

Stratified nanoporous PtTi alloys for hydrolysis of ammonia borane

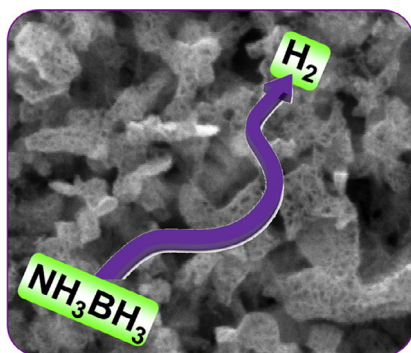


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GRAPHICAL ABSTRACT

Stratified nanoporous PtTi (SNP-PtTi) alloys with different bimetallic ratios are successfully fabricated by first selectively dissolving Al atoms followed by removing part of Ti atoms from the PtTiAl precursor alloy. The as-prepared SNP-PtTi alloys consist of interconnected bimodal nanoporous architecture with two order pore/ligament distributions and interconnected hollow channels extending in all three dimensions. Compared with NP-Pt catalyst, SNP-PtTi alloys show superior catalytic activities toward AB hydrolysis reaction in virtue of the perfect combination of unique stratified nanoporous architecture and alloying effect.



Stratified nanoporous PtTi alloys

ARTICLE INFO

Article history:

Received 23 December 2016

Accepted 12 February 2017

Available online 16 February 2017

Keywords:

Platinum
Dealloying
Nanoporous
Hydrolysis
Ammonia borane

ABSTRACT

Stratified nanoporous PtTi (SNP-PtTi) alloys with bimodal size distributions and different components are successfully prepared by selectively dissolving Al atoms followed by removing part of Ti atoms from the PtTiAl precursor alloy. The as-made PtTi alloys have stratified nanoporous architecture with the first order ligaments around 50 nm and the second order smaller ligaments around 6 nm. The SNP-PtTi alloys with different bimetallic ratios exhibit much higher catalytic activity for the hydrolysis of ammonia borane than NP-Pt catalyst. The SNP-Pt₆₅Ti₃₅ alloy shows superior specific activity toward the hydrolytic dehydrogenation of ammonia borane compared with SNP-Pt₅₀Ti₅₀ and -Pt₈₀Ti₂₀, showing an initial turnover frequency of 51.4 mol H₂ (mol Pt)⁻¹ min⁻¹. The activation energy of SNP-Pt₆₅Ti₃₅ was estimated to be about 39.4 kJ mol⁻¹, which was small compared with most of the reported activation energy values in the literature. In addition, the recyclability tests indicate that the SNP-Pt₆₅Ti₃₅ retained 63% of the initial catalytic activity after the fifth run of hydrolysis. The lifetime of SNP-Pt₆₅Ti₃₅ was measured as 16,380 turnovers over 100 h in the hydrolysis of ammonia borane before deactivation. The SNP-PtTi alloys show potential application prospect in the field of online hydrogen production due to the high catalytic performance and the facile preparation.

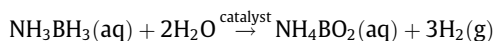
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1. Introduction

With the ever-growing depletion of fossil fuel and environmental contamination, hydrogen energy has attracted great attentions as one of the most promising green fuels for future vehicle-mounted application owing to its high energy efficiency, high power density, as well as zero emissions [1]. For the transportation application, hydrogen can satisfy the requirements of relatively small volume and mass with high energy content. However, its safe and efficient storage proposes one of the technological challenges as an alternative energy carrier [2,3]. Currently, a large number of chemical storage materials have been reported, such as chemical hydrides, metal hydrides, and sorbents [4,5]. Chemical hydrides with high hydrogen content and low molecular weight are the most prospective contenders as potential hydrogen sources [6]. Among the chemical hydrides, ammonia borane (NH_3BH_3 , AB) is the most promising candidate to supply pure hydrogen especially for portable applications owing to relatively lower molecular weight (30.87 g mol^{-1}) and extremely higher gravimetric hydrogen capacity (19.6 wt%) than those of gasoline [7–10]. In addition, AB is environmentally nontoxic with good stability in neutral and alkaline solution, which can release hydrogen by either thermal decomposition or hydrolysis [11–14]. However, the thermal decomposition requires high temperature and high power consumption. In contrast, the catalytic hydrolysis provides a more promising approach for hydrogen generation from AB [15–17]. In the presence of a suitable catalyst, the hydrolysis reaction (the equation below) can be achieved even at ambient temperature [14]. Therefore, the exploration of highly efficient catalysts is a critical prerequisite for the practical application in the catalytic hydrolytic dehydrogenation of AB.



