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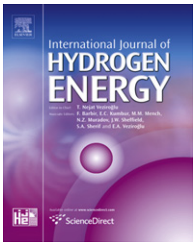

Activity and stability of Pt catalysts supported on carbon nanotubes, active carbon and γ-Al_2O_3 for HI decomposition in iodine–sulfur thermochemical cycle

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ABSTRACT

Pt catalysts supported on carbon nanotubes (CNT), activated carbon and γ-Al_2O_3 were prepared by the electroless plating method. For comparison, the CNT supported Pt was also prepared by the traditional impregnation–reduction method. The physical properties, structure, morphology and Pt loadings of the different catalysts were characterized by BET, XRD, TEM and ICP, respectively. The catalytic activity for HI decomposition was investigated in a fixed bed reactor under atmospheric pressure. The results of XRD and the activity evaluation indicated that the Pt/CNT prepared by the electroless plating method had better catalytic performance than that prepared by the impregnation–reduction method. Among the three kinds of supported Pt catalysts by the electroless plating method, the CNT supported Pt catalyst not only showed the highest activity for HI decomposition, but also had the best stability in specific surface area, structure and morphology.

1. Introduction

Recently, the Iodine-Sulfur thermochemical water splitting cycle (IS cycle) has attracted increasing attention because it is a promising candidate for high efficient and large-scale hydrogen production without CO_2 emissions [1–5]. The IS cycle is composed of the following three chemical reactions [1]:

Bunsen reaction: $SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4$ (1)

H_2SO_4 decomposition reaction: $H_2SO_4 = SO_2 + 1/2O_2 + H_2O$ (2)

HI decomposition reaction: $2HI = H_2 + I_2$ (3)

Since the IS cycle was first proposed by General Atomic (GA) in the 1970s, researchers from different institutes have done many useful studies on the chemistry and the process engineering about the IS cycle [1–20]. In the past decades, studies of IS cycle have been focused mainly on the demonstration of the closed-cycle continuous water splitting. In 2004, Japan Atomic Energy Agency (JAEA) built a glass

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Nomenclature

AC	Active carbon
BET	Brunauer–Emmett–Teller method
CNT	Carbon nanotubes
E-Pt/CNT	CNT supported Pt catalyst prepared by the electroless plating
FWHM	Full width at half maximum
H-Pt/CNT	CNT Supported Pt catalyst prepared by the impregnation–reduction
HTGR	High temperature gas-cooled reactor
ICP-AES	Inductively coupled plasma atomic emission spectrometry
Pt/AC	AC Supported Pt catalyst prepared by the electroless plating
Pt/Al_2O_3	γ-Al_2O_3 Supported Pt catalyst prepared by the electroless plating
S_{BET}	The specific BET surface area
TEM	Transmission electron microscopy
XRD	X-ray diffractometer

apparatus with a hydrogen production rate of about 30 L/h and closed-cycle continuous water-splitting was demonstrated for one week [5,6]. In 2008, an integrated lab-scale test facility with the designed hydrogen production rate of about 200 L/h was constructed with industrial materials by the cooperation of GA, Sandia National Laboratory (SNL), and Commissariat à l'Energie Atomique (CEA) [7]. Recently, the lab-scale H_2 producing apparatuses were also built by Korea Atomic Energy Research Institute (KAERI), Italian National Agency for New Technology, Energy and Environment (ENEA), and INET (Institute of Nuclear and New Energy Technology, Tsinghua University), respectively [8–10]. A nuclear hydrogen research project is being proceeded at INET with the aim of coupling the IS cycle with the High Temperature Gas-cooled Reactor (HTGR) with thermal power of 10 MW [11]. In 2009, a lab-scale glass apparatus IS-10 with a H_2 production rate of 10 L/h was built and the closed-cycle loop was operated stably for several hours [10]. At present, INET is designing and building the bench scale facility IS-100 with a designed H_2 production rate of 100 L/h. In this paper, different supported Pt catalysts were studied in order to prepare suitable catalyst for HI decomposition in the bench scale facility IS-100.

The decomposition of HI is the key reaction to produce hydrogen in the IS cycle and occurs hardly without the catalysts even at 500 °C. In order to make the HI decompose rapidly and effectively, many kinds of catalysts have been used to catalyze this reaction at a certain temperature [12]. Among the various HI decomposition catalysts which mainly included the noble metals (such as Au and Pt), supports materials (such as active carbon, Al_2O_3, and Ce_2O), and supported transition metals (such as supported Pt, supported Ni, and supported Pd) [9,12–23], supported Pt catalysts were found to have good activity for HI decomposition. Furthermore, the catalytic performance of platinum catalyst was support-dependent, which meant the supports played the very important role in dictating the catalyst activity. Among the different supported platinum catalysts, the active carbon (AC) supported platinum catalyst had been verified to show the excellent activity for HI decomposition [12,18].

As a kind of carbon materials, carbon nanotubes (CNT) with special mechanical and electronic properties have been used as a promising support for metal catalysts. For example, CNT supported Pt and Ru nanoparticles performed some unusual catalytic properties [24–26]. However, as far as the authors know, there have been only a few studies so far on the use of CNT as the support of the catalyst for HI decomposition. Liberatore et al. from ENEA first reported that the CNT supported Pt had very good activity for HI decomposition [9]. Recently, in our previous studies of HI catalytic decomposition for the lab-scale H_2 producing apparatus of IS-10, the CNT supported Pt catalyst was found to have better catalytic performance than the active carbon supported Pt catalyst [23]. Researches of ENEA and INET revealed that CNT supported Pt had excellent activity for HI decomposition. However the stability in activity, specific surface area, structure and morphology for CNT supported Pt catalyst in HI decomposition and its comparisons with other conventional supported Pt catalysts (such as active carbon supported Pt, and Al_2O_3 supported Pt) have not been studied systematically. In this paper, the activity and stability of the CNT supported Pt, active carbon supported Pt, and Al_2O_3 supported Pt catalysts prepared by the electroless plating method were studied for HI decomposition. For comparison, the CNT supported Pt prepared by the traditional impregnation–reduction method was also studied. In the course of the study, XRD (X-ray diffractometer), specific surface area (BET), and transmission electron microscopy (TEM) techniques were used to characterize the differences in structure, surface area, and morphology for different supported Pt catalysts before and after HI decomposition.

2. Experimental

2.1. *Catalyst preparation*

The employed support of CNT was obtained from Chemical Engineering Department of Tsinghua University. Pretreatment of the as-received CNT was carried by immersing the material in a solution of 4.5 M H_2SO_4 and 0.38 M $K_2Cr_2O_7$, followed by refluxing at 60 °C for 6 h under vigorously agitation. The recovered materials were filtrated, washed thoroughly with distilled water, dried in air at 120 °C for 4 h, and finally sieved to retain particles with sizes between 40 and 60 mesh.

Two kinds of methods were used to prepare the CNT supported Pt catalysts. One was the conventional impregnation–reduction method. The pretreated carbon nanotubes were added into a certain amount of hexachloroplatinic acid aqueous solution, stirred at room temperature for 4 h, filtrated by membrane, and dried at 120 °C for 4 h in an oven. The resulting solid was reduced by H_2 at 350 °C for 2 h. The resultant catalyst was denoted as H-Pt/CNT. The other preparation method was the electroless plating method [17,20]. First, the pretreated carbon nanotubes were activated by