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The Decomposition of Water on the CO- or H_2-reduced Indium Oxide

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The reduction of In_2O_3 by H_2 or CO and the reoxidation of the reduced oxide by water, accompanying the formation of hydrogen, have been investigated at $\geq$673 K. The reduction of In_2O_3 and the decomposition of water have been expressed by the forward reaction and the backward reaction respectively of this equation: $In_2O_3(s)+xH_2(g)\rightleftarrows In_2O_{3-x}(s)+xH_2(g)$, where $In_2O_{3-x}(s)$ is a mixture of indium metal and In_2O_3. Surface oxygen atoms of fresh In_2O_3 are easily removed by H_2- or CO-reduction at 673 K, but they can not be reformed by oxidation with water. This explains the observation that the quantity of hydrogen produced in the oxidation step was somewhat deficient compared to that consumed by the reduction. The maximum rate of the decomposition of water is observed when the oxide has been reduced up to a 50% reduction-level. However, an excessive reduction (greater than 85%) results in a sharp decrease in the rate of the decomposition of water, probably because of the isolation of metallic indium from the host In_2O_3.

Recently we have proposed a simple two-step water-decomposition process which uses a reduction-oxidation cycle of In_2O_3.[1] In Step 1, the oxide is reduced by various reductants at a high temperature. In Step 2, the reduced oxide is reoxidized by water at a low temperature, producing hydrogen. Since Steps 1 and 2 are carried out separately, pure hydrogen can be obtained in Step 2. Various reducing agents, such as diluted hydrogen, carbon monoxide or light hydrocarbons in waste gas from chemical plants, may be used as reductants in Step 1.

It has also been reported[2] that the reduction of In_2O_3 by hydrogen and the subsequent decomposition of water over the reduced oxide proceed smoothly at 673 K. However. more fundamental studies of the reduction-oxidation cycles are needed in order to develop the two-step hydrogen-production process. This report will present the results of kinetic studies of the reduction of In_2O_3 by hydrogen and carbon monoxide and of the oxidation of the reduced oxide by water. The conditions required for the hydrogen-production and the nature of the reduced In_2O_3 are also discussed.

Experimental

Materials. The In_2O_3 used was a reagent-grade powder (purity>99.9%) obtained from the Wako Pure Chemical Co. The surface area of the fresh In_2O_3, as measured by means of the nitrogen adsorption (BET method), was 13.9 $m^2 g^{-1}$. The hydrogen and carbon monoxide used as reducing gases were purified by passing them through a silica-gel adsorbent cooled at 77 or 195 K. The water was purified three times by trap-to-trap distillation in a vacuum apparatus. The dissolved gases in the water were removed by repeated freeze-degassing-thaw procedures.

Procedure. The apparatus employed was a conventional mercury-free static gas-circulation system with a volume of $\approx$320 ml. Before each run of the experiment, the sample oxide (0.10—0.50 g) in a U-shaped quartz reactor was degassed at 773 K for 2 h. The reduction of the sample was initiated by adding H_2 and CO to the system at 473—773 K. During the reduction, the H_2O and CO_2 produced were removed from the gaseous phase by condensing them into a trap which had been placed in the gas-circulation line and cooled by means of liquid nitrogen. Kinetic curves of the reduction were obtained by measuring the pressure drop of the reducing gas or the change in the gas-chromatographic peak. After In_2O_3 had been reduced to a certain extent, the gases in the reaction system were pumped out; the reoxidation of the reduced oxide was then started by adding and circulating a mixture of water vapor (2.1×10^3 Pa) and nitrogen (1.33×10^4 Pa, added to ensure the gas-circulation). The quantity of hydrogen produced was measured by means o gas chromatography.

