Journal of Alloys and Compounds 744 (2018) 110–115

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Nanoporous Pt and Ru catalysts by chemical dealloying of Pt-Al and Ru-Al alloys for ultrafast hydrogen generation

Levent Semiz, Nazrin Abdullayeva, Mehmet Sankir*

Department of Materials and Nanotechnology Engineering, TOBB University of Economics and Technology, Sogutozu C. No 43, Sogutozu, 06560, Ankara, Turkey

A R T I C L E I N F O

Article history:
Received 7 April 2017
Received in revised form
6 February 2018
Accepted 8 February 2018
Available online 9 February 2018

Keywords:
Alloying
Dealloying
Hydrogen generation
Precious metals
Platinum
Ruthenium

A B S T R A C T

Novel nanoporous catalysts from selective dissolution of alloys have been prepared for fast hydrogen generation from chemical hydrides. Pt and Ru have been used as precious metals in the alloys, while the nonprecious metal is Al. The alloy composition has been arranged by sputtering power of Al, which is varied from 200 to 400 W for Pt-Al and Ru-Al alloys. The influence of particle size on the sputtering power of Al has been demonstrated. The particle size of the Pt nanoparticle decreases from 900 to 90 nm when the sputtering power of Al is increased from 200 to 400 W. However, the particle size of the Ru nanoparticle decreased from 610 to 55 with the same increase in Al sputtering power. The hydrolysis reaction rate of $NaBH_4$ scales with the sputtering power of Al and has been raised from 20 to 90 L $min^{-1}g^{-1}_{catalyst}$ for Pt while it increases from 23 to 110 L $min^{-1}g^{-1}_{catalyst}$ for Ru. The BET analysis has demonstrated that the measured surface areas of the Pt and Ru nanoparticles are approximately 55.5 and 151 m^2 g^{-1}, respectively. Joint like morphology providing the porous structure has been clearly concluded by TEM analysis. The average pore sizes are 1 and 10 nm for the Ru and Pt nanoparticles, respectively. In this study, fast hydrogen generation with lower activation energies of 31.7 and 32.1 kJ mol^{-1} has been achieved for the Pt and Ru nanoparticles, respectively. The critical parameters demonstrating the high catalytic activity in the hydrolysis reaction of $NaBH_4$ are reported for the catalysts developed by the dealloying process.

1. Introduction

Hydrogen generation has been extensively studied by employing a variety of processes including fast pyrolysis of biomass, dark fermentation, microbial electrolysis and thermal and catalytic routes to photo hydrogen generation [1,2]. No matter how hydrogen is produced, ultra-fast and reliable hydrogen generation is desired for many applications [1]. In addition to the need for ultra-fast hydrogen generation rates, on-board hydrogen generation also requires achieving very high volumetric and gravimetric densities of hydrogen storage and supply [3]. Chemical hydrides such as $NaBH_4$, $LiBH_4$, and BH_3:NH_3 are solid hydrogen carriers with high volumetric and gravimetric hydrogen storage densities [1]. There is a great interest in solid hydrogen storage using chemical hydrides for fuel cell systems utilizing hydrogen which is typically produced on demand in a cartridge by mixing the chemical hydride solution with water in the presence of catalysts for accelerating the hydrolysis reaction of chemical hydrides [4]. A typical hydrolysis reaction for $NaBH_4$ is as follows.

$$NaBH_4(s) + (x+2)H_2O(l)NaBO_2xH_2O(aq) + 4H_2(g) + \mathit{heat}. \quad (1)$$

where the x is the hydration factor.

There is a large number of catalysts that have been demonstrated to speed up the reaction given in Eq. (1) [5–11]. However, there is still a need to develop new catalysts to allow the mass production of hydrogen in an inexpensive, safe, robust and very efficient way. Therefore, novel approaches for meeting these demands are very important in the area of hydrogen generation. To date, a remarkable interest has been paid to the dealloying process for its critical roles in several research areas such as actuators, catalysis, capacitors, and battery and fuel cell electrodes [12]. Precious nanoporous metals are usually prepared by dealloying nonprecious metals from the alloys of precious and nonprecious metals. Therefore, the remaining structures become nanoporous at

---

* Corresponding author.
E-mail address: msankir@etu.edu.tr (M. Sankir).

https://doi.org/10.1016/j.jallcom.2018.02.082
0925-8388/© 2018 Elsevier B.V. All rights reserved.

the end of the dealloying process. Dealloying is achieved by either electrochemical or chemical processes. The electrochemical process involves selective dissolution of one of the components of alloys by electrochemically controlled corrosion. Dursun et al. have demonstrated that sponge like morphologies, which are completely interconnected and random in all directions, have been achieved by a electrochemical dealloying process of binary silver and gold alloys [13]. Another similar study for the electrochemical dealloying process is the preparation of the nanoporous platinum with pore sizes varying from 2 to 200 nm [14]. In both studies, influence of types of electrolytes, applied potential, and temperature on the pore size development has been observed by neutron scattering measurements. The drawbacks for the electrochemical dealloying process are the limited sample size and very slow dissolution kinetics. Therefore, chemical dealloying with various acids and bases has been used for the selective dissolution of nonprecious metals from binary alloys [15–19]. These porous nanostructures provide a very high catalytic surface area that enables them appropriate for ultrafast hydrogen generation. In one of our previous studies we have prepared dealloyed thin films and utilized them as an efficient catalyst for hydrogen generation [20]. In order to better understand the influence of the alloying process on hydrogen generation rates, in this study, we are reporting a platinum and ruthenium nanoporous catalyst in a particle form for hydrogen generation using chemical hydrides. Also, the influence of particle size on the hydrogen generation rate is explored.

