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Studies of the Surface of Titanium Dioxide. III. The Electrical Conduction and the Hydrogen Uptake

Toru Iwaki and Masaji Miura

Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

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Synopsis. The changes in the electrical conductance and the hydrogen uptake of titanium dioxide were examined with the introduction of hydrogen at 250—500 °C. The former was found to approach the equilibrium rapidly, compared with the latter above 350 °C.

In a previous paper,[1] it has been suggested that hydrogen atoms adsorbed on the surface of titanium dioxide, during the hydrogen reduction, form hydroxyl groups before the weight of titanium dioxide begins to decrease. Adsorbed hydrogen atoms are well known to influence the electrical conductivity remarkably.[2] In the present study, simultaneous measurements of the electrical conductance and the hydrogen uptake were performed in order to clarify the initial stage of the hydrogen reduction by comparison with the previous results.[1]

Experimental

Materials. The rutile sample was prepared by the hydrolysis of titanium tetrachloride in an aqueous medium, followed by the calcination at 600 °C for 6 h in a stream of oxygen. The surface area obtained from the nitrogen adsorption at 77 K was 11.7 $m^2 g^{-1}$. The average grain size was about 1μ.[3] Hydrogen was purified by passing it through platinum asbestos and a liquid nitrogen trap.

Procedure. The sample was placed in contact with oxygen gas at 600 °C for 30 min and then outgassed at 500 °C and 10^{-5} Torr for 3 h. Hydrogen gas was introduced at temperatures between 250 and 500 °C. A liquid nitrogen trap was installed just before the sample in order to protect it from contamination due to organic substances[4] and to condense the water vapor produced by the hydrogen reduction of the sample. The dc-electrical conductance was measured on the following two kinds of samples. One was an unpressed sample, in which four platinum electrodes were buried, while the other was pressed at 8 t cm^{-2} into a pellet, both sides of which were covered with evaporated platinum films. The hydrogen uptake and electrical conductance were measured simultaneously for the unpressed sample, the former being determined volumetrically. No appreciable hydrogen uptake of the pressed sample could be detected because of an insufficient amount of the sample and probably also because of the slow reaction rate. All experiments were carried out in a static gas system.

Results and Discussion

The electrical conductance of the unpressed sample prior to the introduction of hydrogen ranged from 10^{-9} to 10^{-8} A V^{-1} between 250 and 500 °C. The obtained activation energy is 0.35 eV, indicating that the conduction electrons are provided from the impurity levels, which are composed of oxygen vacancies produced on the surface of titanium dioxide during the activation at 500 °C.[5] Figure 1 shows the change in the electrical conductance of the unpressed sample after the introduction of hydrogen. The electrical conductance increased greatly with a rise in the temperature. The electron mobility in a rutile single crystal in the presence of hydrogen was found to be small, 0.15 $cm^2 V^{-1} s^{-1}$ at 360 °C.[6] The rate of increase in the electrical conductance at the initial stage above 350 °C obeyed the Elovich equation, which had been found to be applicable to the rate of the reduction reaction.[1] Below 350 °C it obeyed t^n partly, where t is the time and n= 0.5—0.7.

Figure 2 shows the change in the electrical con-

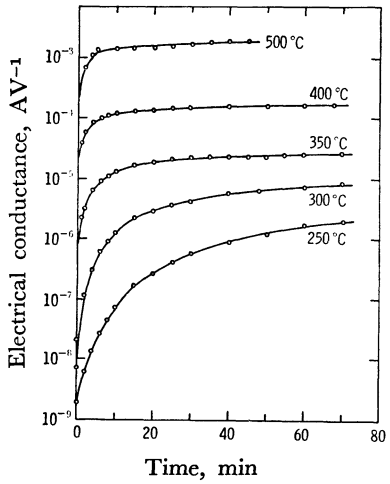

Fig. 1. Electrical conductance of the unpressed sample as a function of time after the introduction of hydrogen at 0.5 atm and several temperatures.