Results

Reduction of In_2O_3. The reductions of In_2O_3 by H_2 and CO occur at temperatures greater than 573 and 473 K respectively under 6.7×10^3 Pa of the reducing gases. Figure 1-a indicates the temperature effect on the kinetics of the consumption of hydrogen during the reduction of In_2O_3. Although the initial pressure of hydrogen was kept constant ($6.74\pm0.08\times10^3$ Pa), the final pressure of hydrogen depended on the reaction temperature (3.02×10^3 Pa at 623 K to 0.76×10^3 Pa at 773 K). The marked decrease in the hydrogen pressure

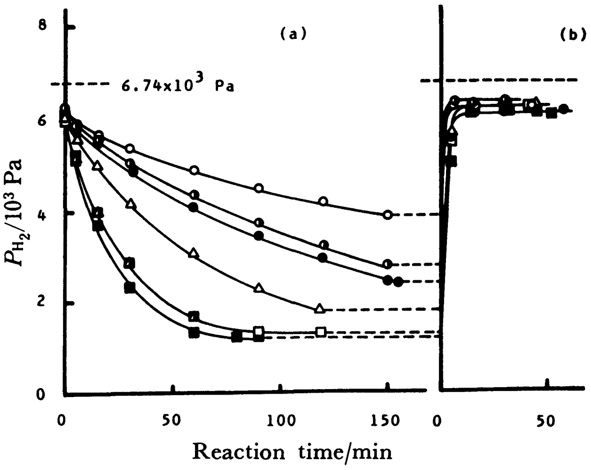


Fig. 1. (a) Kinetic curves of hydrogen-consumption during the reduction of In_2O_3 at 623—773 K. Temperature of reduction: ○: 623 K, ◑: 648 K, ●: 673 K, △: 698 K, □: 723 K, ▲: 748 K, ■: 773 K. The weight of In_2O_3 was 0.50 g. (b) Subsequent reoxidation of the reduced oxide with water accompanying hydrogen-production at 673 K. The symbols in (b) correspond to the samples of the same symbols in (a).

explained the rapid decrease in the reduction rate, especially for the high-temperature runs. For every kinetic curve, a very rapid consumption of hydrogen (≈200 μmol g^{-1}) was observed at the very first contact with the oxide. After the hydrogen and water had been outgassed from the system, the addition of fresh water vapor to the reduced oxide at 673 K caused a rapid formation of hydrogen, as is shown in Fig. 1-b. The decomposition of water finished within 15 min. The amount of hydrogen produced for every kinetic curve was 200±50 μmol g^{-1} less than that of the hydrogen consumed in the preceding reduction. The apparent activation energy of the reduction, as obtained from the initial rates at a 5% degree of reduction, was 72.4 kJ mol^{-1}. The degree of reduction was determined on the basis of the percentage of oxygen atoms removed from the original In_2O_3. Figure 2 shows the effect of pressure of hydrogen on the rate of reduction at 673 K as observed at different degrees of reduction. The rate increases linearly with the pressure of hydrogen, irrespective of the degree of reduction.

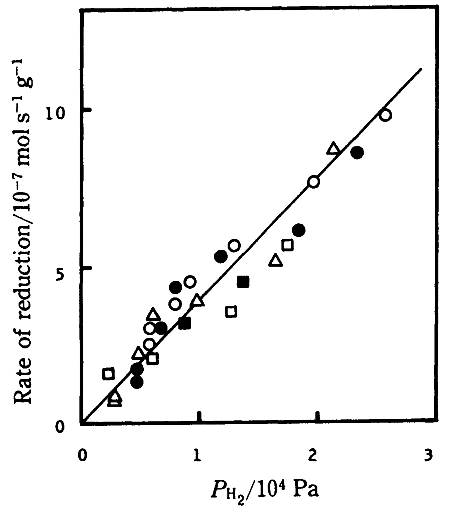
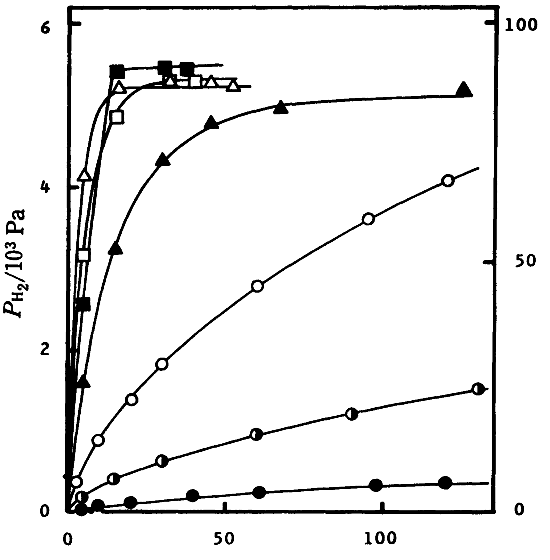


Fig. 2. The effect of pressure of hydrogen on the rate of reduction of In_2O_3 at 673 K.
Degree of reduction of In_2O_3: ○: 2%, ●: 5%, △: 10%, □: 20%, ■: 30%.

