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EFFECTIVE SUPPORTED-In_2O_3 FOR THE PRODUCTION OF HYDROGEN FROM WATER BY THE REDUCTION-OXIDATION CYCLE OF In_2O_3

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Eleven kinds of carriers for In_2O_3 have been tested for the production of hydrogen from water by a reduction and oxidation cycle of In_2O_3. Of these, the most effective carriers were TiO_2, ZrO_2, active carbon and ZnO, because the high enhancing effects on the rates of reduction and oxidation and the high final yields of hydrogen by the reduced In_2O_3 have been observed by using these carriers.

The production of hydrogen by the Steam-Iron Process is considered as one of the prospective methods of making hydrogen in the future.1) The hydrogen by the process is produced by the reduction-oxidation cycle of iron oxide.1-4) Steam reacts with the reduced oxide and gives hydrogen. The operation of the Steam-Iron Process, however, requires higher temperatures than ∿1100 K, and the conversion of steam is limited to ∿40%.5) In contrast with the iron oxide, it has been demonstrated that the production of hydrogen by the same principle using indium oxide proceeds at lower temperatures and the conversion of steam reaches ∿100%.6,7) The reduction-oxidation cycle of the indium oxide can be written as follow;8)

Step 1; the reduction of In_2O_3 by various reductants to indium metal,

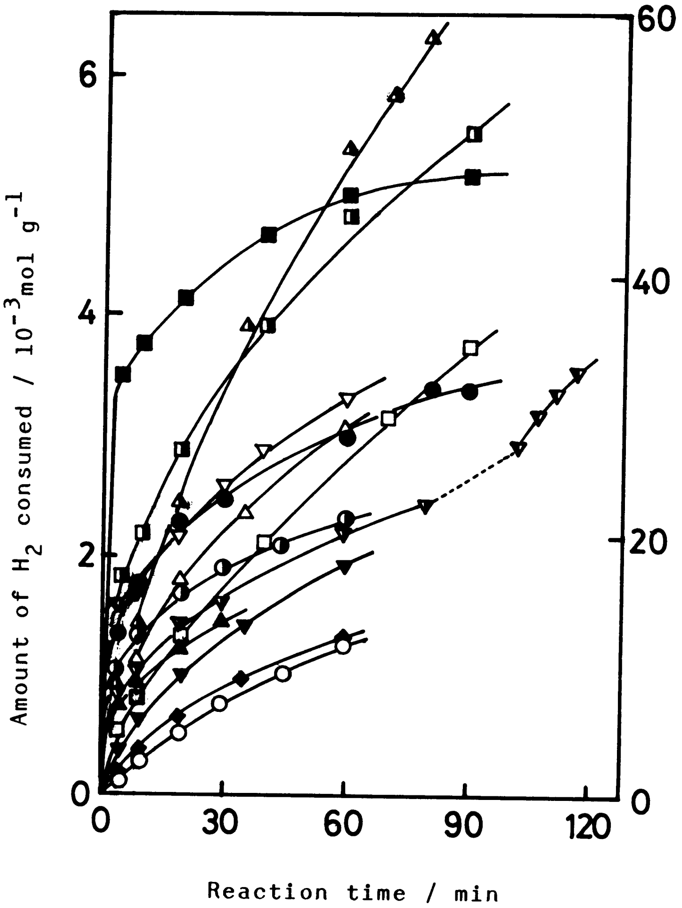
$$In_2O_3(s) + \text{reductant} \longrightarrow 2\,In(liq) + \text{oxidized product} \qquad (1)$$

Step 2; the subsequent oxidation of the indium metal by water regenerating the original oxide and producing hydrogen,

$$2\,In(liq) + 3\,H_2O \longrightarrow In_2O_3(s) + 3\,H_2 \qquad (2)$$

The reactions of eqs. (1) and (2) proceed smoothly at >673 K when CO or H_2 is applied as a reductant on Step 1. It is desirable if the cycle can be operated at lower temperatures. The purpose of this work is to look for an effective carrier for In_2O_3 enhancing the rates of reactions (1) and (2). Hydrogen is used as the reductant in Step 1 because the only product in gas-phase is water and easy to control the degree of reduction of the oxide.

