Catalytic performance of semi-coke on hydrogen iodide decomposition in sulfur-iodine thermochemical cycle for carbon dioxide-free hydrogen production

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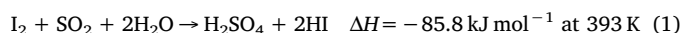
ABSTRACT

Sulfur-iodine thermochemical water splitting cycle is a promising and carbon dioxide-free method for hydrogen production. Among the reactions in this cycle, hydrogen iodide catalytic decomposition is the rate-determining step. In this study, catalytic reactivity test combined with characterizations of nitrogen physisorption, X-Ray diffraction, and Raman spectroscopy provide evidences that hydrofluoric acid modified semi-coke is a promising catalyst candidate for hydrogen iodide decomposition because of its high active and low cost. The raw semi-coke enhanced the hydrogen iodide conversion rate. After modification of hydrofluoric acid, the catalytic activity of semi-coke increased largely. Semi-coke modified by 40 wt% hydrofluoric acid showed better performance than commercial activated carbon catalyst. Combine the characterization results and catalytic reactivity, the graphitic edge carbon atoms in semi-coke are the active sites for hydrogen iodide decomposition. This finding pointed out the direction of carbon material catalyst design for hydrogen iodide decomposition.
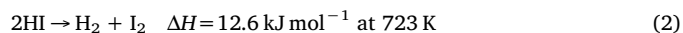
1. Introduction

The development of global economy not only brings better life on this planet but causes rising energy demand [1]. The fossil fuel is playing a dominate role in global energy supply, but it will run out in future. The pollutants (nitrogen oxide, carbon dioxide (CO_2), dust, etc.) released in the utilization process of conventional energy sources, such as fossil fuels, are putting more and more pressures on our environment [2]. Therefore, global energy demand and gas pollutant lead to the introduction of a new and alternative energy carrier: hydrogen (H_2) [3]. Because of its superiorities, such as "clean energy" and "feasible energy carrier", hydrogen has attracted extensive interests in the last decades [4]. Hydrogen could be utilized in various ways, among which, polymeric electrolyte membrane fuel cell (PMEFC) is an effective technologic alternative to generate power from hydrogen without releasing any pollutions. Hydrogen gas produced via conventional processes (steam reforming, dry reforming, and partial oxidation) contains a high concentration of by-product carbon monoxide, which would lead to the poisoning of platinum (Pt) anode in the PMEFC and the significant greenhouse gas emissions [5]. Thermochemical water splitting cycles are efficient to produce hydrogen with low pollution to the environment [6]. In last decade, extensive efforts have been made in sulfur-iodine (SI or IS) thermochemical cycle, a CO_2-free method for hydrogen

production. The schematic of SI thermochemical cycle is shown in Fig. 1; this cycle consists of three reactions ((1)–(3)):
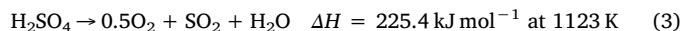
Bunsen reaction:

$$I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \quad \Delta H = -85.8\,kJ\,mol^{-1} \text{ at } 393\,K \quad (1)$$

Hydrogen iodide decomposition reaction:

$$2HI \rightarrow H_2 + I_2 \quad \Delta H = 12.6\,kJ\,mol^{-1} \text{ at } 723\,K \quad (2)$$

Sulfuric acid decomposition reaction:

$$H_2SO_4 \rightarrow 0.5O_2 + SO_2 + H_2O \quad \Delta H = 225.4\,kJ\,mol^{-1} \text{ at } 1123\,K \quad (3)$$

