An experimental study of HI decomposition through adsorption-desorption process in the Sulfur-Iodine cycle

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1. Introduction

The Sulfur-Iodine thermochemical cycle is one of the candidates of effective nuclear hydrogen production processes with VHTR. This cycle includes three steps, Bunsen reaction, sulfuric acid decomposition and hydrogen iodide decomposition step. Among those steps, hydrogen iodide decomposition step is bottleneck of whole hydrogen production efficiency because of low thermodynamic yield and reaction rate. Therefore, there have been number of trials to improve HI decomposition efficiency using various methods, such as distillation and membrane, mainly challenging to overcome thermodynamic equilibrium yield around 25% at 500°C, conventional reaction temperature. In case of catalysts, though platinum or titanium shows high catalytic activity at conventional temperature, costs of those metals are greatly high and physical degradation occurs.

In this article, adsorption-desorption method for overcoming thermodynamic yield and giving low temperature catalytic activity is shown. Using porous support material, selective adsorption-desorption through temperature change can give hydrogen conversion higher than thermodynamic yield because of product loss to maintain reaction equilibrium. Additionally, this method can provide relatively reasonable decomposition yield at lower temperature.

2. HI Decomposition Experiment

We performed the HI decomposition experiment to see whether we can overcome thermodynamic yield or not and to find low temperature catalytic decomposition yield.

2.1 Materials

Hydriodic acid of azeotropic condition(57wt%) is prepared for decomposition test as a reactant and Nickel on silica/alumina(Sigma-Aldrich, surface area=190m^2/g) is catalyst/adsorbent.

2.2 Apparatus and Methods

The electric furnace is used to keep the target temperature for reaction and the reactor consists of quartz pipe in 1 inch diameter. The catalyst are loaded inside of the quartz pipe, using quartz wool to support the powder catalyst at the top and bottom of catalyst level.

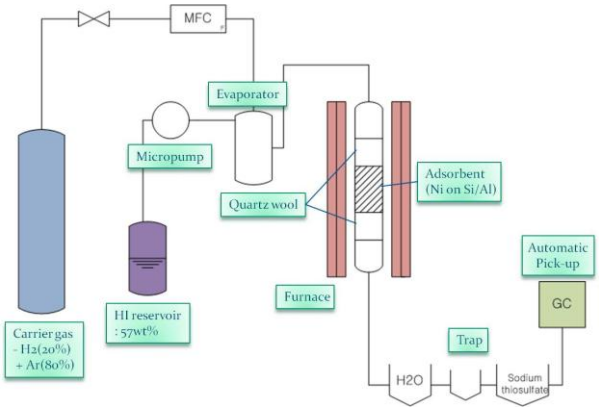

Fig. 1. Experimental apparatus for HI decomposition test.

HI feed is supplied into the evaporator by the micropump with 0.1ml/min, mixed with carrier gas(H_2 20%+Ar 80%) of 20ml/min and moves to the reactor. HI and carrier gas mixture passes catalyst and decomposed. Unreacted HI and iodine molecules are trapped through water and sodium thiosulfate solution. We used gas chromatography(DS6200, DS science) to analyze emerging gas composition.

2.3 Material Analysis

Before starting the experiment, thermogravimetry analysis(TGA) is conducted for an adsorbent to get the adsorption and desorption temperature information about HI and iodine. Hydrogen and water desorb immediately. After reaction, BET, SEM, XRD tests are done to compare used catalyst condition with fresh catalyst,

3. Results and discussion

Figure 2. shows TGA results for HI and iodine molecules. Both materials show a sharp decline in mass around 300°C, which means that the adsorbent adsorbs below that temperature and desorbs as the temperature increases. Using this mechanism, HI is adsorbed at 250°C and then decomposed into hydrogen and iodine, while hydrogen being desorbed out immediately giving lack of product, which causes continual reaction due to Le Chatelier's principle. After decomposition, desorption can occur at increased temperature, around 400°C and can recover adsorption sites to adsorbent. This process is called temperature swing.