The various carriers used were impregnated with aqueous solution of $In(NO_3)_3$. The In_2O_3 supported on the carriers were prepared by the decomposition of $In(NO_3)_3$ in a vacuum at 773 K. The In_2O_3 without carrier was prepared by the decomposition of $In(NO_3)_3$ in a flow of nitrogen at 773 K. The apparatus used was a conventional mercury-free gas-circulation system of ≃285 ml volume. Before each experiment of Step 1, the sample oxide was calcined in an atmosphere of oxygen (1.3×10^4 Pa) at 773 K and degassed for 2 h at the same temperature.



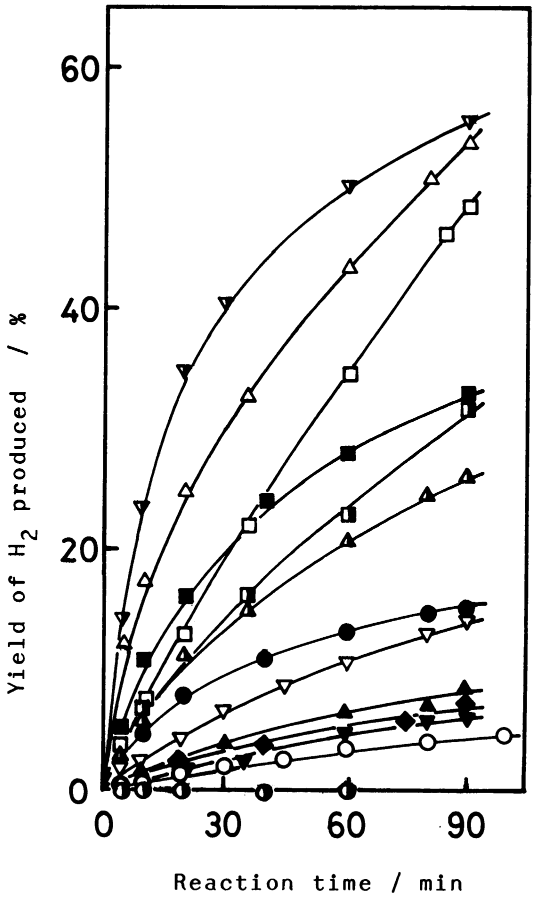


Fig. 1. Kinetic curves of the reduction of In_2O_3 on various carriers at 573 K. In_2O_3 were supported on the following carriers: ◭ ; ZnO, ◧; MgO, ■; Al_2O_3, □; TiO_2, △ ; ZrO_2, ▽; La_2O_3, ●; SiO_2, ◑; WO_3, ▲; $SiO_2 \cdot Al_2O_3$, ⧨; active carbon (at 523 K), ⧨; active carbon (at 573 K), ▼; graphite, ◆; Pt-black mixed, ○ ; In_2O_3 without carrier

Fig. 2. Yield of hydrogen produced on step 2 at 473 K as a function of time. In_2O_3 were supported on the following carriers: ⧨; active carbon, △ ; ZrO_2, □; TiO_2, ■; Al_2O_3, ◧; MgO, ◭; ZnO, ● ; SiO_2, ▽; La_2O_3, ▲; $SiO_2 \cdot Al_2O_3$, ◆ ; Pt-black mixed, ▼; graphite, ◑; WO_3, ○; In_2O_3 without carrier

Figure 1 shows the kinetic curves of the reduction of In_2O_3 (Step 1) supported on various carriers at 573 K under the hydrogen pressure of 1.3 $\sim$1.2 X 10^4 Pa. The formed water was always condensed at 77 K. Most of the carriers tested in this work enhanced the rate of reduction of In_2O_3 compared to the In_2O_3 without carrier (open circles). Pt-black is well known as an effective catalyst for activating hydrogen. However, mixing of Pt-black with In_2O_3 powder did not show any promoting effect on the rate of reduction. For some carriers in Fig. 1 there are very fast consumption of hydrogen at the initial stage of the reaction. The

Table 1. BET surface areas of the carriers (S), weight percents of In_2O_3 supported on the carriers (Wt), degrees of reduction of In_2O_3 in Step 2 (Rd), and the final yields of hydrogen in Step 2

