Journal of Alloys and Compounds 693 (2017) 642–649

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Boron nitride supported Ni nanoparticles as catalysts for hydrogen generation from hydrolysis of ammonia borane

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ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form
18 September 2016
Accepted 20 September 2016
Available online 21 September 2016

Keywords:
Boron nitride
Ni catalysts
Nanoparticles
Ammonia borane
Hydrogen generation

ABSTRACT

We report on Ni nanoparticles supported on boron nitride spheres (BNSP) and sheets (BNSH) as catalysts for hydrogen generation via hydrolysis of ammonia borane (NH_3BH_3, AB). The Ni/BN catalysts were prepared through a redox replacement reaction. The structure, morphology, and chemical composition of the obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDX), and inductively coupled plasma emission spectroscopy (ICP). The characterization results showed that Ni nanoparticles were well dispersed on the BNSP and BNSH supports for the four Ni/BN catalysts prepared (Ni atomic contents of 6.8, 9.0, 9.2, and 12 wt%). The catalytic activity toward the hydrolysis of AB was found to correlate with the loading of the Ni/BN catalysts, which showed great cycle performance. Theoretical calculations revealed that BN sheets significantly influenced the electric character of Ni catalysts and thereby their catalytic properties.

1. Introduction

Nowadays, a great deal of attention has been paid to the use of clean fuel substitutes such as hydrogen in substitution of fossil fuels, for both economic and environmental reasons [1–4]. Ammonia borane (NH_3BH_3, AB) has a hydrogen content of 19.6 wt%, which exceeds those of borohydrides such as $LiBH_4$ (18.3 wt%) and $NaBH_4$ (10.8 wt%), and metal hydrides such as MgH_2 (7.7 wt%) [5,6] and Mg_3La (*ca.* 7.7 wt%) [7,8] typically used for hydrogen generation via hydrolysis. Therefore, AB is an attractive candidate for chemical hydrogen storage applications. When compared to borohydrides which are not chemically stable in water, AB higher solubility in water (33.6 g per 100 mL) while also showing superior stability in neutral aqueous solutions at room temperature [9]. In addition, some researchers have studied the regeneration of AB, which helps to realize its recycling [10]. Thus, AB was identified as one of the leading candidates for serving as a hydrogen reservoir owing to its high hydrogen content, high stability under ordinary fuel cell reaction conditions, and nontoxicity characteristics.

Although the hydrolysis of AB can be catalyzed by acids [10], the corresponding H_2 release rate is relatively low and depends highly on the concentration of acid, which may hinder practical applications. In contrast, metal catalysts can be effectively used in AB aqueous solutions. From the viewpoint of practical applications, the development of efficient and low-cost catalysts achieving improved kinetic properties under moderate conditions is therefore very important [11,12]. Recently, there is a general interest in searching for more abundant transition-metal catalysts (e.g., Fe, Co, Ni, among others) to catalyze the hydrolysis of AB with high efficiency [13–15]. In this sense, a large number of studies focused on the utilization of Ni nanoparticles as catalysts for AB hydrolysis. The Luo's group prepared amorphous Ni catalysts derived from nickel halides, with the halide anions affecting the formation and catalytic activity of Ni (0) catalysts during the hydrolysis of AB [16]. Umegaki prepared Ni nanoparticles by reducing Ni (II) species in an aqueous $NaBH_4/NH_3BH_3$ solution. The catalytic rate of Ni toward the hydrolysis of AB in the presence of L-arginine was 827 mL s^{-1} (mol Ni)$^{-1}$ at the 11th cycle [17]. Xu prepared a Ni@MSC-30 catalyst by a high temperature reaction. The catalysts showed high activity, with a total turnover frequency (TOF) of 30.7 mol of H_2·(mol of Ni)$^{-1}$·min^{-1} [18]. The W. G. Song's group prepared nanoporous Ni catalysts having a TOF value for the hydrolysis for AB of 19.6 mol of H_2·(mol of Ni)$^{-1}$·min^{-1} and an activation energy (Ea) of 27 kJ mol^{-1} [19]. Metin prepared monodisperse Ni nanoparticles via reduction of $Ni(acac)_2$ with oleic acid. The Ni nanoparticles exhibited high catalytic activity for the hydrolysis of an AB complex

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http://dx.doi.org/10.1016/j.jallcom.2016.09.204
0925-8388/

with a TOF value of 8.8 mol of H_2·(mol of Ni)$^{-1}$·min^{-1} [20]. Remarkably, the activity of the Ni nanoparticles is influenced by the nature of the supports to some extent. Thus, utilization of different supports may help improve the catalytic activity of the Ni catalysts.

Hexagonal boron nitride (h-BN), the simplest III–V compound with semiconductor properties, is stable at room temperature and ambient pressure [21]. It is a layered structural material with weak van de Waals interactions between layers. It has a honeycomb structure within each layer composed of alternating boron and nitrogen atoms [22]. h-BN is an insulator with a direct band gap of 5.97 eV [23]. It has superior chemical stability as it is stable in air up to 1000 °C [24]. All these characteristics mentioned above make h-BN a good catalytic support. BN is used to increase the catalytic activity as a catalyst supporter of TiO_2. It is reported that BN promoted the separation of electrons and holes in $TiO_{2-x}N_x$ [25]. It is expected BN can also active the catalysis of Ni for hydrolysis of AB.

