INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

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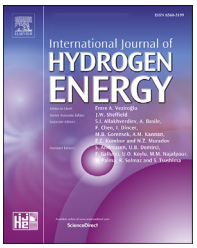

Non-noble metallic nanoparticles supported on titania spheres as catalysts for hydrogen generation from hydrolysis of ammonia borane under ultraviolet light irradiation

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ARTICLE INFO

Article history:
Received 16 May 2018
Received in revised form
3 July 2018
Accepted 9 July 2018
Available online xxx

Keywords:
Ammonia borane
Hydrolysis
Non-noble metallic nanoparticles
Titania spheres
Ultraviolet light irradiation

ABSTRACT

Herein, a report on non-noble metal (Ni, Co, Cu, and their combination) nanoparticles (NPs) supported on TiO_2 spheres as catalysts for hydrogen generation via hydrolysis of ammonia borane (NH_3BH_3, AB) is provided. The TiO_2 spheres were prepared through a template method by using polystyrene (PS). The metallic nanoparticles were synthesized by a redox replacement reaction. The structure, morphology, and chemical composition of the obtained samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS). The characterization results showed that the metallic nanoparticles were well dispersed on the TiO_2 supports. The catalytic activity toward the hydrolysis of AB was found to correlate well with the amount of metallic elements in catalysts while for the multicomponent phases, a synergistic effect was noticed. Theoretical calculations revealed that Ni, Co, and Cu atoms significantly influenced the electronic behavior of TiO_2 and thereby, the catalytic properties of the materials.

Introduction

Hydrogen is known as a clean and renewable energy carrier, properties which recommend it as a suitable and efficient alternative to the fossil fuel feedstocks [1,2]. Ammonia borane (NH_3BH_3, AB) has 6H atoms in the molecule, which is equivalent with a hydrogen content of 19.6 wt%. The hydrogen content of AB exceeds that of many compounds used to generate hydrogen via hydrolysis, such as borohydrides ($LiBH_4$ – 18.3 wt%, $NaBH_4$ – 10.8 wt%) and metal hydrides (e.g., MgH_2, 7.7 wt% and Mg_3La, *ca.* 7.7 wt%). In addition, AB has high chemical stability at room temperature compared to borohydrides [3]. Therefore, AB is considered as an attractive source of hydrogen for fuel cells, because it combines both chemical hydrogen storage and production due to its high hydrogen content and stability at room temperature, conditions in which the fuel cell operates. AB can releases hydrogen by pyrolysis or hydrolysis with a suitable catalyst. The pyrolysis reaction is not very convenient, because it takes place at high

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https://doi.org/10.1016/j.ijhydene.2018.07.049
0360-3199/

temperature, which is not suitable for the fuel cell, while generates toxic byproducts [4]. AB completely decomposes at high temperatures during pyrolysis, so the power consumption does not meet the recent targets imposed by the environmental legislation [5,6]. During the last years, the ionic liquids have been reported to be an appropriate solution to increase the amount of hydrogen released from AB. In this case, the AB is introduced in the ionic liquid that attacks the AB molecule bonds releasing hydrogen [7]. However, the reported ionic liquids are usually complicated organic salts, which are not easy to prepare and not environmentally preferred.

Nowadays, the hydrolysis of AB is accomplished by using metal catalysts, such as Pt, Rh, and Ru [8–10]. Due to the high costs of these noble metals, researchers have recently begun to seek the non-noble metals, which are cost-effective and show relatively high catalytic activity, especially when they are used as nanoparticles whose size is small enough to enhance their catalytic performance [11–13]. Therefore, a tendency to use non-noble metals for the hydrolysis of AB was observed lately. As a result, the cost of the overall process of hydrogen release was reduced due to the practical use [14,15]. Since the monometallic NPs usually manifest poor performance, trimetallic NPs can be considered as better catalysts with enhanced catalytic performance rationalized by the synergistic effect between the neighboring elements in the same NP. In this sense, a large number of studies focused on the catalysts of Cu combined with other metallic nanoparticles for AB hydrolysis. Wang et al. synthesized trimetallic magnetic Cu@FeNi core–shell NPs, which are composed of crystalline Cu cores and amorphous FeNi shells [16]. Cu@FeCo and Cu@CoNi manifested composition dependent activities towards the hydrolysis of AB [17]. Moreover, core–shell structured trimetallic NPs Cu@CoCr and Cu@CoW were synthesized using one-step in-situ synthesis method and evaluated in the hydrolysis of AB [18]. However, these nanoparticles can form large aggregates, whose catalytic activity is reduced accordingly. An efficient strategy to improve their stability consists of loading these nanoparticles on an inorganic support, when the interaction established between the NPs and support surface will stabilize them and thus, the agglomeration will be prevented while the catalytic behavior will be improved.

