 kJ/mol was reported for anatase sample above 150°C.

The sigmoidal curves in Fig. 2 could not be expressed uniquely by any simple reaction equations. The application of Eq. (1) gave two breaks in the plots, i.e., three periods divided according to the reaction degree (at 0.22 and 0.63 of α). Figure 4 shows the pressure dependence of the absolute reaction rate constant, k_m, on the outgassed surface at 300°C. k_m is given by the following relation:

$$k_m = k_e N/60A \text{ molecules/cm}^2 \text{ sec}, \qquad (2)$$

where N is the total number of reacting molecules and A is the surface area of the sample. As is seen in the figure, k_m is found to be proportional to P^n, where n is the reaction order and changed from 0.9 to 1.2 as the reaction progressed.

When hydrogen-reduced anatase sample was reoxidized by oxygen at 20 kPa (0.2 atm) and 500°C for 30 min after a run of equilibration, the HD formation on the surface increased again although it was still less than that on the original outgassed surface, as is shown in Fig. 5. These find-

TABLE 1

Activation Energies of Several Reactions on Titanium Dioxide

Reaction	Sample	Activation energy (kJ/mol)
Weight decrease	Anatase (below 500°C)	50–84
	Anatase (above 500°C)	88–150
	Rutile	140
Hydrogen uptake	Rutile	110
Water desorption	Rutile	110
HD equilibration	Anatase (outgassed) initial	21–25
	final	17–21
	Anatase (hydrogen-reduced)	38

ings are similar to those for the heats of immersion of the reoxidized anatase reduced by hydrogen in water (*9*). The rate of equilibration on outgassed and reoxidized surfaces increases continuously as the reaction proceeds and is larger than that on a hydrogen-reduced one. The hydrogen atoms adsorbed on the former surfaces may catalyze the equilibration reaction either by reducing the surface or, as in spillover, activating the surface.

The equilibration reaction below 200°C was very slow though weight decrease and hydrogen uptake in the previous studies were not observed appreciably below 300°C. The activation energies of the equilibration reaction in this study are compared with those of weight decrease (*1*), hydrogen uptake (*2*), and desorption of water (*10*) on titanium dioxide, rutile or anatase, as was examined in the previous study (*1*) and the results are summarized in Table 1. It should be noted that the equilibration gives a lower activation energy than the others suggesting that the dissociative adsorption of hydrogen is not the rate-determining step for the hydrogen-reduction reaction of titanium dioxide. Dissociatively adsorbed hydrogen may isomerize slowly to some form of reductive adsorption according to the classification for the nature of adsorbed hydrogen on metal oxides (*11*, *12*).

REFERENCES

1. Iwaki, T., Komuro, M., Hirosawa, K., and Miura, M., *J. Catal.* **39,** 324 (1975).
2. Iwaki, T., and Miura, M., *Bull. Chem. Soc. Jpn.* **49,** 2321 (1976).
3. Reymond, J. P., Vergnon, P., Gravelle, P. C., and Teichner, S. J., *Nouv. J. Chim.* **1,** 197 (1977).
4. Reymond, J. P., and Gravelle, P. C., *J. Chim. Phys.* **76,** 879 (1979).
5. Moore, W. R., and Ward, H. R., *J. Phys. Chem.* **64,** 832 (1960).
6. Fujita, K., and Kwan, T., *Jpn. Anal.* **12,** 15 (1963).
7. Urey, H. C., and Rittenberg, D., *J. Chem. Phys.* **2,** 48 (1934).
8. Harris, J. R., and Rossington, D. R., *J. Catal.* **14,** 168 (1969).
9. Iwaki, T., and Miura, M., *Bull. Chem. Soc. Jpn.* **44,** 1754 (1971).
10. Munuera, G., and Stone, F. S., *Discuss. Faraday Soc.* **52,** 205 (1971).
11. Burwell, R. L., Jr., Haller, G. L., Taylor, K. C., and Read, J. F., *in* "Advances in Catalysis and Related Subjects," Vol. 20, p. 1. Academic Press, New York/London, 1969.
12. Burwell, R. L., Jr., and Stec, K. S., *J. Colloid Interface Sci.* **58,** 54 (1977).

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