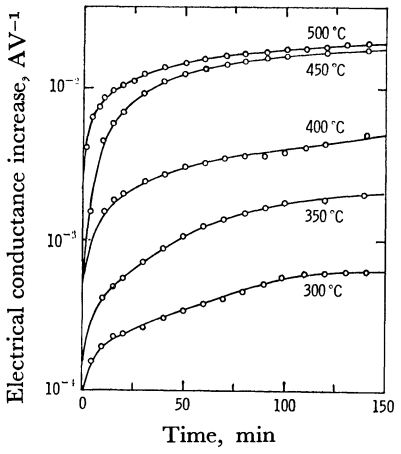

Fig. 2. Electrical conductance of the pressed sample as a function of time after the introduction of hydrogen at 0.5 atm and several temperatures.

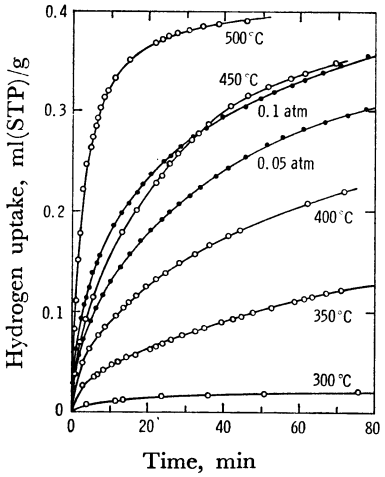

Fig. 3. Hydrogen uptake as a function of time after the introduction of hydrogen at several temperatures. The open circles indicate that the hydrogen pressure is 0.5 atm and the closed circles other hydrogen pressures at 500 °C.

ductance of the pressed sample, where the electrical conductance before the introduction of hydrogen ranged from 10^{-4} to 10^{-3} A V^{-1}. The kinetics was found to obey t^n above 350 °C, where n=0.3—0.6. The remarkable difference between the results in Figs. 1 and 2 may be attributable to the contacts between particles and between electrode and particles and to the mobility of the gas molecules migrating through the opening of the titanium dioxide particles.

Figure 3 shows the hydrogen uptake as a function of the time. The hydrogen uptake increased with an increase in the temperature, analogously to the electrical conductance. The rate of hydrogen uptake was found to obey the parabolic rate law. The activation energy obtained was 26 kcal mol^{-1}, indicating the chemisorption of hydrogen, followed by diffusion through the surface region into the bulk. The time required for the attainment of the equilibrium of the hydrogen uptake was short, compared with that of the weight decrease reported in the previous study.[1] The amount of the hydrogen uptake at 500 °C corresponds to a one percent surface coverage if one hydrogen atom is held to one surface oxygen atom. The differences between these findings and the previous ones may result from differences in the experimental conditions, between the static gas system and the circulating one. Nevertheless, at the initial stage, the rates of changes in both the electrical conductance and the hydrogen uptake were quite large, compared with that in the weight decrease. In the previous study, the rate-determining step in the initial stage of the hydrogen reduction was presumed to be the formation of the hydroxyl groups on the surface. The present results support the previous finding concerning the presence of adsorbed hydrogen atoms before the reduction reaction begins.

A comparison of Fig. 1 with Fig. 3 makes it clear that the electrical conductance approaches the equilibrium more rapidly than the hydrogen uptake, especially above 350 °C. The appreciable changes in both the electrical conductance and the hydrogen uptake below 350 °C are also to be noted, because the weight decrease could not be observed below 350 °C.[1] This implies that adsorbed hydrogen atoms which can not take part in the reduction reaction exist on the surface. This hydrogen may adsorb reversibly because the electrical conductance is restored to the original one by outgassing the sample after a run. Above 400 °C, the oxygen vacancies formed by the hydrogen reduction as well as the adsorbed hydrogen atoms contribute remarkably to the electrical conduction.[5]

References

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