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NEW PROCESS FOR THERMOCHEMICAL HYDROGEN PRODUCTION

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A new water splitting process, "Sb-I Process", was proposed from the simple search method. This process consists of three reactions which proceed to an acceptable degree.

A number of thermochemical processes for hydrogen production from water have been proposed by computer searches in recent years[1∿3]. We propose here a novel water splitting process named "Sb-I Process", which was devised by the following search method.

First, we composed a general three-step process based on the considerations mentioned below.

$$AO_n + B + H_2O \longrightarrow AO_{n+1} + H_2B \qquad (1)$$

$$H_2B \longrightarrow H_2 + B \qquad (2)$$

$$AO_{n+1} \longrightarrow AO_n + 1/2O_2 \qquad (3)$$

where AO_n and AO_{n+1} refer, respectively, to a lower oxide (or a metal) and the higher one, and B for a hydrogen acceptor. The considerations taken into account were;

I) From the viewpoint of overall efficiency, the process should be constructed of basic reactions as few as possible and the number of elements other than hydrogen and oxygen involved should be no more than two.

II) For the oxygen formation step, preferable is a thermal decomposition of a solid oxide, since such a reaction usually yields two easily separable products, the lower oxide and oxygen.

III) The oxidation of the lower oxide should be attained by the water reaction.

For the hydrogen acceptor B, iodine was chosen by considering the corrosive problem and the relative ease of the thermal decomposition of hydrogen iodide. As for AO_n-AO_{n+1} couples, a number of systems in which the higher oxides can dissociate oxygen below 1000°C, a temperature attainable with high-temperature gas-cooled reactors[4], were screened from comprehensive chemistry books such as one by Gmelin[5]. Among these systems, only four, i.e., $3CoO$-Co_3O_4, Cu_2O-$2CuO$, $1/2As_2O_3$-$1/2As_2O_5$, $1/2Sb_2O_3$-$1/2Sb_2O_5$, were thermodynamically acceptable in the reaction (1), being associated with the standard free energy change less than 10 kcal/mol for the reaction like (4) below. Further, preliminary experiments revealed that, of the four, the $1/2Sb_2O_3$-$1/2Sb_2O_5$ couple was the most suitable; the other three systems were excluded because of one or two of such flaws as slow reaction rates, occurence of a side-reaction, and harmfulness of the material. The "Sb-I Process" thus selected is expressed as follows;

$$1/2Sb_2O_3(s) + I_2(s) + H_2O(l) \longrightarrow 1/2Sb_2O_5(s) + 2HI(aq) \qquad (4)$$

$$2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad (5)$$

$$1/2Sb_2O_5(s) \longrightarrow 1/2Sb_2O_3(s) + 1/2O_2(g) \qquad (6)$$

Each reaction of this process is thermodynamically acceptable as shown in Table 1.

Table 1. Thermodynamic data for the "Sb-I Process".

Step	Reaction temperature (°C)	Energies (kcal/mol) for reaction as written	
		ΔH°	ΔG°
(4)	25°C	+10.5	+7.5
(5)	530°C	+ 3.1	+6.0
(6)	980°C	+31.2	+1.1

The reaction (4) is a well-known reaction[6] which has been applied to the volumetric analysis of Sb(III) in a homogeneous system. However, we found that the reaction also took place in heterogeneous systems such as one in which Sb_2O_3 and iodine were mixed with the heterogeneous reaction medium consisting of a water-insoluble organic solvent (e.g. carbon tetrachloride) and a sodium chloride aqueous solution. In addition, the use of such a heterogeneous reaction medium turned out to be advantageous in the subsequent separation process. The unreacted iodine and hydrogen iodide were separated from each other by their selective dissolution into the organic solvent and the sodium chloride aqueous solution phases, respectively, while both the Sb_2O_5 formed and the Sb_2O_3 unreacted precipitated as solid phases. As to the reaction (5), it is well established that hydrogen iodide is 25 per cent dissociated at 530°C[7]. The hydrogen generated can be separated from hydrogen iodide and iodine with a porous membrance. For the last step (6), we observed that Sb_2O_5 decomposed to Sb_2O_3 rapidly at the temperature not exceeding 1000°C, the produced Sb_2O_3 being sublimed to be separated from the reaction system. Published data[8] show that Sb_2O_5 when heated at about 800°C transforms to Sb_2O_4, the complex oxide of trivalent and pentavalent antimony, and that Sb_2O_4 further decomposes to Sb_2O_3 above 930°C. Thys we conclude that these three reactions can be successfully combined to compose a water splitting process. The thermal efficiency (LHV) of this process calculated according to Masuko method[9] is 42 per cent, which is comparable to those of other representative water splitting processes.

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