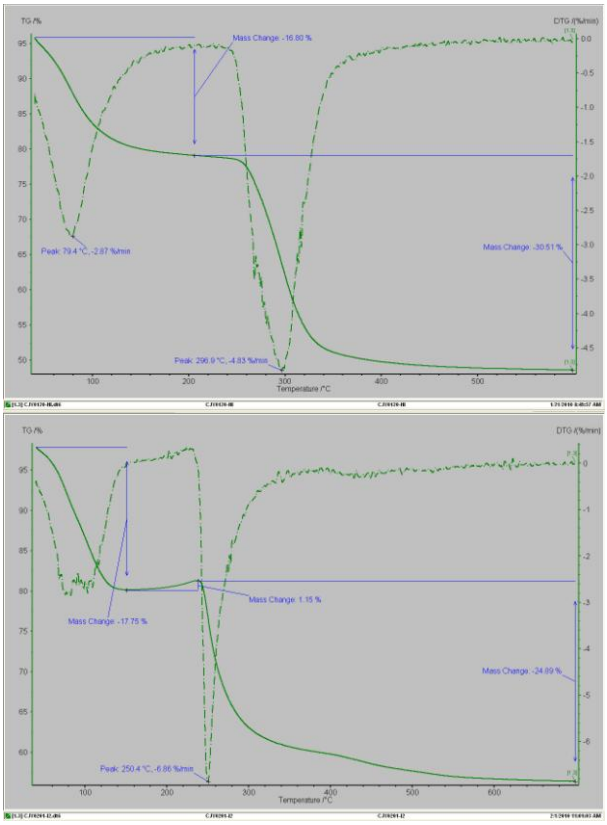

Fig. 2. TGA results for HI(top) and I_2(bottom).

As shown in figure 3, the decomposition experiment at 250°C for 1ml of HI showed 40% of conversion yield at the peak with 3g of catalyst. This value is much above the thermodynamic yield, 15%. Also, we showed that the proper adsorbent regeneration temperature is near 400°C.

However, the temperature swing method needs discontinuity of process and high value of yield declined after number of tests. Therefore, we found an optimal temperature which produces a largest yield during the simultaneous adsorption-desorption process, around 300°C. At this point, HI adsorption and iodine desorption can be balanced to give continuous decomposition though it is low temperature for catalyst.

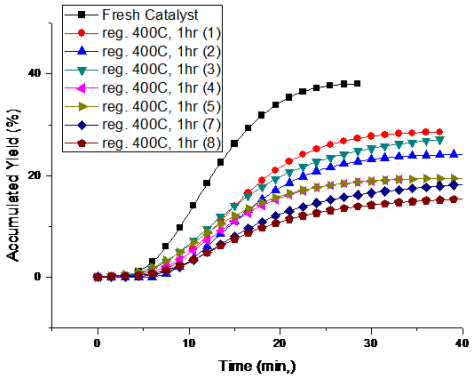

Fig. 3. Hydrogen yield of HI decomposition for 1ml of hydriodic acid at 250°C with regenerations at 450°C.

At 300°C, 0.1ml/min of HI was fed continuously to 3g of catalyst. Results are shown in figure 4. At early phase, conversion yield was almost 20%, and declined to 4.7%. This value was held about 1hr, and is expected to be maintained, because there is almost no thermal degradation due to lower temperature. With 6g of catalyst under the same condition, yield becomes 30% at peak yield and 7.3% during stable yield.

After reaction, BET and SEM analysis showed that the used catalyst has the smaller surface area and smaller average pore size than the fresh catalyst because of site occupation with HI and iodine.

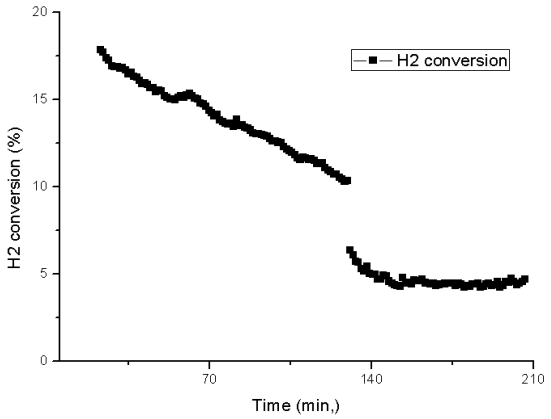

Fig. 4. Hydrogen conversion yield at 300°C for 0.1ml/min. HI feed with 3g of catalyst.

XRD results also told that the used catalyst contains mainly Nickel Iodide Hydrate. After regeneration at higher temperature, main compound changed to Nickel, same as the fresh catalyst but the surface area was not perfectly recovered. From these analysis results, we can assume that physical surface degradation is the main reason of loss of decomposition ability for the temperature swing method.

4. Conclusions

Through the adsorption-desorption process, we showed that we can overcome the limitation of thermodynamic yield. However, this process takes temperature swing and discontinuity on hydrogen production. Thus, we demonstrated the feasibility of the simultaneous adsorption-desorption process providing stable decomposition yield at lower temperature.

Acknowledgements

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