



Catalytic performance of different carbon materials for hydrogen production in sulfur–iodine thermochemical cycle

Yanwei Zhang*, Rui Wang, Xiangdong Lin, Zhihua Wang, Jianzhong Liu, Junhu Zhou, Kefa Cen

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

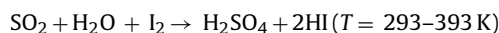
This study examines four carbon materials through a series of characterization methods and a hydrogen iodide (HI) decomposition test. Applying a traditional structure to carbon materials facilitates the quantitative analysis of the four samples. The X-ray diffraction and Raman spectroscopy results indicate that lesser stacked graphite-like layers and shorter lateral diameter L_a result in higher disordering structure. However, the quantity of active sites is not determined only by the degree of disordering. The aliphatic carbon in the inter-layer correlations decreases the amount of graphite carbon and occupies its edge, thereby inhibiting the formation of edge sites in carbon materials. A low ratio of amorphous carbon with a high degree of disordering corresponds to a high concentration of surface active sites associated with the edges of graphite-like layers. The catalytic performance combined with characterization results demonstrates that the edges of graphite carbon are active sites in HI decomposition. A computational chemistry study is also conducted to illustrate the dominant role of edge sites in the reaction. The calculation results build a detailed mechanism of the catalytic decomposition of HI over the carbon materials and verify that the adsorbed I on the edge sites facilitate the HI decomposition.

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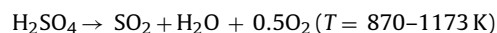
1. Introduction

Hydrogen is considered an alternative source of energy because of its environmentally friendly characteristics. An efficient hydrogen production system is necessary in developing a hydrogen energy system. The thermochemical water-splitting cycle, which produces hydrogen and oxygen from water through a series of correlative chemical reactions, has attracted much attention in current research. The inputs in thermochemical cycles are heat and water; other intermediates are not consumed and are recycled in the process. Among various potential thermochemical cycles, the sulfur–iodine (SI) thermochemical cycle presents significant advantages. The SI cycle involves three reactions:

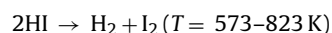
Bunsen reaction :



Sulfuric acid decomposition :



Hydrogen iodide decomposition :



The decomposition of hydrogen iodide (HI) serves as the step toward hydrogen evolution in several thermochemical water-splitting steps. However, the homogeneous gas-phase conversion during the decomposition is rather low, occurring below 833 K. The use of catalysts is therefore desirable to accelerate the reaction rate. Early studies that sought to identify active catalysts were mainly conducted in the late 1970s and 1980s and have been well summarized by O'Keefe et al. [1]. A series of activated carbon (AC)-based catalysts have also been discussed recently [2–8]. Such studies lead to the conclusion that the Pt catalysts have the best catalytic performance, but their catalytic activities are only slightly higher than those of unmodified ACs above 700 K. Thus, AC is an economical alternative to noble metal catalysts for large-scale hydrogen production.

AC has been studied in many catalytic reactions for its high surface area, well-developed porous structure, and variable

* Corresponding author. Tel.: +86 571 87952040; fax: +86 571 87951616.
E-mail address: zhangyw@zju.edu.cn (Y. Zhang).

surface compositions. The performance of a catalyst depends on the availability of suitable active sites capable of chemisorbing the reactants and forming surface intermediates of adequate strength. In last few decades, many papers focused on the structural characterization and nanostructures of AC have been published [9–14], given that knowledge of such structures are bound to directly affect the number of reactive sites [15–17]. The structural analysis of ACs and other disordered carbons provides a direct perspective for the quantitative analysis of reactive sites [15,18]. The structure of the nano-crystalline forms of AC generally consists of what can be described as disordered graphite-like layers with very weak inter-layer correlations or random stacking [19,20]. The disordered graphite-like layers are mainly composed of micro-graphite in nanometer scale with a short-range order that varies across different carbon materials. The inter-layer correlations are usually made up of aliphatic carbon or other saturated carbon species. Various characterization techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), and Raman spectroscopy, have been utilized in examining the structure of carbon materials. Raman spectroscopy has become the standard characterization method for carbon materials because of its capacity to provide information on the crystalline size, ratio of sp^2 (graphite-like layers) to sp^3 (inter-layer correlations), ordering of the graphite-like layers, and many other such unique data [10,21–23]. XRD is the most common method used in describing carbon materials in terms of various parameters, including average in-plane length (L_a), average height (L_c), average inter-planar distance (d_{002}), 3D ordering of the graphite-like layers, and density and type of defects [14,24]. Other characterization methods, such as AFM and STEM, provide an accurate representation of the carbon structure and defect content.

