Bifunctional Characteristics of Al_2O_3 supported Ni in the HI Decomposition of Sulfur-Iodine Process

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Abstract. The Sulfur-Iodine process is in need of catalytic reactor for HI decomposition because the HI decomposition reaction rate is very slow. Nickel as an alternative catalyst for platinum was investigated in this study. Al_2O_3 supported Ni catalysts were prepared by impregnation method. Ni amounts loaded over Al_2O_3 were in the range of 0.1~20 wt. %. HI decompositions were carried out in the temperature range of 573 ~ 773 K using the fixed-bed quartz reactor. The difference of catalysts before and after the reaction was analyzed using BET, CO/H_2 chemisorption, XRD, XRF and SEM. It was confirmed by XRD and SEM-EDX analysis that Ni was converted to NiI_2 during the HI decomposition. Catalyst deactivation due to the formation of NiI_2 leads to a reduction of HI conversion. Although Ni of catalyst converted to NiI_2, HI decomposition with low loading (up to 3 wt. %) catalyst showed a little decrease of HI conversion. However, with more than 5 wt. % catalyst, the initial HI conversion was considerably decreased. In the particular case of 20 wt. %, the initial conversion was increased close to 60 %, which is higher than 20 % as an equilibrium conversion at 723 K. These results showed that Ni had not only a catalytic function for HI decomposition, but also function as a sorbent to absorb I_2 produced from HI.

1 Introduction

Sulfur-Iodine cycle is the promising thermochemical water-splitting process to produce large amounts of hydrogen [1]. Sulfur-Iodine hydrogen production process consists of the following three chemical reactions:

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$$\text{HI decomposition: } 2HI \rightleftharpoons H_2 + I_2 \ (573 \sim 773\ K) \quad (1)$$

$$\uparrow\downarrow$$

$$\text{Bunsen reaction: } SO_2 + I_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2HI \ (293 \sim 393\ K) \quad (2)$$

$$\uparrow\downarrow$$

$$H_2SO_4 \text{ decomposition: } H_2SO_4 \rightleftharpoons H_2O + SO_2 + 0.5O_2 \ (1073 \sim 1173\ K) \quad (3)$$

Bunsen reaction (Eq. (2)) is a water splitting reaction of producing H_2SO_4 and HI. HI and H_2SO_4 can be separated by specific gravity difference. In the H_2SO_4 decomposition process (Eq. (3)), H_2SO_4 is decomposed into H_2O, SO_2 and O_2. Products of H_2SO_4 decomposer are then fed back to Bunsen process. H_2 and I_2 are produced by thermal decomposition of HI (Eq. (1)). I_2 is returned to Bunsen process as complexes of $HIx{\cdot}yH_2O$ [2]. In the temperature range of 600 ~ 800 K, HI conversion is around 20 % in the equilibrium state. In addition, the rate of HI decomposition reaction is very slow without a catalyst [3]. The platinum as a catalyst for the HI decomposition has been mainly studied [4]. Ni catalysts supported on various supports have been investigated for the cost savings resulting from alternating of noble metal. However, the life time of Ni supported catalyst was not good while Pt supported catalysts showed very good performance. Favuzza et al. [5] reported that deactivation of Ni-based catalyst was due to NiI_2 formation. In the present work, Ni catalysts supported on γ-Al_2O_3 were investigated. To identify the optimum loading amounts of Ni, Ni catalysts were prepared in the range of 0.1~20 wt. % by impregnation method. To compare the activities of catalysts, HI decompositions were conducted in the controlled conditions to be below theoretical equilibrium conversion.

2 Experimental

2.1 Preparation of Catalysts.

The Ni supported catalysts on γ-Al_2O_3 were prepared by impregnation method (Fig. 1). As a support, γ-Al_2O_3 (Alfa-aesar, 99 %) was used. Al_2O_3 particles in the range of 300 ~ 450 μm were obtained through pulverizing-sieving. The Al_2O_3 particles were thermally treated to remove impurities at 973 K in the air atmosphere. Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}\ 6H_2O$, Sigma-Aldrich, $\geqq$98.5%) as Ni precursor was used. The Al_2O_3 particles were wetted in Nickel nitrate solution using a rotary vacuum evaporator (BUCHI, R-210). The wetted particles were dried at 373 K for 24 h and then calcined at 973 K for 6 h in 5 vol. % H_2/Ar.

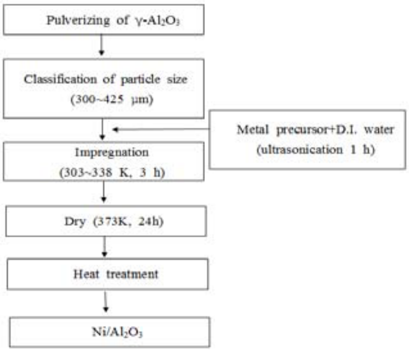

Fig. 1. Preparation procedures of Ni/Al2O3.

