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HYDROGEN PRODUCTION FROM WATER BY In_2O_3 AND K_2CO_3 USING GRAPHITE, ACTIVE CARBON AND BIOMASS AS REDUCTANTS

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The two-step open cycle, the reduction of In_2O_3 by carbon and its reoxidation by water, was applied to produce hydrogen from water. Various carbons could be used as the reductants. Of these, chars from biomass are highly effective to the reduction of In_2O_3, and consequently to the production of hydrogen. K_2CO_3 is also a good catalyst to the two-step hydrogen production.

It has been shown that In_2O_3 is an active oxide for the production of hydrogen from water by the following two-step open cycle in which an active carbon is used as reductant:[1)]

Step (1); Reduction of In_2O_3 by active carbon at >873 K,

$$In_2O_3 + C \text{ (or 2C)} \longrightarrow In_2O + CO_2 \text{ (or 2CO)}$$

where gaseous products are continuously removed from the system.

Step (2); Oxidation of the reduced oxide by water at <673 K,

$$In_2O + 2H_2O \longrightarrow In_2O_3 + 2H_2.$$

Hydrogen is the only product in gas phase in step (2). Since CO and CO_2 are removed from the system by the independent reaction of step (1), pure hydrogen can be obtained by the cycle. This letter reports the availability of various carbon sources as the reductants in the above two-step hydrogen production.

K_2CO_3 is known as an active catalyst for the steam-gasification of coal.[2,3)] The effectiveness of K_2CO_3 for the two-step hydrogen production will also be reported.

In case A, the mixtures of In_2O_3 powder with carbons (graphite and active carbon) or biomass (cellulose, starch, sucrose and glucose) were thoroughly ground. In case B, the active carbon or the graphite was impregnated with an aqueous solution of K_2CO_3 or of $In(NO_3)_3$. The $In(NO_3)_3$ dispersed on the carbons was converted to In_2O_3 by the thermal decomposition at 573 K. The samples thus prepared were degassed in a vacuum at 773 ∿ 923 K for 3 h (step 1),[4)] and water vapour (≃2.7 kPa) was added to the sample at 673 K (step 2). The quantity of hydrogen produced was measured by gas-chromatography.

The In_2O_3 and K_2CO_3 decompose water only when the carbons or the biomass are mixed with them. Table 1 shows the hydrogen yields under various experimental conditions, where the amounts of carbon used in step (1) were less than 5% of the

Table 1. Water Decomposition over In_2O_3 and K_2CO_3 Reduced by Various Carbon Sources.

Catalyst[a]	Reductant	Catalyst/Reductant (weight ratio)	Reduction temperature (K)	Hydrogen yield at 673 K in 120 min (μmol $g\text{-}cat^{-1}$)
In_2O_3(A)	Graphite	1.0	923	4.9
In_2O_3(A)	Active carbon	1.0	773	0.0
		1.0	823	18
		1.0	873	90
In_2O_3(A)	Cellulose	5.0	773	65[b]
In_2O_3(A)	Starch	5.0	773	102[b]
In_2O_3(A)	Sucrose	5.0	773	106[b]
In_2O_3(A)	Glucose	5.0	773	96[b]
In_2O_3(B)	Graphite	0.39	923	17.4
In_2O_3(B)	Active carbon	0.39	773	94
		0.39	873	3658
K_2CO_3	Graphite	1.0	923	40
K_2CO_3	Active carbon	1.0	773	135
K_2CO_3		1.0	873	735

[a] (A) and (B) indicate the preparation methods of cases A and B described in the text, respectively.

[b] Quantity formed in 100 min.

original carbon sources. The degassing treatment of the In_2O_3-starch mixture at the temperatures below 573 K produced volatile materials but gave a small amount of hydrogen from water at 573 K (<12 μmol g-oxide^{-1}) compared with the 773 K-degassed sample(55 μmol g-oxide^{-1}). This fact indicates that the volatile materials formed during pyrolysis of the biomass sources below 573 K would not reduce In_2O_3 appreciably. The high yields of hydrogen from the biomass sources (Table 1) show that the chars formed by their decompositions can be used as efficient reductants for In_2O_3 even at the reduction-temperatures less than 773 K.

The higher activity of the In_2O_3(B) than that of the In_2O_3(A) may be explained not only by a better dispersion of the former oxide on the carbons but also by the oxidation of the carbons by HNO_3 or NO_2 gas evolved during the decomposition of $In(NO_3)_3$. In fact, the oxidation of the active carbon by HNO_3 aqueous solution enhanced the hydrogen production.

The results in Table 1 show that K_2CO_3 catalyst is as active as In_2O_3(B).

The two-step cycle for the K_2CO_3-catalyzed decomposition of water may be written as follows:[5,6]

$$\begin{array}{lll}
\text{Initiation;} & K_2CO_3 + C \longrightarrow K_2O + 2CO \\
 & \text{or} \\
 & K_2CO_3 \longrightarrow K_2O + CO_2 \\
\text{Step (1);} & K_2O + C \longrightarrow 2K + CO \\
\text{Step (2);} & 2K + H_2O \longrightarrow K_2O + H_2
\end{array}$$

The changes in the quantity of hydrogen production with the repetition of the two-step cycle are shown in Table 2. The activities of the In_2O_3(A) and K_2CO_3 are reduced with the repetition of the cycle. However, the deactivation of K_2CO_3 is not so appreciable as that of In_2O_3(A). The deactivation of In_2O_3(A) may be ascribed to the decrease in the number of contact points between carbon and catalyst surfaces due to a sintering of the oxide particles or to the consumption of the carbons in contact with the oxide.

Table 2. Changes in the Activities of In_2O_3 and K_2CO_3 for Hydrogen-production with the Repetition of the Two-step Cycle.[a]

Catalyst	Reductant	Quantity of hydrogen produced at each cycle (μmol g-cat^{-1}) Number of cycle 1st	2nd	3rd	4th
In_2O_3(A)	Acitive carbon	90	87	49	54
In_2O_3(A)	Cellulose	65	41	37	b
In_2O_3(A)	Glucose	96	56	30	b
In_2O_3(A)	Starch	102	42	b	b
K_2CO_3	Graphite	40	35	30	34

[a] The cycles were carried out without taking out the samples from the reactor. Experimental conditions are same as shown in Table 1.

[b] Not observed.

References and Note

1) K. Otsuka, Y. Takizawa, and A. Morikawa, submitted for publication.
2) W.P. Haynes, S.J. Gasior, and A.J. Forney, Adv. Chem. Ser., 131, 179(1974).
3) M.J. Veraa and A.T. Bell, Fuel, 57, 194(1978).

4) For the active carbon and the graphite, CO, CO_2, H_2O and CH_4 were desorbed or produced during the degassing process. For the biomass sources, CO, CO_2, H_2O and volatile materials were formed by their thermal pyrolysis.

5) D.W. Mckee and D. Chatterji, Carbon, 16, 53(1978).
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