The initial rate of reduction of In_2O_3 by carbon monixide is one order of magnitude greater than that by hydrogen at the temperatures of 473—773 K under a pressure of 6.7×10^3 Pa. This fact shows that carbon monoxide is a stronger reducing agent for In_2O_3 than is hydrogen. The deficiency of ≈200 μmol g^{-1} in the amount of produced hydrogen compared to that of the consumed carbon monoxide in the preceding reduction was also observed in this case. The apparent activation energy of the reduction by carbon monoxide at a 2% degree of reduction was obtained as 59.4 kJ mol^{-1}.

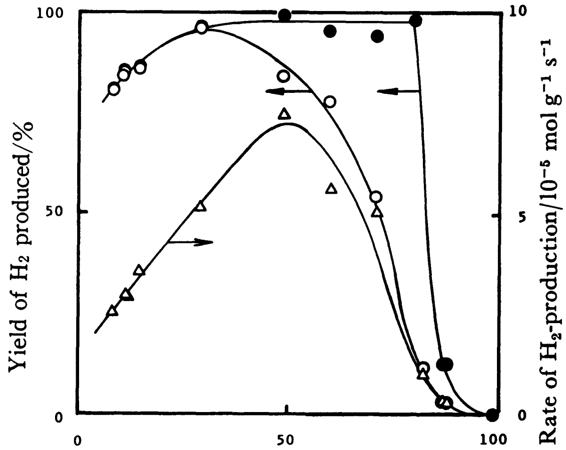
Decomposition of Water. The decomposition of water on the H_2- or CO-reduced indium oxide occurs at temperatures higher than ≃423 K. Figure 3 shows the kinetic curves of the formation of hydrogen at different temperatures for the sample with a 14% degree of reduction. The reaction at >673 K was to rapid to be measured accurately. The vertical axis of the right-hand side indicates the yield of hydrogen production on the basis of the quantity of oxygen atoms transferred from water to the reduced oxide compared to that removed from In_2O_3 during the preceding reduction. The decomposition of water was completed within 15 min when the temperature was higher than 673 K. The yield of hydrogen production never reached 100%, not even at 873 K. The Arrhenius plot of the initial rate of hydrogen production, as evaluated from the slopes of the kinetic curves (423—573 K) in Fig. 3, gave the apparent activation energy of 50.1 kJ mol^{-1}.



Reaction time/min

Fig. 3. Kinetic curves of the formation of hydrogen at different temperatures.
□: 873 K, ■: 773 K, △: 673 K, ▲: 573 K, ○: 523 K, ◑: 473 K, ●: 423 K. The weight of In_2O_3 used was 0.50 g.

All the results described above have been obtained for the oxide with a degree of reduction of less than 30%.



Degree of reduction of In₂O₃/%

Fig. 4. The yield and rate of H_2-production as functions of the degree of reduction of In_2O_3.
○: Yield at 20 min, ●: yield at 100 min, △: initial rate of H_2-production.

Figure 4 shows the yield of water decomposition as a function of the degree of reduction. The pre-reduction of In_2O_3 had been carried out by the use of hydrogen at 673 K, and the subsequent oxidation by water was conducted at the same temperature. The triangles in Fig. 4 indicate the initial rate of water-decomposition: The quantity of hydrogen produced in 5 min divided by the time. The open and closed circles are the yields of the production of hydrogen at 20 and 100 min respectively. The results in the figure show that the maximum in the rate of hydrogen-production lies at a $\approx$50% degree of reduction. Although the rate of reaction decreases as the degree of reduction increases above the 50% level, the reaction is complete within 100 min when the reduction-level is lower than 85% (closed circles).

