Energy Conversion and Management 117 (2016) 520–527

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Catalytic performance and durability of Ni/AC for HI decomposition in sulfur–iodine thermochemical cycle for hydrogen production

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A R T I C L E   I N F O

Article history:
Received 6 January 2016
Received in revised form 3 March 2016
Accepted 23 March 2016
Available online 29 March 2016

Keywords:
Sulfur–iodine cycle
HI decomposition
Ni content
Catalytic activity
Durability

A B S T R A C T

This work reports the Ni content effect on the Ni/AC catalytic performance in the HI decomposition reaction of the sulfur–iodine (SI) thermochemical cycle for hydrogen production and the Ni/AC catalyst durability in a long-term test. Accordingly, five catalysts with the Ni content ranging from 5% to 15% were prepared by an incipient-wetness impregnation method. The activity of all catalysts was examined under the temperature range of 573–773 K. The catalytic performance evaluation suggests that Ni content plays a significant role in the Ni dispersion, Ni particle size, and eventually the catalytic activity in HI decomposition. 12% is the optimal Ni content for Ni/AC catalysts in HI decomposition which is balanced between poor dispersion of Ni particles and increasing active center. The results of 24 h durability test, which incorporated with BET and TEM investigations of the 12%Ni/AC catalyst before and after the reaction, indicate that establishing a better Ni particle dispersion pattern and improving the stability of Ni particles on the support should be considered in the future.

1. Introduction

The global economy has grown rapidly after the Second World War, causing a burgeoning demand for energy resources. More and more fossil fuels are consumed annually, giving rise to the vast greenhouse gases emissions. Thus, the emission control of greenhouse gases has gradually become the consensus globally. Hydrogen produced by renewable sources without CO_2 emission has drawn increasing attentions in recent years [1–5]. Thermochemical water splitting cycles powered by solar or nuclear energy are efficient, CO_2 free methods to produce hydrogen [6–8]. Among them, the sulfur–iodine (SI) thermochemical cycle proposed by General Atomics Co. is the ideal one according to many strict criterions [2,9–12]. The SI process was shown in Fig. 1 and this cycle consists of three parts:

$$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI \quad (1)$$

$$2HI \rightarrow H_2 + I_2 \quad (2)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + 0.5O_2 \quad (3)$$

$$\text{In total} \quad H_2O \rightarrow H_2 + 0.5O_2 \quad (4)$$

Reaction (1) is called Bunsen reaction. SO_2 is absorbed by I_2 in the aqueous phase (with H_2O added from a source outside the cycle) to produce H_2SO_4 and HI. Then, the two acid solutions are separated into two parts by the presence of an excess I_2. The light part is called H_2SO_4 phase, with a small amount of I_2 and HI. The heavy part is denoted as HIx phase, containing some H_2SO_4. Both of the two phases are purified by reverse Bunsen reaction ($2HI + H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2$) at 423 K. Accordingly, HI is separated from the purified HIx phase by distillation and catalytic decomposed into H_2 and I_2 at about 723 K gradually (Reaction (2)). The purified H_2SO_4 is concentrated and catalytically decomposed into SO_2, H_2O and O_2 at about 1123 K (Reaction (3)). The overall reaction is exactly water decomposition at relatively low temperature due to all the productions except H_2 and O_2 are fully recycled.

The hydriodic acid (HI) decomposition section (Reaction (2)) is a highly energy consuming part in the SI cycle due to the azeotrope phenomena in the HIx phase and the low homogeneous conversion rate of HI decomposition reaction [13,14]. The thermodynamic equilibrium conversion of HI decomposition is only 0.23 at 773 K and the reaction rate is also very low. Several approaches have been proposed to solve these problems by various institutes. The General Atomics Co. advanced an extractive distillation technique which uses phosphoric acid (H_3PO_4) to break the azeotrope of HI–H_2O binary system for acquiring pure HI vapor in 1982 [11]. However, the concentration of the remaining phosphoric acid also needs a large amount of energy which decreases the thermal

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Abbreviations: SI, sulfur–iodine; AC, activated carbon; Ni/AC, activated carbon with Ni impregnated; XRD, X-ray diffraction analysis; TEM, transmission electron microscope; BET, Brunauer–Emmett–Teller method.

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http://dx.doi.org/10.1016/j.enconman.2016.03.065
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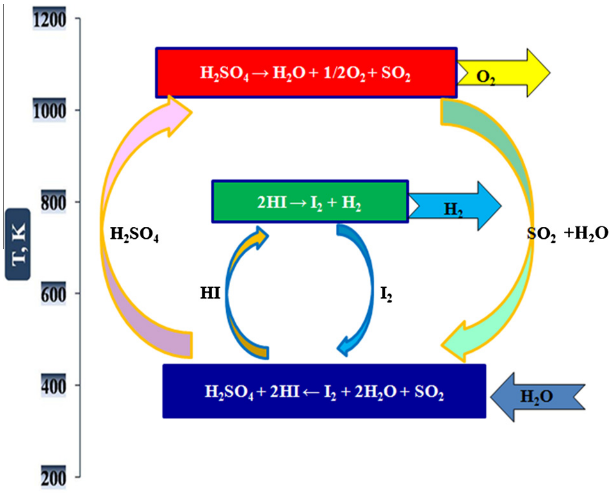

Fig. 1. SI thermochemical cycle for hydrogen production.