A variety of catalysts, such as noble metal and non-noble metal catalysts, have been developed for the hydrolysis reaction [18–21]. Among them, platinum (Pt) represents one of the most widely investigated catalysts due to its extraordinary catalytic activities toward the hydrolytic dehydrogenation of AB [22,23]. In order to decrease the Pt utilization as well further improve its catalytic performance, the fabrication of Pt alloy nanomaterials combined with 3d transition metals, such as Fe, Co, and Ni, has been demonstrated to be an effective strategy in terms of the structural and electronic effects [22–24]. Moreover, alloy catalysts are preferable for boost the catalytic activity and stability compared with their monometallic counterparts because the introduction of another metal could provide new active sites as well produce synergistic catalytic effects [24–26]. Titanium (Ti) is one of the most stable transition metals, which has good corrosion resistance in a wide range of chemical environments [27]. The combination of Ti and Pt generates a large negative formation enthalpy, thus resulting in the strong chemical bond between Pt and Ti in PtTi alloy [28]. In addition, a number of theoretical studies and experiments have reported that Ti can generate the slight electronic modification for Pt, leading to its activity enhancement [27,29]. In the previous study, it has been found that combining Ti with Pd or Pt could dramatically improve their oxygen reduction activities [30,31]. Therefore, it is interesting to explore the catalytic performance of Pt-Ti alloy toward the hydrolysis of AB. However, there is still a lack of systematic investigations on the catalytic performances of PtTi alloy nanomaterials for the hydrolysis of AB up to now. It is noted that in previous reports the particle-type PtTi alloy nanomaterials were prepared by reducing the Pt and Ti precursors under the assistance of capping agents [28,32]. This type of method is difficult to achieve the good control to the composition, morphology, and structure uniformity for the resulted alloy nanomaterials.

Besides, the particle-type alloy catalysts tend to aggregate during the long term usage, resulting in the degradation of catalytic activities. Thus, it is necessary to design and fabricate Pt-Ti alloy nanocatalysts with the simple and controllable method to optimize the alloy ratios as well explore their effects on the catalytic activities toward the hydrolysis of AB.

Recently, dealloying has been demonstrated to be a flexible method to fabricate nanostructured bimetallic catalysts in tailoring the morphology and alloy compositions [33–35]. The selective dissolution of one or more elemental components from a multicomponent alloy can generate three dimensional bicontinuous network structure. Thus, nanoporous metals fabricated by dealloying have received great attention as a particular class of heterogeneous catalysts because the interconnected nanoscaled backbone can effectively bypass the issues of particle aggregation compared with the particle-type catalysts [36,37]. For example, Duan et al. [38] reported that nanoporous PtFe alloys by dealloying exhibit excellent electrocatalytic activity for oxygen reduction reaction compared with the PtFe/C and Pt/C catalysts. Chen et al. [39] found that nanoporous PdAu bimetallic catalysts by electrochemical dealloying show superior electrocatalytic performances toward ethanol electrooxidation in comparison with commercial Pt/C. In current work, we focused on the fabrication of stratified nanoporous PtTi (SNP-PtTi) alloy with bimodal size distributions based on the two-step dealloying to further enhance the catalytic activity and utilization of Pt. In the typical fabrication process, the well designed PtTiAl source alloy was first selectively etched in alkaline solution to remove the Al atoms to form the first order pore and ligament. And then, the dissolution of part of Ti atoms were controlled in HCl solution to generate the second pore/ligament structure on the initial porous surface. By only tuning the redealloying time, SNP-PtTi alloy with different bimetallic ratios can be easily fabricated. The whole dealloying/redealloying process can achieve a good control on the bimetallic ratio and structure uniformity in terms of an easy operation. It is found that the as-prepared SNP-PtTi alloy with different components show superior catalytic performance compared with NP-Pt for the hydrolytic dehydrogenation of AB under ambient atmosphere at room temperature.

2. Experimental

2.1. Sample preparation

$\text{Pt}_{20}\text{Al}_{80}$ and $\text{Pt}_{4.2}\text{Ti}_{12.8}\text{Al}_{83}$ (at.%) alloy foils were made by refining high-purity Pt, Ti, and Al (>99.99%) in an arc furnace, and followed by melt-spinning under the protection of high-purity argon. In the typical fabrication process, $\text{Pt}_{4.2}\text{Ti}_{12.8}\text{Al}_{83}$ alloy foils were first dealloyed in 0.5 M NaOH solution for 48 h and following by immersing in 5 M NaOH for 12 h to obtain NP- $\text{Pt}_{25}\text{Ti}_{75}$ alloy [31]. The as-made NP-PtTi alloy was further treated in 4 M HCl solution at room temperature for 10, 15, and 20 min to prepare SNP- $\text{Pt}_{50}\text{Ti}_{50}$, SNP- $\text{Pt}_{65}\text{Ti}_{35}$, and SNP- $\text{Pt}_{80}\text{Ti}_{20}$ alloys, respectively. $\text{Pt}_{20}\text{Al}_{80}$ alloy was dealloyed in 1 M HCl solution for 48 h to obtain the NP-Pt. The prepared samples were washed clean with ultrapure water (18.2 M Ω) and dried at room temperature in air. Ammonia borane (AB, 97%) was provided by Aldrich.

2.2. Sample characterization

Powder X-ray diffraction (XRD) measurement was performed on a Bruker D8 advanced X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of $0.02 \text{ }^\circ\text{s}^{-1}$. The morphology and chemical composition of all samples were observed by using a JEOL JSM-6700F field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer

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