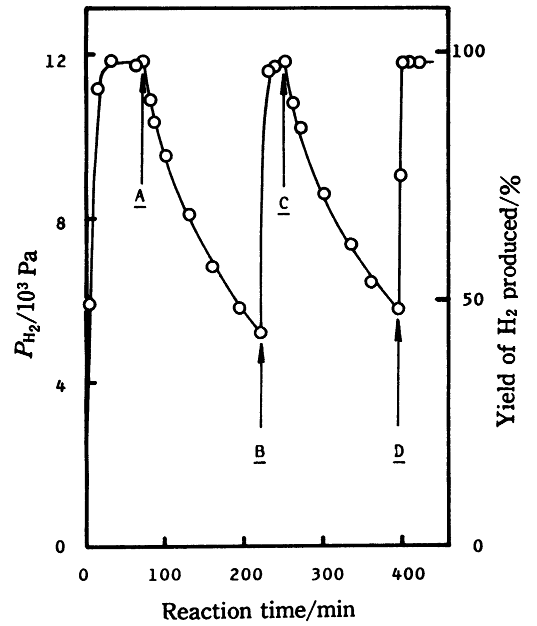


Fig. 5. Reproducible oxidation and reduction of indium oxide at 673 K.
The weight of In_2O_3 used was 0.50 g.

Figure 5 shows the progress of the oxidation-reduction cycles at 673 K: the sample oxide had been reduced by hydrogen to the degree of 29.2% before the experiments. The condensation of water vapor in the circulating gas at 77 K (Point A) caused the backward reaction; *i.e.*, the reduction of the oxide was initiated. The evaporation of the condensed water at Point B caused the decomposition of water to be resumed. The subsequent reduction and oxidation were recommenced at C and D respectively. The results shown in Fig. 5 show that smooth and repeating reduction-oxidation cycles can be operated at 673 K.

The ratio of the pressure of the water vapor to that of hydrogen under apparent equilibrium conditions has been measured using two initial systems: a partially reduced In_2O_3–water system and an In_2O_3–hydrogen system. The ratio obtained after 200 min standing at 673 K was in the range of 0.011±0.003.

Discussion

The Reduced State of the Oxide. The lower valent oxides of indium than In_2O_3 suggested their existence are InO and In_2O. InO is very unstable and has been detected spectroscopically under indium-arc burning in air.[3] There is no clear evidence for the existence of InO under mild conditions. The formation of In_2O by the reduction of In_2O_3 with hydrogen was reported by Klemm and Vogel.[4] The existence of crystalline In_2O was suggested by several workers.[5,6] However, Brewer[7] concluded in his review that the supposedly crystalline In_2O is a stoichiometric mixture of indium and In_2O_3 or is a metastable homogeneous phase. Broch and Christensen[8] attempted to prepare crystalline In_2O; they came to the conclusion, after a detailed X-ray analysis of the products, that no proof for the existence of crystalline In_2O could be given. Wit *et al.*[9] commented, with regard to the existence of crystalline In_2O, that an indium suboxide like In_2O exists only as a parasitic phase, in combination with the contacting indium metal and In_2O_3, and is highly nonstoichiometric. Thus, there is still controversy with regard to the existence of crystalline In_2O. Our X-ray spectroscopic studies of the partially reduced In_2O_3 could establish only the existence of In_2O_3 and indium metal.

Therefore, let us tentatively write the following equation for the reduction of In_2O_3:

$$In_2O_3(s) + xH_2(g) \longrightarrow In_2O_{3-x}(s) + xH_2O(g), \qquad (1)$$

where $In_2O_{3-x}(s)$ might be a crystalline In_2O or mixture of indium metal and In_2O_3. The ratio (0.011±0.003) of the equilibrium pressure of water vapor to that of hydrogen over the oxide at 673 K observed in this work is very close to the value (0.0091) from the table[10] for the following equilibrium:

$$In_2O_3(s) + 3\,H_2(g) \rightleftharpoons 2\,In(l) + 3\,H_2O(g). \qquad (2)$$

This fact supports the idea that the $In_2O_{3-x}(s)$ in Eq. 1 is a mixture of indium metal and In_2O_3 under the experimental conditions applied in this work. When the sample was reduced excessively ($>\approx$85%-degree of reduction), the formation of indium metal particles was observed at the bottom of the reactor.