efficiency of the SI cycle. Aachen University introduced the conception of reactive distillation which combines reaction and separation together to produce hydrogen effectively [13]. In order to decompose HI in the reactive distillation column, the temperature and pressure should be raised very high, usually reach 535 K and 22 bar, respectively. Furthermore, the HIx mixture is extremely corrosive which contains HI, I_2, H_2 and H_2O at such high temperature and pressure. As a result, it is very hard to find suitable materials for reactive distillation column economically. An electro-electrodialysis (EED) was also proposed by the Japan Atomic Energy Agency to overcome the azeotrope of HIx before HI decomposition [15]. After EED, the HIx phase was concentrated by distillation and then decomposed into H_2 and I_2. To overcome the problem of low conversion rates, various catalysts are developed for HI decomposition [16–32]. Generally, these catalysts can be classified into three categories: noble metal based catalysts [16,17,22,25–28,32], carbon materials (e.g. activated carbon, carbon nanotubes and carbon molecular sieve) [18–20,24,29], and non-precious catalysts [21,23,30,31]. Among them, noble metal based catalysts demonstrated the highest catalytic activity and thus attracted intensive researches. Wang et al. studied the catalytic performance of Pt loaded on various carbon materials and found that the carbon nanotubes supported Pt demonstrates the best activity for HI decomposition, because of the special structure of carbon nanotubes and good Pt dispersion [17]. Mesoporous zirconium oxide supported platinum catalysts were synthesized and applied to HI decomposition by Varma et al. [27]. The results indicate that the Pt catalyst could significantly increase the conversion for HI to H_2 reaction. Several platinum supported catalysts with different Pt loadings were prepared by Park et al. for HI decomposition reaction [16]. The experiments found that with 5 wt% of Pt loading, the catalyst could lead to 22.5% HI conversion at 823 K, which almost equivalent to the theoretical thermodynamic yield (the maximum conversion of HI when this reversible reaction reached equilibrium). However, Pt is quite expensive and its stability does not seem satisfactory. Wang et al. found that during the HI decomposition, Pt particles were sintered in a short time, resulting in a fast decrease of the catalytic performance [32]. Park also discovered the size of Pt particles on the catalysts surface became larger after HI decomposition reaction and the morphologies of the used catalysts changed to a large extent [16]. These results suggest that Pt is not a stable and economical candidate for a large-scale SI hydrogen production system in the future. Because of low cost, non-toxicity, and high activity, Ni has elicited considerable attention of researchers [21,23,30,31]. The experimental investigation of Favuzza et al. [21] reported that γ-alumina-supported Ni catalyst owned a high catalytic performance in HI decomposition at 773 K. Choi et al. [23] prepared Ni catalysts supported on mesoporous Al_2O_3 for HI decomposition. The evaluation results showed Ni catalysts achieved 23% HI conversion yield at 923 K, indicating that Ni catalysts have high reactivity and is a considerable candidate for HI decomposition. Lin et al. [30] demonstrated that Ni supported on $Ce_{0.8}Zr_{0.2}O_2$ strongly advanced the conversion rate of HI decomposition. In our previous work Zhang et al. [31], the reported high activity of Ni supported on activated carbon (Ni/AC) in HI decomposition uncovered that Ni/AC had the potentiality to be a good catalyst choice for HI decomposition in a large-scale SI hydrogen production system. However, the Ni content effect on the Ni/AC catalyst performance, the Ni/AC catalyst durability for a long-term run, and changes of specific surface area and morphology for Ni/AC before and after a HI decomposition reaction have not been systematically studied, aspects of which are partially addressed in this work.

2. Experimental

Five Ni/AC catalysts were prepared with varying the Ni content (loading). Their catalytic performances were evaluated for HI decomposition from 573 K to 773 K. By using BET, XRD and TEM analysis, Ni/AC catalysts before and after HI catalytic decomposition experiments were characterized. In addition, a 24 h lifetime track record was carried out under the following condition: 1 g 12%Ni/AC, 0.7 mL/min hydriodic acid flow rate and operating temperature at 773 K.

2.1. Catalyst preparation

All five catalysts were prepared by an incipient-wetness impregnation method [33]: The applied AC support (100–200 mesh, from Shanghai Activated Carbon Co.. The results of characterizations of AC support could be found in supplementary material) was first dried at 393 K for 2 h. Nickel nitrate salt ($Ni(NO_3)_2 \cdot 6H_2O$, analytical reagent, Hangzhou Chemical Reagent Co.) was used as the Ni precursor. The impregnation solution, which prepared by a calculated amount of $Ni(NO_3)_2 \cdot 6H_2O$ and deionized water, was added into the pretreated AC support (an example of calculated amount of materials could be found in supplementary material). Thereafter, the mixture was stirred at room temperature for 24 h and dried at 383 K for 12 h. The resulting solid was calcined in flowing hydrogen by increasing the temperature at 5 K/min to 823 K from room temperature, and then holding isothermally at 823 K for 3 h. Based on the Ni content, also known as Ni loading, which is the mass percentage of metal Ni in the whole catalyst, the samples are denoted as 5%Ni/AC, 7%Ni/AC, 9%Ni/AC, 12%Ni/AC and 15%Ni/AC, respectively.

2.2. Catalyst characterization

Surface areas, pore volumes and pore sizes for the samples were measured at 77 K by Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2020 using static adsorption procedure. A sample weight of approximately 100 mg was used for each analysis and each sample was degassed at 523 K for at least 5 h, until a pressure of 10^{-5} Pa was attained. The BET surface area was calculated from N_2 adsorption data at a relative pressure of $0.05 < P/P_0 < 0.3$. The total pore volume (TPV) was calculated from the amount of N_2 adsorbed at $P/P_0 = 0.99$. The density functional theory (DFT) model was employed to analyze the results.

The X-ray diffraction (XRD) analyses of catalysts were obtained with the assistance of a Rigaku K/MAX2550/PC X-ray powder