

HYDROGEN PRODUCTION FROM WATER BY  $\text{In}_2\text{O}_3$  AND  $\text{K}_2\text{CO}_3$  USING  
GRAPHITE, ACTIVE CARBON AND BIOMASS AS REDUCTANTS

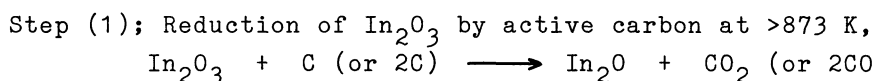
Kiyoshi OTSUKA,\* Yoshihisa TAKIZAWA,

Shin-ichi SHIBUYA, and Akira MORIKAWA

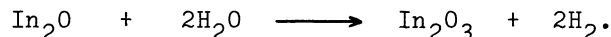
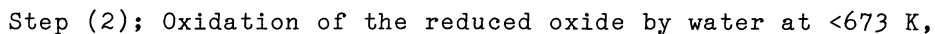
Department of Chemical Engineering, Tokyo Institute of  
Technology, Meguro-ku, Tokyo 152

The two-step open cycle, the reduction of  $\text{In}_2\text{O}_3$  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  $\text{In}_2\text{O}_3$ , and consequently to the production of hydrogen.  $\text{K}_2\text{CO}_3$  is also a good catalyst to the two-step hydrogen production.

It has been shown that  $\text{In}_2\text{O}_3$  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:<sup>1)</sup>



where gaseous products are continuously removed from the system.



Hydrogen is the only product in gas phase in step (2). Since CO and  $\text{CO}_2$  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.

$\text{K}_2\text{CO}_3$  is known as an active catalyst for the steam-gasification of coal.<sup>2,3)</sup> The effectiveness of  $\text{K}_2\text{CO}_3$  for the two-step hydrogen production will also be reported.

In case A, the mixtures of  $\text{In}_2\text{O}_3$  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  $\text{K}_2\text{CO}_3$  or of  $\text{In}(\text{NO}_3)_3$ . The  $\text{In}(\text{NO}_3)_3$  dispersed on the carbons was converted to  $\text{In}_2\text{O}_3$  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),<sup>4)</sup> and water vapour ( $\approx 2.7$  kPa) was added to the sample at 673 K (step 2). The quantity of hydrogen produced was measured by gas-chromatography.

The  $\text{In}_2\text{O}_3$  and  $\text{K}_2\text{CO}_3$  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  $\text{In}_2\text{O}_3$  and  $\text{K}_2\text{CO}_3$  Reduced by Various Carbon Sources.

Catalyst <sup>a</sup>	Reductant	Catalyst/Reductant (weight ratio)	Reduction temperature (K)	Hydrogen yield at 673 K in 120 min ( $\mu\text{mol g-cat}^{-1}$ )
$\text{In}_2\text{O}_3$ (A)	Graphite	1.0	923	4.9
$\text{In}_2\text{O}_3$ (A)	Active carbon	1.0	773	0.0
		1.0	823	18
		1.0	873	90
		5.0	773	65 <sup>b</sup>
$\text{In}_2\text{O}_3$ (A)	Cellulose	5.0	773	65 <sup>b</sup>
$\text{In}_2\text{O}_3$ (A)	Starch	5.0	773	102 <sup>b</sup>
$\text{In}_2\text{O}_3$ (A)	Sucrose	5.0	773	106 <sup>b</sup>
$\text{In}_2\text{O}_3$ (A)	Glucose	5.0	773	96 <sup>b</sup>
$\text{In}_2\text{O}_3$ (B)	Graphite	0.39	923	17.4
$\text{In}_2\text{O}_3$ (B)	Active carbon	0.39	773	94
		0.39	873	3658
$\text{K}_2\text{CO}_3$	Graphite	1.0	923	40
$\text{K}_2\text{CO}_3$	Active carbon	1.0	773	135
$\text{K}_2\text{CO}_3$		1.0	873	735

<sup>a</sup> (A) and (B) indicate the preparation methods of cases A and B described in the text, respectively.

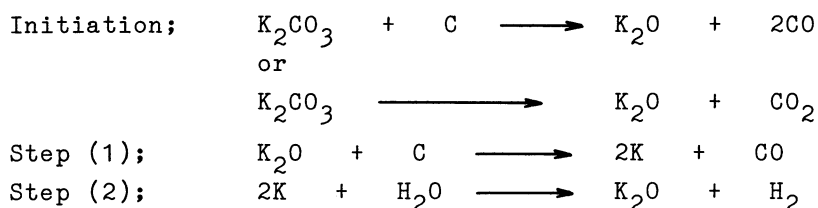
<sup>b</sup> Quantity formed in 100 min.

original carbon sources. The degassing treatment of the  $\text{In}_2\text{O}_3$ -starch mixture at the temperatures below 573 K produced volatile materials but gave a small amount of hydrogen from water at 573 K ( $<12 \mu\text{mol g-oxide}^{-1}$ ) compared with the 773 K-degassed sample ( $55 \mu\text{mol g-oxide}^{-1}$ ). This fact indicates that the volatile materials formed during pyrolysis of the biomass sources below 573 K would not reduce  $\text{In}_2\text{O}_3$  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  $\text{In}_2\text{O}_3$  even at the reduction-temperatures less than 773 K.

The higher activity of the  $\text{In}_2\text{O}_3$ (B) than that of the  $\text{In}_2\text{O}_3$ (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  $\text{HNO}_3$  or  $\text{NO}_2$  gas evolved during the decomposition of  $\text{In}(\text{NO}_3)_3$ . In fact, the oxidation of the active carbon by  $\text{HNO}_3$  aqueous solution enhanced the hydrogen production.

The results in Table 1 show that  $\text{K}_2\text{CO}_3$  catalyst is as active as  $\text{In}_2\text{O}_3$ (B).

The two-step cycle for the  $K_2CO_3$ -catalyzed decomposition of water may be written as follows:<sup>5,6)</sup>



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.<sup>a</sup>

Catalyst	Reductant	Quantity of hydrogen produced at each cycle ( $\mu\text{mol g-cat}^{-1}$ )			
		Number of cycle			
		1st	2nd	3rd	4th
$In_2O_3(A)$	Active 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

<sup>a</sup> The cycles were carried out without taking out the samples from the reactor. Experimental conditions are same as shown in Table 1.

<sup>b</sup> Not observed.

#### References and Note

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- 3) M.J. Verrea and A.T. Bell, Fuel, 57, 194(1978).

- 4) For the active carbon and the graphite, CO, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> were desorbed or produced during the degassing process. For the biomass sources, CO, CO<sub>2</sub>, H<sub>2</sub>O and volatile materials were formed by their thermal pyrolysis.
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