The Presence of Highly Reducible Surface Oxygen Atoms. In the case of the reduction of fresh In_2O_3, a very rapid initial consumption of hydrogen was always observed, irrespective of the pressures and temperatures for the reduction. The quantity of the initial hydrogen-consumption and the BET surface area of the sample have been measured after each reduction-oxidation cycle. The results showed that the quantity of the initial rapid consumption of hydrogen decreased from 200±20 (fresh sample) to 20 (second reduction) and 16 μmol g^{-1} (third reduction). The surface areas of the sample before each reduction were 13.9 (fresh sample), 5.3 (after the first oxidation), and 3.6 $m^2\,g^{-1}$ (after the second oxidation). The decrease in the quantity of the initial rapid consumption of hydrogen is too large to be explained by the decrease in the surface area of the sample. Let us assume that there are highly reactive surface oxygen atoms on fresh In_2O_3 and that, by the use of hydrogen, they are rapidly removed as water from the surface at the very first stage of the reduction; the oxygen atoms, however, can not be recovered after the oxidation with water. This assumption explains the remarkable decrease in the quantity of the initial rapid consumption of hydrogen observed in the second and third reduction experiments compared to that for the fresh sample. The quantity of hydrogen produced on the first water-decomposition was deficient by the quantity of 200 ± 50 μmol g^{-1} compared to that consumed in the first reduction of fresh In_2O_3 (Figs. 1 and 3). The deficiency corresponds approximately to the quantity of hydrogen which had been consumed by fresh In_2O_3 at the very first stage of the reduction. Thus, the deficiency in the yield of hydrogen for the first cycle can be ascribed to the surface oxygen atoms, which are not regenerated by oxidation with water. Further studies are, however, needed to clarify the state and the nature of the active surface oxygen atoms (or might be molecules) described above.

Information from Kinetic Studies. In general, the rate of the reduction of crystalline metallic oxides to their lower oxidized states or metals is a function of three quantities: the rate of nucleation, the rate of the propagation of the interface between the reduced states and the oxide, and the size and shape of the particles. The energetics (*i.e.*, the activation energy) of the reduction process are primarily dependent upon the second of these quantities. However, the results in this work can shed little light on these factors. The rate of the reduction of In_2O_3 did not decrease, but increased for the second reduction compared to the first reduction, despite the fact that the surface area of the sample had decreased from 13.9 to 5.3 $m^2 g^{-1}$. The fact that the reduction rate increases in proportion to the pressure of hydrogen, irrespective of the degree of reduction (Fig. 2), indicates that the change in the surface area of the sample does not influence the rate of reduction. These observations can not yet be explained satisfactorily.

The kinetic curves of the oxidation of reduced-In_2O_3 by water did not obey a simple rate law, such as logarithmic, linear, parabolic, or cubic. Therefore, no simple oxidation mechanism can be applied for the oxidation of the reduced-In_2O_3.

Conditions Required for the Hydrogen Production. The findings on the temperature effect on the rates of reduction of In_2O_3 (Fig. 1) and of hydrogen-production (Fig. 3) show that both the reactions proceed rapidly at ≥ 673 K. This has been confirmed by the smooth and repeated cycles of the reactions at 673 K (Fig. 5). The results of Fig. 4 show that the reduction level around 50% is suitable for the hydrogen-production as far as the rate of reaction is concerned. The lower yield of hydrogen-production at a reduction level lower than 30% can be ascribed to the non-recovery of the surface oxygen atoms, as has been described earlier. The ratio of the quantity of surface oxygen atoms to that of the total hydrogen consumed for the reduction of In_2O_3 becomes smaller as the reduction level increases, which explains the $\simeq 100\%$ yield of hydrogen at higher reduction levels. When the oxide experienced too much reduction ($> \approx 85\%$ degree of reduction), the rate of reoxidation of the reduced oxide decreased sharply (Fig. 4). The formation of indium metal particles shows a clear separation of the metal phase from In_2O_3 at $>85\%$-degree of reduction. The drop in the rate of recovery of In_2O_3 above an 85%-degree of reduction might be ascribed to the change in the physical or chemical nature of the reduced phase due to the isolation of the metal phase from the oxide.

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