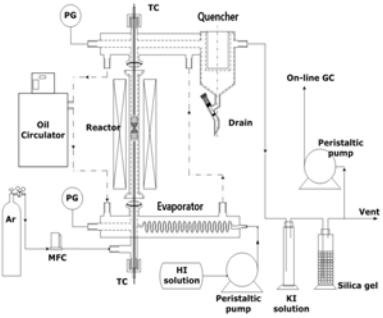

Fig. 2. Activity test apparatus of catalyst for HI.

2.2 Characterization and Activity Test of Prepared Catalysts.

Surface area and pore size distribution were measured by BEL-sorp mini. Metal dispersion and specific metal surface area were measured by BELCAT-B. 10 vol. % CO/He and 5 vol. % H_2/He were used as absorbing gas. The XRD (DMAX-2500, Rigaku) and SEM (S-4800, HITACHI) analysis were carried out to identify the physical and chemical change of catalysts before and after the activity test.

Activity test apparatus (Fig. 2) consisted of the evaporator of HI acid solution, the quartz tubular reactor with catalyst, traps and gas chromatograph. Activity tests were carried out with the vertical fixed-bed quartz reactor (9 mm inside and 13 mm outside diameter). Catalysts were used about 0.4 g (catalyst bed height: about 11 mm). The reaction temperature was kept at 723 K using heating jacket. HI aqueous solution (56 wt. %, Kanto) was fed into the evaporator in 0.2 mL/min using a peristaltic pump (Cole-Parmer, Masterflex L/S). Ar (99.999 %) as the carrier gas was fed in 50 mL/min into the quartz reactor.

The reacted gas was cooled to room temperature to trap I_2, H_2O and unreacted HI as soon as it was passed through the reactor. The resulting gas was then passed through the scrubber with the 2 M KI solution, in order to identify H_2 amount using the gas chromatograph (7890A, Agilent Technologies).

3 Results and Discussion

Specific surface area (BET) was measured before and after loading Ni on the support. BET of Ni loaded catalyst was lower than that of support. BET of Al_2O_3 as purchased was 218 m^2/g. BET of Ni loaded catalysts was decreased owing to clogging of pores of support with increasing of loading amount of Ni. BET of Ni loaded catalyst decreased down to 128 m^2/g when the Ni loading amount was 20 wt. %.

Metal dispersions were measured by following CO and H_2 chemisorption, respectively. Metal dispersion values detected by CO chemisorption showed fluctuating results. CO adsorption on supported Ni is considerably more complex, the stoichiometry of which varies with equilibrium pressure, temperature, metal crystallite size, and metal loading [6]. Therefore, CO adsorptions were not accepted as results in the present work. The table shows results measured by H_2 chemisorption. Metal dispersions were not measured when the Ni loading amount was less than 3 wt. %. The Ni dispersion was decreased with increasing the Ni contents of the catalyst.

Table 1. Surface Characteristics Of Support And Prepared Catalysts

Sample	BET (m^2/g)	Metal dispersion (%)
Al_2O_3	218	-
5.0 wt.% Ni/Al_2O_3	176	1.815
10 wt.% Ni/Al_2O_3	161	1.624
20 wt.% Ni/Al_2O_3	128	0.5374

The evaluation of catalytic activity was performed in the temperature range of 573 ~ 773 K. The HI conversions were increased with increasing the reaction temperature [7]. Fig. 3 represents the results at 723 K graphically with Favuzza's result at 773 K [5]. The gas hourly space velocity was controlled to 34750 h^{-1} in order to be below than theoretical equilibrium conversion. The HI conversions were linearly increased with increasing Ni contents of catalyst up to 3 wt. %. However, it showed the similar results between 3 and 10 wt. % of Ni/Al_2O_3 catalysts. The decomposition results were less than Favuzza's because of the high GHSV and the low reaction temperature. It was necessary to note the variation in the onset of decomposition.

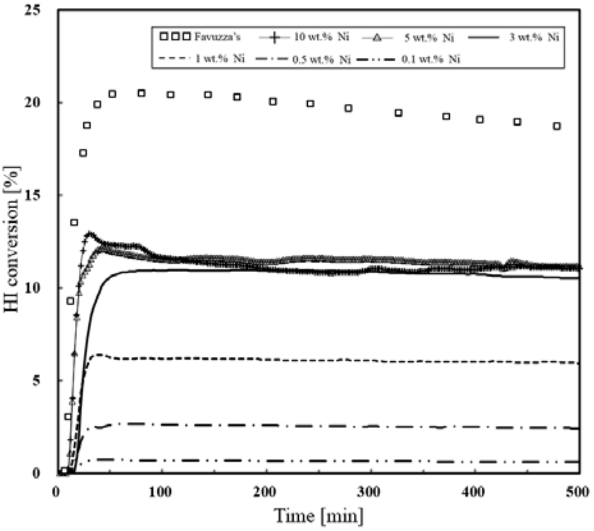

Fig. 3. HI decomposition against the Ni loading contents at 723 K; □ Favuzza's.