2. Experimental

2.1. Materials

Platinum (Pt), ruthenium (Ru) and aluminum (Al) targets (99.99% pure) are purchased from Plus Materials. Hydrochloric acid (37 %w/w) is received from Sigma Aldrich. Deionized water with resistivity of 18.2 M ohm cm (ELGA Purelab Option-Q) is used in the experiments. Teflon™ sheets (OZKA metal) are used as the supporting material during cosputtering.

2.2. Precious metal nanoparticle preparation

Precious metal targets (Pt or Ru) with Al target are simultaneously cosputtered on Teflon™ to prepare the alloys using a Vaksis Midas PVD-MT/2M2T system. The argon gas flow rate is set to 45 sccm and the reservoir pressure is kept at 6.5×10^{-3} Torr during deposition.

The total active area after sputtering is approximately 45.1 cm^2. The sputtering power of the precious metal (Pt or Ru) is kept constant at approximately 50 W, while it is varied for Al from 200 to 400 W. The sputtering period lasts for 5 min. Then the Al in the alloy is removed by the chemical etching method. Selective etching is achieved by using hydrochloric acid. In order to assure that all the Al in the alloy is removed, the alloy is kept in aqueous HCl (37 wt %) for 24 h. The rest of the Pt and Ru nanoparticles are filtered and washed with deionized water several times to remove the HCl residues. After the washing step Pt and Ru nanoparticles are dried under vacuum (1.0 mmHg) at 25 °C overnight.

2.3. Catalyst characterization and measuring the hydrogen generation performances

The adsorption-desorption isotherms of nitrogen are obtained by using Brunauer-Emmett-Teller (BET) method. BET characterization is performed via a Quantachrome iQ-C BET Analysis device. The experimental weight percentages of Pt and Al in the alloy are determined with EDX analysis method. TEM analysis is done with FEI Tecnai G2 F30 transmission electron microscope and particle size measurements are performed with Malvern Zeta Sizer Nano ZS. The hydrogen generation performance measurement system (Fig. 1) includes a sodium borohydride ($NaBH_4$) solution tank, peristaltic pump, reactor equipped with constant temperature water bath, silica dryer and computer controlled mass flow meter. In a typical measurement, $NaBH_4$ solution (1.0 M) is pumped through the reactor containing nanoparticle catalysts (5 mg) and hydrogen generation immediately initiates. Then humidified hydrogen gas from the reactor is fed to a silica gel dryer to remove the water and arrives to a mass flow meter which continually measures the amount of hydrogen with the unit of L min^{-1}. It has been previously demonstrated by our research group that weight normalized hydrogen generation rates are questionable and they can only be used for comparison purposes [5]. Therefore, throughout the study we have used weight normalized reaction rates with the unit of L min^{-1} $g^{-1}_{catalyst}$.

3. Results and discussion

Selective dissolution of nonprecious component of alloys results in the formation of nanoporous catalysts, which are then used in the area of hydrogen generation. The alloying and dealloying processes for preparing nanoporous catalysts reported in this study are very simple, efficient and cost effective. The alloying process is achieved by cosputtering of precious metal (Pt and Ru) with a nonprecious one (Al) on a flexible Teflon™ substrate, which makes the thin film catalyst very easy to handle. The sputtering power plays an important role during the alloy formation. Basically, the smaller the sputtering power the less material is deposited on the substrate. Since we are aiming to minimize the amount of precious metal in the catalyst formulation due to nanoparticle formation after the dealloying process and also to reduce costs, the sputtering power is set to a lower number, which is about 50 W. On the other hand, the sputtering power for the nonprecious metal, Al, is varied from 200 to 400 W. Therefore, the influence of the sputtering power on the catalyst composition as well as the hydrogen generation rates has been investigated. The selective dissolution of Al is achieved by one step chemical treatment of the alloy with aqueous HCl, which is a powerful etchant for aluminum. As seen in Table 1, the Al is successfully dealloyed from the Pt-Al alloy especially with the higher sputtering power of Al. On the other hand, Al free ruthenium nanoporous catalyst is obtained for a sputtering power of Al higher than 200 W. As a result, EDX analysis proves that the nanoporous catalyst only consists of a precious metal that has been successfully achieved with a very simple and one step cost effective method.

Particle size analysis of nanoporous catalysts obtained from Pt-Al and Ru-Al alloys by the selective etching are shown in Fig. 2. Characteristic sizes of Pt particles decreased with increasing Al sputtering power. When the Al sputtering power is increased from 200 to 400 W, Pt and Ru particle sizes reduced from 900 to 90 nm and 610 to 55 nm, respectively. This relates to alloy composition before selective dissolution. The alloy composition before dealloying consists of 74 and 26 percent by weight of precious metal Pt and Al, respectively, when the sputtering power is 200W, while the weight ratio for the precious metal Pt to Al becomes almost unity when the sputtering power of Al reaches 400 W. Therefore sputtering power is a key issue for obtaining nanoparticles with the size of 55 and 90 nm from Ru-Al and Pt-Al alloys, respectively. Bigger particles are obtained when the weight ratio of Pt to Al before dealloying is larger than unity, since the higher amount of the precious metal in the alloy results in bigger clusters after dealloying. Similar behavior is observed during dealloying of Al in Ru-Al alloys. Clearly, it can be concluded that the precious metal nanoporous nanocatalysts are achieved once the alloys with the highest