

Reproducible Hydrogen Production from Water by Indium Oxide

The two-step hydrogen production from water by a reduction (step 1) and oxidation (step 2) cycle of metal oxides has been proposed (1, 2). The metal oxides reduced by various reductants are reoxidized by water, producing hydrogen. The principal advantages of this process are the following: (a) Since reduction and oxidation of metal oxides are carried out separately, pure hydrogen can be obtained. (b) Various cheap reductants, such as coal, chars from biomass (2), or diluted hydrogen or carbon monoxide in waste gas from chemical plants, may be used in step 1. Among the oxides tested previously, In_2O_3 was one of the most active oxides for the two-step water decomposition (1). In order to apply the oxide for the two-step cycle, smooth and repeating reduction and oxidation of the oxide are required. In this report we intended to demonstrate the easy and reproducible reduction and oxidation of indium oxide by hydrogen and water, respectively.

The In_2O_3 used was a reagent-grade powder (purity >99.9%) obtained from Wako Pure Chemical Company. The experiments were carried out using a conventional mercury-free gas-circulation apparatus with a 320-ml dead volume, capable of achieving a vacuum to 1.3×10^{-4} Pa.

Figure 1 shows the kinetic curves of the consumption and the formation of hydrogen in the system for the repeated cycles of reduction-oxidation of indium oxide at 673 K. Before each cycle, the same In_2O_3 powder (0.50 g) in a U-shaped quartz reactor was degassed under vacuum at 773 K. The initial pressure of hydrogen added in step 1 was 66.7×10^2 Pa. The water formed through the reduction of In_2O_3 was always condensed at 77 K in a U-shaped trap placed in the gas-circulation line. The re-

duction was discontinued at 120 min by outgassing hydrogen from the system. The degrees of reduction of the In_2O_3 for each cycle were $10.4 \pm 0.7\%$ which were calculated on the basis of the oxygen atoms removed from the oxide. In step 2, the reduced indium oxide was brought into contact with water vapor maintained at 21×10^2 Pa. The production of hydrogen was completed within 15 min for every cycle. The amounts of hydrogen consumed in step 1 were reproduced in step 2, except the first cycle. BET surface area of the sample measured after the reduction or the oxidation under the same experimental conditions as those applied in Fig. 1 has been shown in Table 1. The areas were measured by nitrogen adsorption at 77 K. The value decreased to one-fourth of that of fresh In_2O_3 during the first oxidation-reduction cycle. However, after the first cycle, the surface area remained unchanged within experimental error ($\pm 0.1 \text{ m}^2 \text{ g}^{-1}$). The decrease in the surface area during the first cycle does not reduce but slightly increases the initial rate of the reduction for the second cycle, which cannot be explained at the moment. As can be seen in Fig. 1, the reproducible

TABLE 1
Surface Area of the Sample after Its
Reduction and Oxidation

	Surface area ($\text{m}^2 \text{ g}^{-1}$)
Fresh In_2O_3	13.9
After first reduction	9.8
After first oxidation	5.3
After second reduction	3.5
After second oxidation	3.6
After third reduction	3.5
After third oxidation	3.4

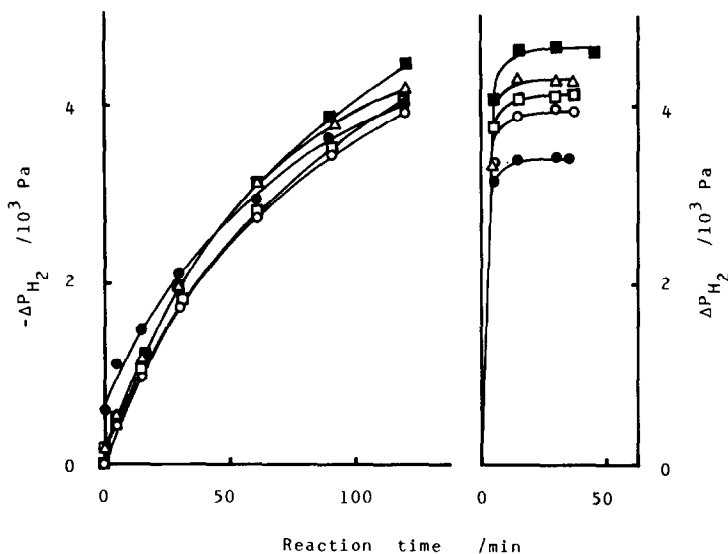


FIG. 1. The kinetic curves of the decrease and increase of hydrogen pressure for each reduction-oxidation cycle. The order of the two-step cycle: ●, first; △, second; □, third; ○, fourth; ■, fifth.

reduction and oxidation were observed after the first cycle. Figure 2 shows the progress of continuous oxidation-reduction of indium oxide at 673 K, where the oxide has previously been reduced by hydrogen to the reduction degree of 29.2%. The formation of hydrogen was initiated over the reduced oxide by the addition of water vapor

of 21×10^2 Pa. The condensation of the water vapor at 77 K (Fig. 2, point A) caused the reaction to go backward, i.e., the reduction of the indium oxide. Evaporation of the condensed water at point B initiated again the decomposition of water. The following reduction and oxidation were recommenced at C and D, respectively. The results in Figs. 1 and 2 show that the reduction and oxidation of indium oxide occur smoothly and reproducibly at 673 K. Thus, we believe that In_2O_3 is a potential oxide for the two-step water decomposition.

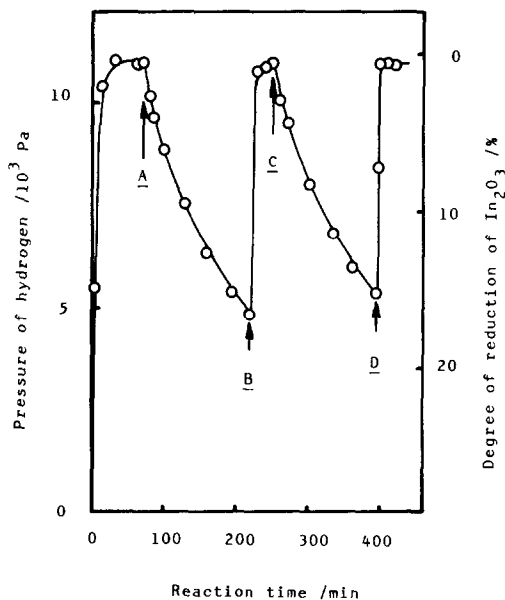


FIG. 2. Reproducible oxidation and reduction of indium oxide.

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