



Hydrogen generation from the hydrolytic dehydrogenation of ammonia borane using electrolessly deposited cobalt–phosphorus as reusable and cost-effective catalyst



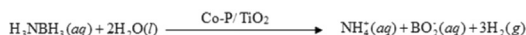
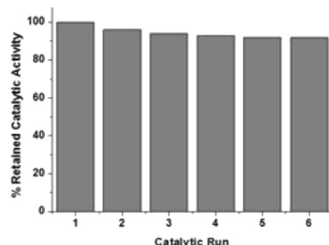
Murat Rakap*

Department of Chemistry, Yüzüncü Yıl University, 65080 Van, Turkey

HIGHLIGHTS

- Co–P/TiO₂ is efficient, reusable, and low-cost catalyst for hydrolytic dehydrogenation of AB.
- The catalyst is reusable with minimal loss of activity for several cycles.
- Arrhenius activation energy is found to be 48.1 ± 2 kJ mol⁻¹.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form

17 April 2014

Accepted 23 April 2014

Available online 2 May 2014

Keywords:

Electroless deposition

Cobalt

Ammonia borane

Hydrolytic dehydrogenation

Hydrogen

ABSTRACT

The development of catalytically active, low-cost, and reusable catalysts is very vital for on-demand hydrogen generation systems for practical onboard applications. Titanium dioxide supported-cobalt–phosphorus (Co–P/TiO₂) catalyst prepared by electroless deposition has been shown to effectively promote the release of hydrogen from the hydrolytic dehydrogenation of ammonia borane. The catalyst is very stable to be isolated as solid material and characterized by XRD, SEM-EDX, and XPS. It is redispersible and reusable as an active catalyst in the hydrolytic dehydrogenation of AB. The activation energy (E_a) for the hydrolytic dehydrogenation of ammonia borane catalyzed by Co–P/TiO₂ catalyst is 48.1 ± 2 kJ mol⁻¹. Maximum hydrogen generation rate in the hydrolytic dehydrogenation of ammonia borane catalyzed by Co–P/TiO₂ catalyst is 2002 mL H₂ min⁻¹ (g catalyst)⁻¹.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

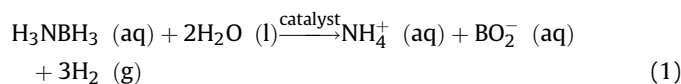
Hydrogen has become one of the most promising future energy carriers in recent years due to the concerns over the depletion of fossil fuels supplies, environmental pollution and global warming which is attributable to the greenhouse effect caused by a steep

increase in carbon dioxide and other gases [1,2]. However, the lack of effective and safe hydrogen-storage materials is the most important challenge toward hydrogen-powered society as a long-term solution for a secure energy future [3]. Recently, ammonia borane (H₃NBH₃, AB) has been considered to be a promising candidate as an efficient hydrogen-storage material to meet the 2010 targets (6 wt % and 45 g L⁻¹) and potentially meet the 2015 targets (9 wt % and 81 g L⁻¹) set by the U.S. Department of Energy (DOE) [4,5] due to its high hydrogen content (19.6 wt % H₂) and low molecular weight (30.7 g mol⁻¹) [6,7]. It is highly soluble in water

* Tel.: +90 432 225 17 01; fax: +90 432 486 54 13.

E-mail addresses: mrtrakap@gmail.com, mrtrakap@gmail.com.

and its solution is stable at room temperature. However, it releases hydrogen gas upon hydrolytic dehydrogenation at room temperature in the presence of suitable catalysts (Eq. (1)) [8].



So far, various catalyst systems consisting of noble and non-noble metals have been tested as catalysts for hydrogen generation from the hydrolysis of AB. Generally, the catalysts composed of noble metals showed higher catalytic activities. However, development of low-cost and efficient catalysts is desired for practical uses. Recent advances in catalyst preparation technologies have led to significant improvements in the catalytic activity of transition metal catalysts, even to a level comparable to that of the noble metal catalysts [9]. Particularly, supported non-noble transition metals can be employed as active catalysts in practical applications owing to their easy separation from the solution and reusability [10]. Some of the non-noble catalysts used for the hydrolysis of AB are hollow titania–nickel composite [11], graphene supported cobalt(0) nanoparticles [12], amorphous Co–B catalyst [13], mesoporous silica supported Co–B [14], Co–B, Ni–B, Cu–B [15], hollow nickel–silica composite [16], Co–B [17], amorphous nickel catalyst [18], polymer-stabilized iron(0) nanoclusters [19], hydroxyapatite-supported cobalt(0) nanoclusters [20], Co/IR-120 [21], Co–P–B/Ni foam [22], Co–B/C [23], silica embedded Co(0) nanoclusters [24], Co₃O₄ [25], Co–W–B–P/Ni [26], Co–SiO₂ nanosphere [27], intrazeolite cobalt(0) nanoclusters [28], nanoparticle-assembled Co–B [29], Co nanoparticles [30], Co–Mo–B/Ni [10], Fe–Ni alloy [31], PVP-stabilized nickel [8], and Co–M–B–P [32].

