



Ruthenium nanoparticles supported over carbon thin film catalyst synthesized by pulsed laser deposition for hydrogen production from ammonia borane

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ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form 21 January 2015

Accepted 22 January 2015

Available online 30 January 2015

Keywords:

Ammonia borane

Hydrolysis reaction

H₂ generation

Ru/C thin film catalyst

Laser ablation

ABSTRACT

Ruthenium nanoparticles (NPs) supported over carbon thin films (Ru/C thin films) catalysts were synthesized by pulsed laser deposition and used as catalysts for hydrolysis of ammonia borane (AB). Highly irregular and porous carbon films with high surface area were deposited by varying Ar gas pressures during the deposition. By taking the advantage of phase explosion phenomena, occurring at high laser fluence, the surface of the carbon films were decorated with crystalline Ru NPs with size below ~10 nm. Ru/C thin film catalyst produced H₂ with 6 times higher H₂ generation rate as compared to unsupported Ru NPs assembled film, and with a high turnover frequency value of 70.5 mol H₂ mol⁻¹ Ru min⁻¹. A combination of morphological features and high content of sp² bonded C atoms provides good dispersion of Ru NPs over a large surface area. Both these features contribute in generating large number of active sites leading to the increase in catalytic efficiency. A possibility of using the present form of catalyst as an ON/OFF switch for H₂ production was also tested. Although the catalytic activity decreased with the number of hydrolysis cycles, Ru/C thin film catalyst was able to generate the expected amount of H₂ gas in each cycle when it was reused several times. The observed low activation energy (~28 kJ mol⁻¹) and high H₂ generation rate (15.5 L H₂ min⁻¹ g⁻¹ of Ru) by hydrolysis of AB suggest that Ru/C thin film catalyst is highly efficient.

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1. Introduction

A proton exchange membrane fuel cell (PEMFC), using pure hydrogen as a fuel, is a clean and efficient alternative power source for transportation and personal electronic appliances, where system weight and portability features are important [1]. At present, H₂ required for PEMFC is mostly produced at industrial scales using the steam reforming of natural gas. These industries leave CO and CO₂ into atmosphere which are the major known culprits to the devastating climate changes witnessed today. Moreover, improper separation of these carbon contaminations from H₂, especially CO (even at ppm level), affects the performance of PEMFC by catalyst poisoning [2]. A system with high gravimetric and volumetric capacity of storing H₂ for safe transportation, along with the ability to supply pure hydrogen conveniently is still under

development. Ammonia borane (NH₃BH₃, AB), which is a strong candidate material for such a system, is stable, non-flammable, non-toxic, and is able to store hydrogen with a capacity of 19.6 wt.% [3,4]. Most importantly AB provides pure hydrogen at room temperature through solvolysis reaction. These distinct advantages of AB make it a promising on-board hydrogen generation method for portable PEM fuel cells.

Catalyst is the key material to control the H₂ generation rate (HGR) during the hydrolysis reaction of AB. Heterogeneous route of catalysis involving metal catalysts has been found to be very efficient in accelerating HGR. Various noble and non-noble metal catalysts like Rh [5], Pd [6], Ru [7], Co [8], Ni [9] and Fe [10] nanoclusters, Ru/C powder catalyst [6], K₂PtCl₆ [11], NiAg [12], Ni@Ru [13], Ru, Rh and Pt supported over γ-Al₂O₃ [14], Co/γ-Al₂O₃ [15], nickel and cobalt borides [16–19], etc., have been generally used to produce hydrogen by hydrolysis of AB. Among all the catalysts, platinum group metals including Pt [14], Rh [20] and Ru [7] based catalysts have delivered a remarkable performance in hydrogen production as compared to other catalysts, and have been identified as a stable catalyst against deactivation. However, recently, Ru-based catalysts are highly investigated for

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hydrolysis of AB namely: ruthenium (0) nanoparticles (NPs) supported on hydroxyapatite [21], bimetallic-based RuCo and RuCu alloy supported on γ -Al₂O₃ [22], graphene supported Ru NPs [23], water soluble laurate-stabilized ruthenium (0) nanoclusters catalyst [7], Ru/ γ -Al₂O₃ nanopowder [24,25], Ru(acac)₃ [26], Ni@Ru [13], NiRu alloy [27], and PSSA-co-MA stabilized ruthenium (0) nanocluster catalyst [28], etc. Nevertheless, all the catalysts used are in powder form which has the problem related to separation and aggregation during the course of the reaction. These problems can be overcome by using a catalyst in the form of a supported thin film. Along with easy recovery and reusability properties, supported thin film catalyst can also serve as suitable tool for ON/OFF switch for H₂ production in transport vehicle thus exhibiting the tag of “green catalyst”. In addition, surface morphology and structure can be tuned to acquire better catalytic properties by just controlling the thin film deposition parameters. In our previous works [29–32], thin film nano-catalysts synthesized by pulsed laser deposition (PLD) in form of nanoparticles (NPs) assembled films, showed outstanding performance for hydrogen production in catalytic hydrolysis reaction of NH₃BH₃ and NaBH₄.