Net reaction:

$$H_2O \rightarrow H_2 + 0.5O_2 \quad (4)$$

During Bunsen reaction, sulfuric acid (H_2SO_4) and hydrogen iodide (HI) are produced by the redox reaction of sulfur dioxide (SO_2), iodine (I_2), and water (H_2O). Then, the two acid solutions are separated into two parts by the presence of an excess I_2. The light part is denoted as H_2SO_4 phase, with small amount impurities of I_2 and HI. The heavy part is HIx phase (HI-I_2-H_2O), 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
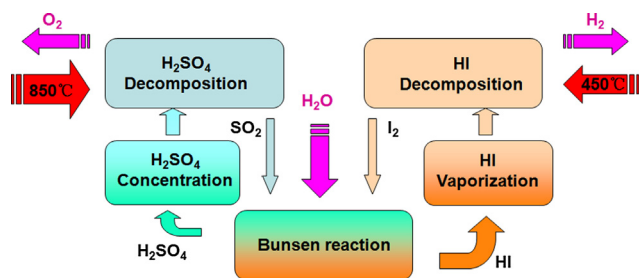

Fig. 1. Schematic of sulfur-iodine cycle for hydrogen production.

purified HIx phase by distillation and then thermally decomposed into H_2 and I_2 at about 723 K. The purified H_2SO_4 is concentrated and catalytically decomposed into SO_2, H_2O and oxygen (O_2) at about 1123 K. The net reaction is exactly water decomposition at relatively low temperature (< 1123 K) because all the productions except H_2 and O_2 are fully recycled during SI cycle.

HI decomposition reaction (reaction (2)) is the key reaction in SI thermochemical cycle. It is a step of hydrogen evolution and it consumes extensive energy because of the low homogeneous conversion rate of HI decomposition (only 2.2% at 773 K). Consequently, high active catalysts are mandatorily employed to increase the reaction rate of HI decomposition. Small transition metal clusters (e.g. Pt, palladium (Pd), Iridium (Ir), nickel (Ni) and cobalt (Co)) dispersed on high surface area substrates could largely enhance HI conversion [7]. General Atomic Co. (GA) and the National Chemical Laboratory for Industry (NCLI), Japan, reported that dispersed Pt clusters showed an excellent activity for the conversion of HI to hydrogen [8]. Zhang et al. synthesized high active Pt/cerium oxide (Pt/CeO$_2$) catalyst by doping Pt into pure CeO$_2$ [9]. Considering the high cost of noble metals (e.g. Pt, Pd, and Ir), nickel and cobalt has drawn many attentions in recent researches. Ni/CeO$_2$ showed good catalytic performances, which provided this metal with a potential to be used in the HI decomposition [10]. Pt/MCM-41 were found to be effective and stable catalyst [11]. And Ni/Activated Carbon (Ni/AC), relatively low-cost catalyst, showed good catalytic activity in HI decomposition at 773 K, even equivalent to the thermodynamic yield [12]. However, the dispersed metal clusters were deactivated fast with time-on-steam due to the high temperature (723–773 K) and corrosive chemical environment (HI-H$_2$O-I$_2$ ternary system). Wang et al. reported that after catalyzing HI decomposition reaction at 723 K, the average size of Pt cluster sintered from 25 nm to 45 nm [13]. Fu et al. also discovered the average diameter of dispersed Ni cluster increased dramatically from 11.4 nm to 94 nm after catalytically converting HI to hydrogen at 773 K for 24 h [14]. The agglomeration of metal clusters leads to a significant loss in catalytic activity. To date, many carbonaceous materials, such as activated carbon (AC), carbon molecule sieve (CMS), and graphene, have been proposed as catalysts for HI decomposition. The structure analysis reveals that activated carbon was composed by disordered graphite-like layers with weak inter-layer correlations [15]. The experimental results demonstrate that this disordered graphite-like structure remains a very high activity in HI decomposition reaction for a long time; no obvious deactivation was observed during lifetime evaluation in HI decomposition at 773 K for 12 h [4].

