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Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen iodide in the sulfur–iodine cycle for hydrogen production

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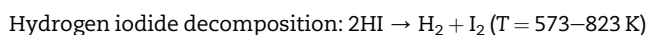
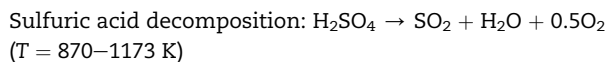
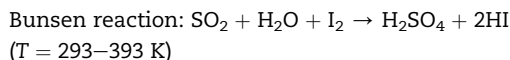
ABSTRACT

Coal-based activated carbon (AC-COAL) catalysts subjected to acid treatment were tested to evaluate their performance on hydrogen-iodide (HI) decomposition for hydrogen production in sulfur-iodine (SI or IS) cycle. The effects of acid treatment on catalysts and the relations between sample properties and catalytic activities were discussed. The AC-COAL obtained by non-oxidative acid treatments had the best catalytic activity. However, the catalytic activity of AC-COAL decreased after the treatment of nitric acid. Higher surface area, higher carbon contents, lower ash contents and fewer surface oxidation groups contributed to the catalytic activity of ACs. HI decomposition on the AC surface itself may be due to high densities of unpaired electrons associated with structural defects and edge plane sites with similar structural ordering. Moreover, the oxygen-containing groups reduced the electron transfer capability associated with the basal plane sites.

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1. Introduction

Hydrogen is a kind of environmentally friendly fuel, and it has the potential to replace fossil fuels. Since the late 1970s, thermochemical water-splitting cycles for hydrogen production have been studied. Such cycles produce hydrogen from water via a series of chemical reactions at much lower temperature than direct thermal decomposition. The sulfur–iodine (SI or IS) cycle is proposed by General Atomics [1], and it is one of several promising candidates for large-scale hydrogen production. This cycle involves three reactions:



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Table 1 – Conditions of the acid treatments applied to the AC catalysts.

Samples	Conditions
AC-COAL	Original samples obtained from SHHXTC
COAL-CLF	Both 5 M hydrochloric acid and 25 wt.% hydrofluoric acid treatment on AC-COAL at 60 °C for 3 h
COAL-30HN	2 M nitric acid treatment on COAL-CLF at 30 °C for 3 h
COAL-60HN	2 M nitric acid treatment on COAL-CLF at 60 °C for 3 h
COAL-90HN	2 M nitric acid treatment on COAL-CLF at 90 °C for 3 h

The overall cycle is quite similar to water decomposition, which produces hydrogen and oxygen. In the cycle, SO₂ and I₂ are fully recycled. The high-temperature heat applied in the cycle can be supplied by nuclear or solar energy.

The HI decomposition is the key reaction to produce hydrogen in several thermochemical water-splitting cycles. However, the homogeneous gas-phase conversion during the decomposition is rather low below 833 K. Thus, the use of catalysts is desirable to accelerate the reaction rate. The early studies on identifying active catalysts were conducted and summarized in 1980s [2]. A series of activated carbon (AC)-based catalysts were discussed recently [3–5]. It could be concluded that the Pt catalysts had the best catalytic performance, but their catalytic activities were 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. Carbon materials have been commercially produced and widely used as catalysts. ACs are considered as amorphous carbon materials. They possess a microcrystalline structure, where aromatic grapheme layers are disordered and separated by distances. In addition, their well-developed porous structure, high surface area and multiple surface compositions result in distinct differences in their reactivity. The structural ordering of an AC depends on the preparation method and on the precursor [6]. The catalytic activity of different kinds of ACs was examined to understand the relations between sample properties and catalytic activity in the literature [7–9]. However, no clear relations were found, because the AC catalysts were obtained either from different raw materials [7] or different activated methods [8].

In the current work, coal-based activated carbon (AC-COAL) catalysts subjected to acid treatment were tested for the decomposition of HI to explore the effects of acid treatment on catalysts and the relations between sample properties (especially surface chemistry) and catalytic activities, thus ensuring that the structural ordering of each catalyst is similar. Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), proximate and elemental analyses, scanning electron microscopy (SEM), as well as temperature-programmed desorption (TPD)-mass spectrometry (MS) were carried out for the catalyst characterization.

2. Experimental

2.1. Catalyst preparation

Commercial AC-COAL, provided by Shanghai Activated Carbon Co., Ltd., was used as starting materials. The AC catalysts used in this study were crushed into powder (40–60 ASTM mesh fraction) and then vacuum dried for 2 h. ACs with different sample properties such as textural features and surface chemistries were chemically obtained by different acid treatments. In the acid treatments, 50 cm³ of acids was added to 5 g of AC-COAL which was put in a conical glass flask equipped with a condenser to prevent the acid leakage. The mixture was heated in water bath with continuous stirring for 3 h, then filtered, washed with distilled water, and oven dried at 383 K. Table 1 summarizes the conditions of acid modification treatment for AC-COAL catalysts used in this study. Thus, the ash compounds of AC-COAL were removed with hydrofluoric and hydrochloric acids, and the obtained COAL-CLF was oxidized with nitric acid. The AC catalysts produced by nitric acid treatment at different temperatures were denoted as COAL-30HN, COAL-60HN and COAL-90HN.

2.2. Catalyst characterization

The surface areas and pore volumes of the samples were determined at 77 K by the BET method, and the adsorption measurements were performed on a Micromeritics ASAP 2020. Powder XRD patterns were obtained from a Rigaku K/MAX2550/PC X-ray powder diffractometer with Cu-K α radiation. The surface morphology of the catalysts was observed on a Hitachi S-4800. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur was determined on a LECO CHNS-932 Elemental Analyzer. Proximate analysis of the air-dried ACs was performed on a thermogravimetric analyzer (TGA/SDTA851). The proximate analysis was measured following the ISO 11722, 351, 17246 and 1171, while the elemental analysis was measured following the ISO 17247. The surface oxygen groups were obtained by TPD-MS with a custom built apparatus, consisting of a Micromeritics AutoChem II 2920 and a Hiden QIC20 quadrupole mass spectrometer.

2.3. Activity tests

Fig. 1 shows the experimental setup built of quartz and glass. The catalytic decomposition was conducted in a quartz tubular reactor (inner diameter = 18 mm) at atmospheric pressure. The evaporator was set at 433 K to ensure the flash vaporization of HI solution. N₂ was employed to drive the vaporized HI through the system. Unreacted HI, H₂O and I₂ were trapped and collected by a spiral condenser. The gaseous products (H₂ and N₂) could be measured by an online hydrogen analyzer (K522, HITECH INSTRUMENTS Ltd) after purification with NaOH solution and silica gel. The other apparatus included a BT100-2J peristaltic pump (LongerPump) and a mass flow controller (Alicat Scientific) for N₂.

The catalytic decomposition of HI was performed at 573–823 K. About 1 g of catalysts was uniformly mixed with coarse quartz chips fixed in the quartz tube reactor. HI

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