In this study, the characteristics of AC and other three carbon materials were examined through a series of instruments and were associated with the catalytic activities of the carbon materials. A traditionally structured model was applied to the four materials for the quantitative analysis of the carbon structure. The quantities of the active sites in the materials were evaluated through an effective structural model with several characterization methods. A detailed mechanism of the catalytic decomposition of HI over the carbon materials was also established.

2. Experimental setup

2.1. Catalyst preparation

The four samples—AC, multiple-walled carbon nanotubes (MWCNT), carbon black (CB), and carbon molecular sieves (CMS)—were obtained from JCNANO Co. The AC used in this study is coconut-shell activated carbon, and it is produced by $ZnCl_2$ activation. They were crushed into powder (40–60 ASTM mesh fraction) and vacuum dried for 2 h. All of the four samples were heated from room temperature to 873 K under flowing nitrogen at 5 K/min and then kept at that temperature for 3 h to remove their functional groups.

2.2. Catalyst characterization

The porosity of each sample was analyzed using a Micromeritics 2020 ASAP porosimeter. Their nitrogen adsorption and desorption isotherms were obtained at 77 K after degassing. The BET surface area was calculated from the N_2 adsorption data at relative pressures of $0.05 < P/P_0 < 0.3$. The total pore volume was calculated from the amount of N_2 adsorbed when $P/P_0 = 0.99$. The

density functional theory (DFT) model was used to analyze the results.

The XRD patterns of the catalysts were acquired using a Rigaku K/MAX2550/PC XRD. Cu K- α radiation was employed at a working voltage and current of 40 kV and 100 mA, respectively. The XRD patterns were recorded at intervals of 0.02° in the range of $10^\circ \leq 2\theta \leq 80^\circ$. The PeakFit v4.12 was used to deconvolute the diffraction patterns in the 2θ region of $15\text{--}32^\circ$. The broad hump in this region was fitted to two Gaussian peaks around 20° and 26° , which represented the γ - and π -bands (d_{002}), respectively. The areas below the γ - and π -peaks are theoretically acknowledged to be equal to the number of aromatic and aliphatic carbon atoms, respectively. The aromaticity (A_{arom}) of the studied carbon materials—the ratio of carbon atoms in aromatic rings to the aliphatic chains—was calculated based on the literature [25].

Scanning electron microscopy (SEM) observation of the catalysts was performed on a Hitachi S-4800 operated at 5–20 kV. Samples were mounted on aluminum stubs using double-sided tapes. The images were obtained in the secondary electron mode in conjunction with SEM imaging.

The crystallite structure of the four catalysts was characterized by high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20). The powders were gently ground and dispersed in carbon film-coated copper grids by dipping the grids into a methanol suspension of the powder.

The surface oxygen-containing groups of the supports were characterized by the temperature-programmed desorption mass spectrometry (TPD-MS) method with an apparatus consisting of a Micromeritics AutoChem II 2920 and a Hiden QIC20 quadrupole mass spectrometer. Approximately 0.1 g of the sample was loaded into a quartz U-tube with an inner diameter of 10.0 mm. Prior to the desorption experiments, the samples were degassed for 1 h in a helium stream [50 cm^3 (STP)/min] at 383 K. The temperature was then increased to 1373 K at a heating rate of 10 K/min. The evolution of carbon dioxide ($m/z = 44$) and carbon monoxide ($m/z = 28$) was monitored by the quadrupole mass spectrometer.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo XPS ESCALAB 250Xi instrument with Al K α (1486.8 eV). The X-ray source and samples were maintained under ultra-high vacuum conditions ($<10^{-9}$ mbar). The binding energies were calibrated using the containment carbon (C 1s = 284.5 eV). XPS Peak 4.1 was applied to deconvolve the C 1s peaks using the Shirley-type baseline and an iterative least-squared optimization algorithm.

A model of the DXR smart Raman spectrometer (Thermo Fisher, USA) was used to analyze the structure of the materials at a laser wavelength of 532 nm, power of 3.0 mW, and collection exposure time of 7.5 s. The deconvolution of the Raman spectra was conducted using PeakFit v4.12.

2.3. Activity tests

Fig. 1 shows the schematic illustration of the experimental setup consisting of quartz and glass. The catalytic reaction was conducted at the atmospheric pressure in a quartz tube reactor (inner diameter = 18 mm) placed vertically in an electrically heated tube furnace. The heated evaporator was set at 433 K to ensure the flash vaporization of the HI solution flash. N_2 was used to drive the vaporized HI through the system. Unreacted HI, H_2O , and I_2 were trapped and collected through a spiral condenser. The gaseous products (H_2 and N_2) were analyzed using an online hydrogen analyzer (K522, HITECH INSTRUMENTS Ltd) after purification with NaOH solution and silica gel. Other apparatuses included a BT100-2J peristaltic pump (LongerPump) and a mass flow controller (Alicat Scientific) for N_2 . The catalytic decomposition of HI was performed from 573 K

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