In_2O_3/carrier	S $/m^2g^{-1}$	Wt /%	Rd /%	Final H_2-yield /%
In_2O_3 without carrier	9	-	57.6	103
In_2O_3/ZrO_2	29	11.1	57.3	98
In_2O_3/TiO_2	11	11.1	58.2	100
In_2O_3/ZnO	6	11.1	58.2	93
In_2O_3/MgO	251	11.1	58.1	86
In_2O_3/Al_2O_3	237	11.1	57.4	42
In_2O_3/La_2O_3	-	11.1	58.8	41
In_2O_3/WO_3	7	11.1	55.0	13
In_2O_3/graphite	-	11.1	60.3	74
Pt-black mixed	-	6.1[a)]	52.8	82
$In_2O_3/SiO_2 \cdot Al_2O_3$	511	13.0	32.2	27
In_2O_3/SiO_2	655	19.2	31.9	31
In_2O_3/active carbon	941	28.1	32.7	90

a) Weight percent of Pt-black mixed with In_2O_3.

quantities of water produced were always 10 ∿ 50% less than those estimated from the consumed hydrogen. This fact implies that the fast initial consumption of hydrogen in Fig. 1 is ascribed to its adsorption or spill-over to the carriers. After the experiments shown in Fig. 1 the samples were reduced at 623 K until the degrees of reduction shown on the fourth column in Table 1 were obtained. The samples thus prepared were subjected to the experiment of Step 2.

Figure 2 shows the yield of hydrogen production as a function of time at 473 K under 2.1×10^3 Pa of water vapor. The yield of hydrogen was determined by the amount of produced hydrogen against the quantity consumed in Step 1. It is clarified in Fig. 2 that most of the carriers have favourable effects on the rate of hydrogen production compared to the sample without carrier (open circles). Of these, active carbon, ZrO_2 and TiO_2 are most effective in increasing the rate. Although the BET surface area of the TiO_2 or ZrO_2 carrier is much lower than those of SiO_2, Al_2O_3 or silica-alumina (second column of Table 1), the former carriers more enhanced the rate of hydrogen production. The final yields of hydrogen, which was measured at 673 ∿ 773 K just after the experiments shown in Fig. 2, are listed on the last column of Table 1. The results for pure In_2O_3, In_2O_3/ZrO_2 and In_2O_3/TiO_2, show that the hydrogen consumed on Step 1 was almost recovered on Step 2 within experimental error ($\pm$3% yield).

ZrO_2, TiO_2, active carbon and ZnO which show the high enhancing effects on both rates of Steps 1 and 2 and the high final yields of hydrogen on Step 2 are the most suitable carriers for In_2O_3. The reactions of eqs. (1) and (2) using these carriers proceeded smoothly at 573 and 473 K, respectively. The favourable action of the carriers may be discussed by measuring the activation energies for the reactions (1) and (2) for some samples. There was no appreciable difference in the apparent activation energies of Step 1 among the samples of In_2O_3/TiO_2, In_2O_3/ZrO_2, and In_2O_3 without carrier (65.7 ± 2.5 kJ mol^{-1}). This implies that the favourable action of carriers on the rate of Step 1 can be ascribed to the high dispersion and stabilization of small particles of In_2O_3 preventing their aggregation during Step 1. The reduction of pure In_2O_3 at 573 K did not proceed at all when the sample was tested at second and third cycles, probably due to the sintering of the particles during the first reduction. However, for In_2O_3/TiO_2 and In_2O_3/ZnO the reaction of Step 1 proceeded smoothly at second and third cycles, though the rates of reaction decreased to $\sim$50% of that at the first cycle. The carriers must prevent the aggregation of the In_2O_3 particles. The activation energies of Step 2 for In_2O_3/TiO_2, In_2O_3/SiO_2, and In_2O_3/ZnO were 13 $\sim$ 3 kJ mol^{-1} lower than that for pure In_2O_3 (60.2 kJ mol^{-1}). This suggests that the carriers play an important role for the activation of water in Step 2. The repetition of the two-step cycles, examined for In_2O_3/TiO_2 and In_2O_3/ZnO, indicated only a slight decrease in the rate of hydrogen production with the cycles.

Although the detailed enhancing-mechanisms of the carriers are not known at the moment, the In_2O_3 supported on TiO_2 , ZrO_2,active carbon or ZnO can be used as a potential metal oxide for the production of hydrogen by the repeated two-step cycles.

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