In this work, Ni nanoparticles were synthesized through a redox replacement reaction employing h-BN as a support. The h-BN used herein showed high surface area such that Ni can distribute on its surface uniformly. The as-prepared Ni/BN catalysts exhibited promising catalytic activities toward the hydrolysis of AB. Therefore, these Ni/BN catalysts might find application in fuel cells as a hydrogen supplier via catalytic hydrolysis of AB. Theoretical calculations were carried out with the aim to study the changes in the electronic properties of the reaction system and to confirm the effect of BN on the catalytic activity of Ni.

2. Experimental

2.1. Preparation of Ni/BNSP and Ni/BNSH catalysts

BNSP and BNSH were synthesized according to previously reported procedures [26]. The rest of reagents were of analytical grade and used without further purification. The initial nanoparticles were prepared by reduction of Ni^{2+} with $NaBH_4$. The redox process can be expressed as:

$$Ni^{2+} + BH_4^- + 2H_2O \rightarrow Ni + BO_2^- + 2H^+ + 3H_2 \quad (1)$$

A certain amount of a $NiNO_3$ solution was first placed in a sealed three-neck flask. 0.5000 g of BNSP or BNSH were added to the solution and dispersed by ultrasonic vibration. The mixture was stirred vigorously for 1 d. The solid obtained was subsequently collected by centrifugation and washed thoroughly with distilled water in order to remove the Ni^{2+} in the solution. A 0.1 M $NaBH_4$ solution was subsequently added to the mixture dropwise under an ice water bath upon stirring to react with Ni^{2+}. The molar ratio of $NaBH_4$ to $NiNO_3$ was 1:1. After *ca.* 1 h, the resulting Ni/BNSP and Ni/BNSH catalysts were collected from the solution by centrifugation, washed thoroughly with distilled water and anhydrous ethanol to remove residual ions, and finally vacuum dried in vacuum at 60 °C for 12 h. Four catalysts with different Ni loading (i.e., 6.8, 9.0, 9.2, and 12 wt%) were prepared by appropriately selecting the added amount of reactants. An unsupported Ni catalyst was also prepared by a similar process without adding BN to the reactant solution.

2.2. Catalyst 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 coupled with energy dispersive X-ray spectroscopy (SEM-EDX, JEOL JSM-6700F), inductively coupled plasma emission spectroscopy (ICP, ICP-9000, Thermo Jarrell-Ash Corp.), and transmission electron microscopy (TEM, Philips Tecnai F20, 200 kV).

2.3. Hydrogen generation measurements

An AB solution was placed in a sealed flask fitted with an outlet tube for collecting the evolved H_2. The outlet tube exhaust was placed under an inverted, water-filled gas burette that was situated in a water-filled vessel. A certain amount of catalysts was added to the solution without stirring. The hydrolysis reaction was carried out at controlled temperatures using an electric-heated thermostatic water bath. The volume of generated H_2 was measured by the water displacement method. The process of AB hydrolysis can be described as follows [27]:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2\uparrow \quad (2)$$

Once the hydrolysis reaction was completed, the residual solution was filtered and the catalyst was saved.

2.4. Computational methods

All the calculations were carried out using the density functional theory (DFT) method implemented in the DMol^3 code [28]. The generalized gradient approximation was used by combining the Perdew–Wang correlation functional with the Becke exchange functional [29]. Self-consistent field calculations were conducted with a convergence criterion of 10^{-6} a.u. for the total energy. We adopted a hexagonal 4 × 4 × 1 supercell for an h-BN sheet. In the case of the h-BN sheet, the vacuum region in the z direction was employed to eliminate the sheet-sheet interactions. 5 × 5 × 1 Monkhorst–Pack k-points meshes were used for structural optimization, while 3 × 4 × 1 k-points were employed for electronic structure calculations. The adsorption energy (E_{ads}) was obtained from the following expression:

$$E_{ads} = E(Ni/BN) - E(BN) - E(Ni) \quad (3)$$

where E(Ni/BN), E(BN), and E(Ni) stand for the total energies of the Ni-adsorbed h-BN sheet, the pristine h-BN sheet, and bare Ni, respectively. By this definition, Eads <0 corresponds to an exothermic adsorption leading to minima stable toward dissociation.

3. Results and discussion

3.1. Catalyst characterization

The Ni/BN catalysts were prepared by an *in situ* redox reaction between Ni and $NaBH_4$ over the BN support. The first step involved the preparation of Ni^{2+} ions adsorbed on BN. The formation of Ni nanoparticles attached to BN was achieved in the second step via the redox reaction between $NaBH_4$ and Ni^{2+}. The extent of this reaction for BNSP and BNSH supports is summarized in Table 1. As can be seen from Table 1, BNSH adsorbed Ni^{2+} to a larger extent as compared to BNSP. Thus, Ni/BNSH catalysts are more suitable for the hydrolysis of AB as compared to Ni/BNSP.

Fig. 1a–e shows the XRD patterns of the Ni catalysts. The diffraction peak at a 2θ value of 44.5° in Fig. 1a corresponded to the

Table 1
Extent of reaction during the preparation of the Ni catalysts for different BN supports.

Samples	Ni/BNSP1	Ni/BNSP2	Ni/BNSH1	Ni/BNSH2
$NiNO_3$(g)	1.4540	2.908	1.4540	2.908
BN(g)	0.5000	0.5000	0.5000	0.5000
Ni:(Ni + BN)(wt%)	6.8	9.0	9.2	12