In order to support thin film catalyst, porous materials such as carbon, silica, and alumina, are usually chosen as they provide a large active surface area and better dispersion of an active phase due to their intrinsic morphology. In addition, support can retard the sintering of an active phase, improve the dissipation of the reaction heat, increase the poison resistance and facilitate the diffusion of reactants through the pores. High chemical inertness, particularly in strong basic and acid environments, and good interactive nature with the active metals, make carbon the most promising support for an active catalyst [33–35]. It also provides flexibility to produce selected morphology and porosity [36]. The absorptive properties of carbon can be tuned by simply decorating the surface of carbon with oxygen-containing groups with acidic, neutral, or basic nature [37]. Ru supported over black carbon [6], multi-walled CNT [38], and graphene [22], displayed outstanding catalytic activity for hydrolysis of AB with very high stability. In all the cases, the enhanced activity is attributed to the role played by carbon in providing high surface area and in dispersing the Ru NPs on the surface to make available good number of active sites. However because in all the cases, Ru was in powder form, the separation and aggregation problems discussed earlier still remains as a barrier for scalability. In addition, none of the above mentioned literatures on supported Ru catalyst have examined the role of morphology and structure of carbon-based support on the dispersion and catalytic activity of Ru active metal.

In the present work, Ru NPs supported on carbon thin film (Ru/C thin film) catalyst was synthesized using PLD. Rough and porous morphology of carbon film, synthesized under different Ar gas pressures, provides high surface area and enhances dispersion of Ru NPs to significantly improve the HGR by hydrolysis of AB. Ru/C thin film catalyst was also tested as an ON/OFF switch for H₂ production along with its reusability property.

2. Experimental

2.1. Catalyst synthesis

Deposition of all the films were performed by PLD technique in a stainless steel vacuum chamber evacuated to a base pressure of 10⁻⁴ Pa. KrF excimer laser (Lambda-Physik, LPX 220i) having wavelength of 248 nm and a pulse duration of 25 ns was used for the ablation. The targets were irradiated with a laser beam tilted at an angle of 45° by focusing through an aperture using fused silica lens (400 mm focal length). Further details about the deposition apparatus are reported in Ref. [39]. Highly oriented pyrolytic

graphite (99.99%) and pure ruthenium (99.9%) targets were ablated to deposit the C and Ru films, respectively, by keeping target-to-substrate distance of around 4 cm for all the experiments. Carbon films were deposited by using the laser fluence of 4 J/cm² under vacuum condition and under different Ar pressures ranging from 30 to 50 Pa. Deposition of Ru was later carried out in situ, at room temperature, over the carbon films under vacuum condition with laser spot energy density of 5 J/cm². In order to study the role of the carbon support, pure Ru film was deposited directly on a glass slide in absence of carbon support film. All films were deposited on glass substrates for measuring their catalytic activity and on silicon substrates for morphological, compositional and structural characterizations. Weight of all the catalyst films was maintained constant (Ru/C ~3 mg, with 10 wt.% Ru) which was confirmed by measuring the weight of the glass slide (with surface dimensions of 76 mm × 46 mm), before and after deposition.

2.2. Catalyst characterization

The surface morphology of all the catalyst samples was studied by scanning electron microscope (SEM-FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy analysis (EDS, INCA PentaFET-x3) to determine the composition of the samples. Particle size and the structure of the Ru and Ru/C thin film catalysts deposited on copper grid were examined using a transmission electron microscope (TEM, JEOL-JEM 2100F and energy of 200 keV). Raman spectra of the carbon films, prepared at different pressures, were recorded by using HORIBA JobinYvon Lab RAMAramis Raman spectrometer with diode pumped solid state laser at 532 nm.

2.3. Hydrogen generation measurement

Aqueous solution of ammonia borane (Sigma–Aldrich) of 0.25 wt.% was prepared for catalytic activity measurements performed by gas volumetric method. Detailed description of the measurement apparatus can be found elsewhere [40]. For all the reported experiments, fixed volume of above AB solution was maintained at desired temperature and then the catalyst film was inserted into this solution under constant stirring. H₂ production rate was evaluated by curve-fitting the plot of the amount of H₂ produced, measured from the weight of the water displaced, against the reaction time. To determine the activation energy involved in the catalytic hydrolysis, H₂ generation rate was measured at different solution temperatures. Reaction kinetics dependency on the amount of active metal catalyst was also investigated.

3. Results and discussion

3.1. Morphological analysis of Ru and Ru/C thin film catalysts

SEM images of pure Ru film and Ru supported on carbon film (Ru and Ru/C thin films) are presented in Fig. 1. The surface of the Ru film (Fig. 1a) was composed of non-spherical particles with narrow size distribution in the range of 4–10 nm with an average size of ~6.5 nm (Fig. 1b). The presence of these NPs is due to the phase explosion process induced by high laser fluence during ablation of target material [41]. In this process the high energy density of laser beam irradiation causes a superheating of the region below the target surface beyond the limit of thermodynamic stability of the material (~90% of the thermodynamic critical temperature, T_c) inducing a homogeneous nucleation of vapor bubble [42]. The target surface then makes a rapid transition from superheated liquid to a matrix of vapor and nano-size liquid droplets, which leave the irradiated target surface and get deposited on the substrate. Since these Ru NPs were deposited on plane glass substrate, the active surface is basically 2D. In addition, the Ru NPs are attached to each

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