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THERMOCHEMICAL HYDROGEN PRODUCTION BY THE MAGNESIUM-SULFUR-IODINE CYCLE

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A new thermochemical cycle for hydrogen production is presented. It consists of (i) redox reaction of sulfur dioxide and iodine with magnesium oxide in an aqueous solution, (ii) hydrolysis of magnesium iodide, (iii) thermal decomposition of magnesium sulfate and (iv) thermal dissociation of hydrogen iodide. Key reactions (i) and (ii) were experimentally verified.

The sulfur-iodine cycle comprising the following three reactions has been noticed as one of the most promising schemes for thermochemical hydrogen production:

$$I_2(c) + SO_2(g) + 2H_2O(liq) \longrightarrow H_2SO_4(aq) + 2HI(aq) \qquad (1')$$

$$H_2SO_4(g) \longrightarrow H_2O(g) + SO_2(g) + (1/2)O_2(g) \qquad (2')$$

$$2HI(g) \longrightarrow H_2(g) + I_2(g). \qquad (3')$$

The key operation of the cycle is the separation process of the acid mixture (H_2SO_4-HI) formed by Reaction (1') since distillation causes a reverse reaction resulting in formation of I_2 and SO_2. Several proposals have been reported as for the separation; addition of excess iodine to form polyiodides (HI_x)1), use of nickel metal2) and electrolytic promotion of the reaction(1').3)

The present authors have examined effects of addition of a series of metal ions to the acid mixture4)5) and found out that magnesium ions effectively prevented the reverse reaction during heating of the acid mixture, and made it possible to generate hydrogen iodide and sulfur trioxide separately at different temperatures. It was unnecessary to separate $MgSO_4$ and MgI_2 since the temperatures of their thermal decomposition and hydrolysis are far apart.

Thus, a new thermochemical cycle using magnesium, sulfur and iodine was successfully constructed:

$$2MgO(c) + SO_2(aq) + I_2(c) \xrightarrow{70°C} MgSO_4(aq) + MgI_2(aq) \qquad (1)$$

$$MgSO_4(aq) + MgI_2(aq) \xrightarrow{400°C} MgSO_4(c) + MgO(c) + 2HI(g) + nH_2O(g) \qquad (2)$$

$$MgSO_4(c) \xrightarrow{1100°C} MgO(c) + SO_2(g) + (1/2)O_2(g) \qquad (3)$$

$$2HI(g) \xrightarrow{300\text{-}700°C} H_2(g) + I_2(g). \qquad (4)$$

Since Reactions (3) and (4) are well known to proceed, experimental verification was focused on Reactions (1) and (2).

Reaction (1)

Iodine powder (552 mg) was added to 2 cm^3 of approximately 2.0 mol% aqueous solution of sulfur dioxide and the mixture was agitated until a colorless solution was obtained. Then, 174 mg of MgO powder, prepared by the decomposition of magnesium sulfate, was added to the solution at 70 °C while stirring. Magnesium oxide dissolved after several minutes. Thus, 100% yield and high reaction rate were confirmed.

Reaction (2)

The mixed solution of $MgSO_4$ and MgI_2 produced by Reaction (1) was heated in a nitrogen atmosphere at 100, 200, 240, or 350 °C. The solid residues were examined by X-ray analysis. Thermal analyses (TG and DTA) were also performed for the mixed solution. The results indicated that MgI_2 hydrate decomposed to the oxide in three steps, while $MgSO_4$ hydrate was dehydrated as follows:

$$MgSO_4(aq) + MgI_2(aq) \xrightarrow{\sim 100°C} MgSO_4 \cdot H_2O(c) + MgI_2 \cdot 8H_2O(c) \qquad (2\text{-}1)$$

$$MgSO_4 \cdot H_2O(c) + MgI_2 \cdot 8H_2O(c) \xrightarrow{\sim 200°C} MgSO_4 \cdot H_2O(c) + Mg(OH)I \cdot H_2O(c) + HI(g) + 6H_2O(g) \qquad (2\text{-}2)$$

$$MgSO_4 \cdot H_2O(c) + Mg(OH)I \cdot H_2O(c) \xrightarrow{\sim 240°C} MgSO_4 \cdot H_2O(c) + (1/2)Mg_2(OH)_3I(c) + (1/2)HI(g) + (1/2)H_2O(g) \qquad (2\text{-}3)$$

$$MgSO_4 \cdot H_2O(c) + (1/2)Mg_2(OH)_3I(c) \xrightarrow{\sim 350°C} MgSO_4(c) + MgO(c) + (1/2)HI(g) + (3/2)H_2O(g). \qquad (2\text{-}4)$$

The reaction products were chemically analyzed for each of the steps. Amounts of $[I_2]$, $[I^-]$, $[SO_3^{2-}]$ and $[SO_4^{2-}]$ contained in the evolved vapors and solid residues were determined by thiosulfate iodometric titration and sulfate gravimetry. No evolution of SO_2 was found in the range of 25-300 °C, while some amounts of I_2 and SO_2 were generated at 300-430 °C. Quantitative analyses confirmed that the overall yield of Reaction (2) was 95%; a 5% portion of the reactants underwent the reverse reaction at about 350 °C to regenerate I_2 and SO_2. According to the previous work6) on hydrolysis of $MgI_2 \cdot 6H_2O$, the rate of each of the above steps is sufficiently fast.

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