



Catalytic hydrolysis of ammonia borane for hydrogen generation using cobalt nanocluster catalyst supported on polydopamine functionalized multiwalled carbon nanotube



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ABSTRACT

Hydrogen was generated from ammonia borane complex by hydrolysis using cobalt nanocluster catalyst supported on polydopamine functionalized MWCNTs (multi-walled carbon nanotubes). The impregnation-chemical reduction method was used for the preparation of the supported catalyst. The nanocluster catalyst support was formed by in-situ oxidative polymerization of dopamine on the MWCNTs in alkaline solution at room temperature. The structural and physical-chemical properties of the nanocluster catalyst were characterized by FT-IR (Fourier transform infrared spectroscopy), EDX (energy-dispersive X-ray spectroscopy), SEM (scanning electron microscope), XRD (X-ray diffraction) and TEM (transmission electron microscopy). The nanocluster catalyst showed good catalytic activity for the hydrogen generation from aqueous ammonia borane complex. A reusability test to determine the practical usage of the catalyst was also investigated. The result revealed that the catalyst maintained an appreciable catalytic performance and stability in terms of its reusability after three cycle of reuse for the hydrolysis reaction. Also, the activation energy for the hydrolysis of ammonia borane complex was estimated to be 50.41 kJmol⁻¹, which is lower than the values of some of the reported catalyst. The catalyst can be considered as a promising candidate in developing highly efficient portable hydrogen generation systems such as PEMFC (proton exchange membrane fuel cells).

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1. Introduction

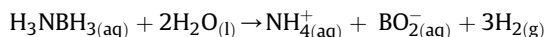
Renewable energy sources are on high demand for sustainable energy future as a result of vast pressure on the depletion and use of fossil fuel. Hydrogen is an environmentally benign energy source and a well known clean energy carrier molecule. Hydrogen can be used for future applications such as heating, transportation, mechanical power and electricity generation [1–3]. Currently, hydrogen gas are stored in tanks in the form of compressed or liquefied hydrogen but in this state, it is unsuitable to be use in portable hydrogen fuel systems such as PEMFC (proton exchange membrane fuel cells) due to safety issues. PEMFC converts the chemical energy of hydrogen gas into electrical energy and it has been demonstrated to be applicable in a variety of portable devices

such as mobile devices, thus the subject of hydrogen fuel cells is attracting great interest nowadays [4].

Chemical hydrides such as NaBH₄, KBH₄, LiBH₄ and NH₃BH₃ as hydrogen chemical storage have been studied as hydrogen sources for portable PEMFC due to their high releasing hydrogen capacities [5–7]. The safe storage and generation of hydrogen are very important in the practical application of PEMFC in the hydrogen economy. Among these chemical hydrides, ammonia borane complex (NH₃BH₃, AB) is regarded as one of the appropriate chemical hydrogen storage due to its high hydrogen content (19.6 wt%) [8], low molecular weight (30.7 g/mol) [9], non toxicity [10], high stability in water under ambient conditions and high solubility (33.6 g NH₃BH₃/100 g H₂O) [11]. Thermolysis, catalytic methanolysis and catalytic hydrolysis are among the processes that can release hydrogen from AB complex. The relatively high temperature needed for thermolysis in order to release hydrogen from an AB complex (greater than 100 °C) [12] has caused great interest in the catalytic hydrolysis of AB complex using transition metal catalyst such as platinum [13], ruthenium [14], palladium [15], iron [16],

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cobalt [17] and nickel [18]. Hydrogen can be released from ammonia borane complex at room temperature upon hydrolysis only in the presence of a suitable catalyst according to the equation.



A higher catalytic activity is attainable with these transition metals for the hydrogen generation; however their high cost makes them impractical to apply them on a larger scale. The catalytic performance of most of these metal nanoparticles depends highly on the dispersion of the active metals. Therefore, their aggregation into clumps and ultimately into their bulk forms can lead to a decrease in their catalytic activity and lifetime; thus suffer in long-term stability. Low-cost metal catalysts normally show relatively low activities compared to precious metal catalysts. Therefore, the synthesis of low-cost, stable and highly efficient catalyst to release hydrogen gas for practical use is one of the important issues in current research [19–21]. Hydrogen generation from metal salts alone encounter problems relating to the feasibility, control of reaction and separation of the catalyst from spent solution. These problems can be eliminated by using supported catalysts [22].

MWCNTs (multi-walled carbon nanotubes) have been used as a support for catalyst in many applications such as in sensors, energy storage and catalysis. This is as a result of its various properties such as unique molecular structure, tunable surface, high electrical conductivity, specific surface area and thermal and chemical stability. The immobilization of nanoparticles of metals and their oxides on MWCNTs surface are attainable with these useful properties to form a composite material [23–25]. However, the relatively surface chemical inertness of MWCNTs limits their affinity for water thereby decreases their catalytic efficiency as catalyst support. The dispersion and increase of the number of anchoring sites for metal nanoparticles on the surface of MWCNTs can be solved by functionalizing the surface of MWCNTs either by physical or/and chemical treatments [26].