TiO_2 is a well-known photocatalyst for many chemical reactions due to its chemical inertness, cost-effective, and long-term stability against chemical-corrosion [19]. Moreover, it can be used as a suitable support for functional materials. Murat Rakap et al. loaded Pd on TiO_2 NPs, and the resulted material was found to be highly active and reusable in the hydrolysis of AB, even at low temperature and concentration [20]. Recently, the incorporation of metal within TiO_2 has been shown to be a good strategy to produce excellent photocatalysts toward hydrogen release from AB [21–23]. The metallic catalysts supported on TiO_2 showed strong metal-support interaction (SMSI), an effect that highly increases the catalytic activity. The high photocatalytic activity is explained by the good separation of electrons and holes. However, all the TiO_2 used as supports were nanofibers synthesized by electrospun method. Therefore, other methods to prepare TiO_2 support with different morphologies are highly encouraged, especially since the morphology of the support can play a significant role in the dispersion of the active phase, which is intimately related to the catalytic performance.

In this study, $Ni_{0.3}Co_{0.3}Cu_{0.4}$ NPs were synthesized through a redox replacement reaction using TiO_2 spheres as a support. The TiO_2 spheres display high surface area on which the tricomponent $Ni_{0.3}Co_{0.3}Cu_{0.4}$ NPs can be uniformly dispersed. The as-prepared $Ni_{0.3}Co_{0.3}Cu_{0.4}/TiO_2$ catalysts exhibited promising catalytic activities toward the hydrolysis of AB under ultraviolet light (UV-light) irradiation. Theoretical calculations were carried out aiming to study the changes in the electronic properties of the reaction system, which cause the SMSI effect, and to confirm the effect of TiO_2 on the catalytic activity of $Ni_{0.3}Co_{0.3}Cu_{0.4}$.

Experimental

Preparation of polystyrene (PS) spheres

The monodisperse PS spheres were prepared by emulsifier-free emulsion polymerization according to reference [24]. In a typical synthesis, 10.0 g of styrene, 1.5 g of poly (vinyl pyrrolidone) (PVP) K30 (Mw ≈ 40000), 0.26 g of cationic initiator 2, 2′-azobis-(isobutyramidine) dihydrochloride (AIBA), and 100.0 g of distilled water were loaded into a 250 mL three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a N_2 inlet, a Graham condenser, and a heating oil bath. The air in the flask was removed from the reaction solution by bubbling N_2 at room temperature for 90 min. Then, the reaction was performed at 343 K for 24 h under a stirring rate of 150 rpm. The obtained PS suspension was centrifuged (6000 rpm, 5 min), washed in ethyl alcohol for at least three times, and the content of PS suspension was then washed by ethanol.

Preparation of catalysts

0.03 g of $Ni(NO_3)_2{\cdot}6H_2O$ (99%), $Co(NO_3)_2{\cdot}6H_2O$ (99%), or $Cu(NO_3)_2{\cdot}6H_2O$ (99%), 12–36 mL of 28 wt% aqueous ammonia solution, and 160 mL of ethyl alcohol were added into 20.0 g of the PS suspension. The sol–gel reaction was carried out at 323 K for 1.5 h, and the metal composite spheres (M/TiO_2, M = Ni, Co, Cu or their compounds) were obtained. After drying in a vacuum oven at 323 K overnight, the resulted fine powders were used as catalysts.

Catalysts characterization

The as-synthesized catalysts were characterized by powder X-ray diffraction (XRD, Rigaku D/max-2500 X-ray generator, Cu Ka radiation), scanning electron microscopy (SEM, JEOL JSM6700F), inductively coupled plasma emission spectroscopy (ICP-9000, Thermo Jarrell-Ash Corp.), transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM and EDX, Philips Tecnai F20, 200 kV), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), and UV-Vis diffuse reflectance spectroscopy (DR UV-Vis, Hitachi U-3900H).

Please cite this article in press as: Yang XJ, et al., Non-noble metallic nanoparticles supported on titania spheres as catalysts for hydrogen generation from hydrolysis of ammonia borane under ultraviolet light irradiation, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.049