It was thought that the high conversion in the onset of the reaction was occurred since Ni catalyst had the bifunctional characteristics of the sorbent of I_2 produced from HI decomposition, as well as the catalyst. These effects took place in the case of the high Ni contents of the catalyst. The another concern was that NiI_2 had the catalytic activity in the HI decomposition.

Fig. 4 shows the XRD patterns of 10 wt. % Ni/Al_2O_3 before and after the HI decomposition. The Ni and Al_2O_3 peaks were detected in the catalyst before the reaction. In the catalyst after the HI decomposition, it was found that most of the Ni was converted to NiI_2. Therefore, the HI decomposition in the end of the reaction could be thought as results due to the catalytic properties of NiI_2.

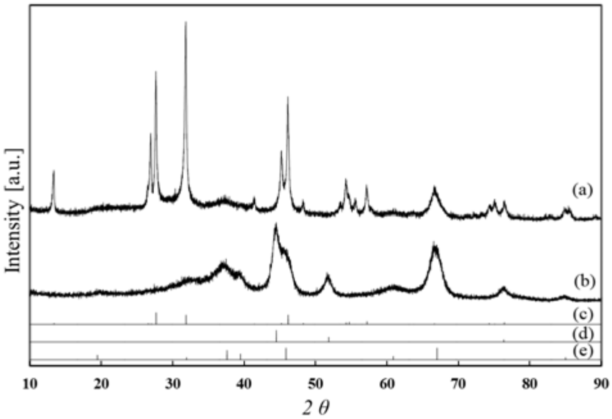

Fig. 4. XRD patterns of 10 wt.% Ni/Al2O3 catalyst before and after the HI decomposition; (a) after, (b) before, (c)NiI2,(d) Ni and (e) Al2O3.

In order to determine the characteristics of Ni as a sorbent and NiI_2 as a catalyst, HI decomposition was conducted with the high Ni contents (20 wt. % Ni/Al_2O_3) in the condition of low GHSV of about 4,630 h^{-1}. HI conversion was increased close to 60 % in the onset of the reaction and then decreased to 20 %. HI decomposition was maintained in the equilibrium state of 20 % after 50 minutes. When H_2 or I_2 is removed, the conversion rate exceeding 20 % that is the theoretical equilibrium conversion value occurs. Hence, the conversion rate of 60 % was caused by removing I_2 from the product gas.

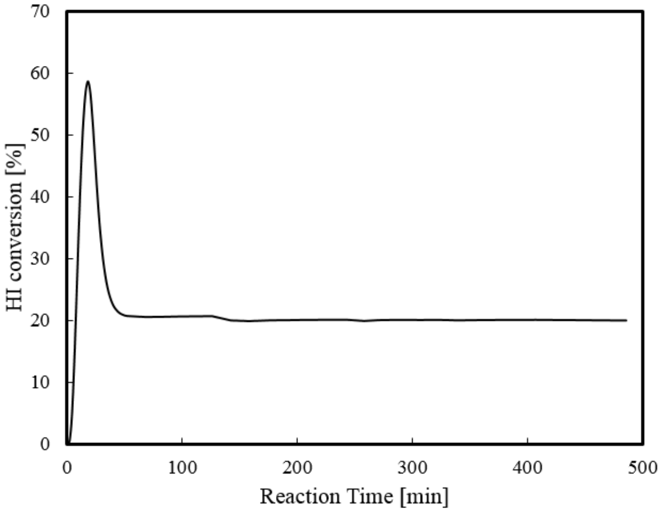

Fig. 5. Variation of HI conversion with 20 wt.% Ni/Al_2O_3 catalyst of at 723 K; 3 g loading amounts.

As a result, the Al_2O_3 supported Ni metal in the HI decomposition showed the characteristics of a catalyst as well as the sorbent. It was also revealed that the NiI_2 formed from HI decomposition had the catalytic activity.

4 Conclusion

In this study, HI decompositions were performed to identify characteristics of Al_2O_3 supported Ni catalyst. The HI conversions were increased with increasing the reaction temperature in the temperature range of 573 ~ 773 K. It was confirmed from XRD analysis that Ni was converted to NiI_2 during the HI decomposition. The results exceeding the theoretical equilibrium took place in the case of the high Ni contents of the catalyst. In the case of high Ni contents and low GHSV, HI conversion was increased close to 60 % in the onset of the reaction. It was reconfirmed that Ni catalyst had the bifunctional characteristics of the sorbent of I_2 produced from HI decomposition, as well as the catalyst. It was also revealed that the NiI_2 formed from HI decomposition had the catalytic activity.

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