Herein, the preparation and characterization of electrolessly deposited Co–P catalysts on TiO₂ and their use as catalyst in the hydrolytic dehydrogenation of ammonia borane is reported. Electroless deposition, an autocatalytic redox reaction process which provides a uniform and dense coating on all surface area of the plating support regardless of the configuration or geometry of the support [33], is the most popular and efficient method to prepare supported non-noble transition metal catalysts [34]. Indeed, a study [35] has shown that Co–Ni–P catalyst prepared by electroless deposition method on the surface TiO₂ can be used as active catalyst in the hydrolytic dehydrogenation of AB. In the light of the results of kinetic studies (depending on the catalyst amount, substrate concentration, and temperature) and the reusability experiment, Co–P/TiO₂ catalysts can be regarded as efficient, low-cost, and reusable catalysts in the hydrolytic dehydrogenation of AB to produce hydrogen. The main advantages of the catalyst are its low-cost and high reusability.

2. Experimental section

2.1. Materials

Cobalt sulfate heptahydrate, sodium hypophosphite monohydrate, EDTA, gluconic acid, boric acid, ammonium hydroxide, sodium potassium tartrate, ammonia–borane complex (97%), palladium acetate, butvar (B98), and titanium dioxide (Degussa P-25) were purchased from Aldrich. All chemicals were used as received. Deionized water was distilled by water purification system.

2.2. Preparation of the Co–P catalyst

The Co–P catalyst was prepared and supported on Pd–TiO₂ by using electroless deposition method. Cobalt sulfate heptahydrate

Table 1

Bath composition and the operating conditions employed for preparing electrolessly deposited Co–P catalyst on TiO₂.

Catalyst	Co–P
<i>Bath composition</i>	
Cobalt sulfate heptahydrate (mM)	53.08
Sodium hypophosphite monohydrate (M)	0.094
Gluconic acid (M)	0.023
EDTA (M)	0.013
Sodium potassium tartrate (M)	0.035
Boric acid (M)	0.162
<i>Operating conditions</i>	
pH	10.5
Temperature (°C)	75 ± 2
Time (min)	45

was used as the source of cobalt. Sodium hypophosphite was used as the reducing agent, which also forms the source of phosphorus in the deposit. EDTA was used as the complexing agent to control the rate of release of free metal ion for the reduction reaction. In addition to other constituents, ammonium hydroxide was added to adjust the pH of the bath solution. During plating, the bath was maintained at a temperature of 75 ± 2 °C by a constant temperature bath. The bath composition and operating conditions employed for the preparation of electroless Co–P alloy deposits are given in Table 1.

Since the electroless deposition of Co–P alloy requires a catalytically active surface, titanium dioxide surface has to be activated. For this purpose, 1 g of titanium dioxide was mixed with 12 g of catalyst ink solution by a method described in detail elsewhere [36,37]. The polymer-stabilized palladium catalyst ink solution was prepared by dissolving a specified amount (0.2–0.5 g) of analytical reagent grade palladium acetate trimer [CH₃(CO₂)₂Pd] (47.05% Pd) from Aldrich–Sigma Co, in 2.0 mL NH₄OH. The palladium mixture was then added with stirring for several hours into a base solution of poly vinyl butyral (PVB) in methanol. The alcoholic-polymer base solution contained 2.0 g poly (vinyl) butyral (Solutia Inc.'s Butvar B-98) in a known volume (100–200 mL) of methanol. The amount of PVB dissolved in alcohol can be used to adjust the catalyst ink viscosity. After a thorough mixing, the as-prepared catalyst solution can be preserved for years without loss in its activity.

The titanium dioxide-catalyst ink mixture was stirred to prepare Pd-activated TiO₂ for 2 h at room temperature, and kept at 270 °C for 48 h and then 350 °C for 6 h. To initiate the electroless

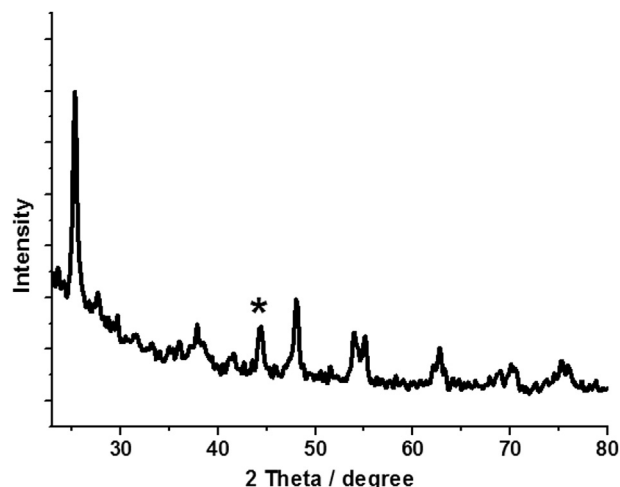


Fig. 1. XRD patterns of the Co–P/TiO₂ catalyst prepared by electroless deposition.

Download English Version:

<https://daneshyari.com/en/article/1284042>

Download Persian Version:

<https://daneshyari.com/article/1284042>

[Daneshyari.com](https://daneshyari.com)