Concerning the high price of graphene, CMS and AC, a lower cost of stable carbon material needs to be developed for HI decomposition. Semi-coke (SC) is a by-product of coal pyrolysis at relative low temperatures (~ 873 K). In many developing countries, such as China and India, coal industry produced very large amount of semi-coke every year. How to use the semi-coke is becoming a thorny problem in these countries. Consequently, semi-coke is much cheaper than Pt, Pd, Ni, CMS, Graphene, etc. Semi-coke is composed of carbon, ash, and volatile. Due to its special physical, chemical, and mechanical properties, semi-coke has been employed as a catalyst in some reactions (e.g.

methane dry reforming [16] and desulfurization [17]). Herein, evidences were provided to prove that semi-coke modified by hydrofluoric acid (HF) could be a highly active and low cost catalyst for HI decomposition. Raw semi-coke shows a good activity in converting HI to hydrogen; hydrofluoric acid treatment further improves its catalytic activity to a large extent. Semi-coke modified by 40 wt% hydrofluoric acid (SC-40HF) shows even higher activity than AC, a good commercial catalyst, in all investigated temperature range, indicating that SC-40HF would be a promising catalyst candidate for HI decomposition in large-scale SI thermochemical cycle in the future.

2. Experimental details

The commercial catalyst AC was purchased from Shanghai Activated Carbon Co., Ltd. The raw semi-coke (denoted as SC) was produced directly from Zhaotong lignite coal by heating at 0.167 K s^{-1} in flowing nitrogen (N$_2$) to 1073 K and then holding isothermally at 1073 K for 1 h, prior to cooling down to room temperature. The modified SCs (SC-10HF, SC-25HF, and SC-40HF) were treated by hydrofluoric acids (analytical reagent; Shanghai Chemical Reagent Co.) of different concentrations (10%, 25%, and 40%, respectively). Typically, 100 cm^3 hydrofluoric acid of certain concentration was added to 10 g of SC, which was in a Teflon flask equipped with a condenser. The mixture was kept isothermally at 353 K for 3 h in the water bath under server stirring and then filtered, washed in deionized water until pH reached 7. After washing, the modified SC was dried in vacuum at 383 K overnight prior to reactivity test and characterization.

N$_2$ adsorption isotherms, specific surface areas, pore volumes, and pore sizes of the samples (AC, SC, SC-10HF, SC-25HF, and SC-40HF) were characterized at 77 K by Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2020 apparatus. X-ray diffraction (XRD) profiles of the samples were acquired by employing a Rigaku K/MAX2550/PC X-ray powder diffractometer with a Cu K-a radiation. The XRD patterns were recorded in the range of $10° \leq 2\theta \leq 90°$ with intervals of 0.02°. The Raman spectra were recorded on a Raman Spectrometer (Themo Fisher, USA) at room temperature with a laser wavelength of 532 nm, and power of 3.0 mW in the investigation range of 900–3300 cm^{-1}. Peakfit v4.12 was used to analyze the Raman spectra by peak fitting with different peak combinations and the results are discussed.

The catalytic activity measurement system was schematically showed in Fig. 2. Typically, the catalytic activities of the five carbon material samples (AC, SC, SC-10HF, SC-25HF, and SC-40HF) were measured in a micro-catalytic plug flow reactor (quartz, 18 mm inner diameter) equipped with a K-type thermocouple that was placed at the outside of the packed catalyst bed. 0.7 mL/min hydroiodic acid (55 wt% HI solution from RiZhaoLiDeShi Chemical Co.) was pumped into an evaporator by a peristaltic pump (BT100-2J, LongerPump Co.). N$_2$ was employed as a carrier gas by thermal mass flow controller (Alicat 111579) to maintain a constant space velocity of 3600 cm^3 g$_{cat}$$^{-1}$ h^{-1}.
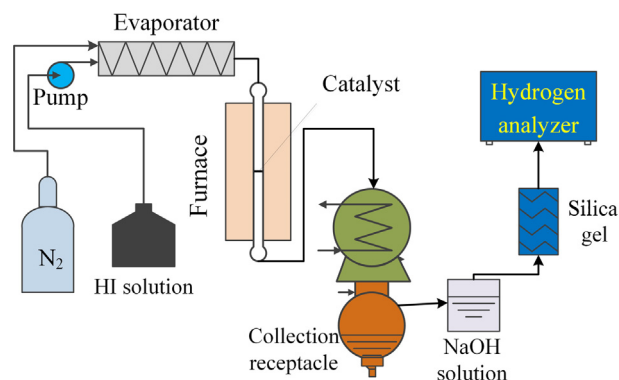

Fig. 2. Schematic of the experimental setup for activity measurement.