Self-polymerization of dopamine to form Pdp (polydopamine) has been discovered to coat many surfaces with multifunctional groups such as amine and phenolic hydroxyl groups. This adhesion layer can then serve to immobilize metal nanoparticles on many surfaces. The amine and phenolic hydroxyl groups from Pdp coated on the surface of MWCNTs could serve as a binding agent as well as reactive site for metal nanoparticles upon reduction [27,28]. Recently, there has been reported synthesis of metal nanoparticles such as platinum and palladium catalysts supported on Pdp modified MWCNT which were used for electrocatalytic applications and also found to be environmentally friendly [29,30].

Inspired by the properties of dopamine and using a similar preparation method, MWCNTs were functionalized with Pdp to offer hydrophilicity, reactivity and stabilizing of cobalt nanocluster as low-cost catalyst. The metal-binding ability of catechol and nitrogen containing groups in the Pdp structure will serve as a reaction assistant to immobilize the cobalt nanoclusters on the surface of MWCNT upon reduction. This supported catalyst was then used for hydrogen generation from ammonia borane via hydrolysis. So the objectives of this work are to report the preparation of cobalt nanocluster supported on polydopamine functionalized MWCNT as low-cost catalyst, its catalytic activity and also its stability in terms of its reusability.

2. Materials and method

2.1. Materials

Multi-walled carbon nanotubes (length 5 μm , diameter 20 nm) were purchased from Carbon Nano-material Technology Co., Ltd

in Korea. Ammonia borane (97%), dopamine hydrochloride and 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) and cobalt (II) nitrate hexahydrate were purchased from Sigma Aldrich. Nitric acid (61%), sodium hydroxide and sodium borohydride were purchased from Showa and used as received. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 100 °C.

2.2. Catalyst preparation

The MWCNT was acid treated to introduce oxygen functional groups on its sidewall. 3 g of MWCNT was dispersed in 150 ml of concentrated HNO_3 (61%) solution and refluxed at 140 °C for 24 h. It was then allowed to cool to room temperature, filtered, washed with distilled water until neutral and dried for 12 h at 80 °C in vacuum oven.

A simple approach used to coat the o-MWCNT (oxidized MWCNTs) with Pdp is based on the spontaneous oxidative polymerization of dopamine in alkaline solution. The polydopamine functionalized o-MWCNTs were prepared by simple immersion of o-MWCNTs into a dopamine solution which contains Tris-HCl. 200 mg dopamine was dissolved in 100 ml of 10 mM Tris-HCl solution (pH = 8.5) and then 200 mg of o-MWCNT was added to the resulting solution which was then stirred for 12 h at room temperature. The resulting product was washed with distilled water and then dried overnight at 80 °C in a vacuum oven.

Wetness impregnation-chemical reduction method was used to immobilize the metal catalyst onto the functionalized MWCNT. An amount of the Pdp-o-MWCNT (polydopamine functionalized MWCNT) powder was ultrasonicated for 1 h with different concentration of cobalt aqueous solution. This was followed by vigorous stirring for 12 h after which 10 ml of 1 M alkaline NaBH_4 solution was added dropwise to the suspended solution to reduce

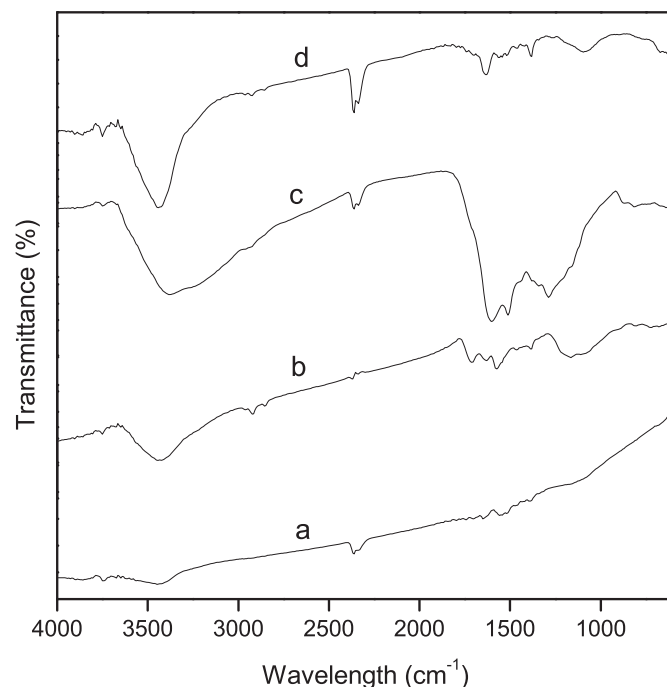


Fig. 1. FT-IR spectra of (a) pristine MWCNT, (b) o-MWCNT, (c) Pdp, and (d) Pdp-o-MWCNT.

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