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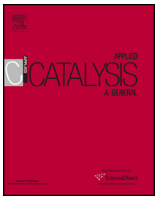

Enhanced H_2 production from hydrolysis of sodium borohydride using Co_3O_4 nanoparticles assembled coatings prepared by pulsed laser deposition

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ABSTRACT

Nanocatalysts, in the form of nanoparticles assembled coatings (NPACs) of Co_3O_4, were synthesized by pulsed laser deposition (PLD) with optimized parameters. Phase explosion phenomena occurring at high laser fluences produce nanoparticles (NPs) with an average size of ~5 nm having narrow size distribution (3–10 nm) and low degree of agglomeration, which are randomly arranged in the form of coating on the substrate surface. In comparison with chemically synthesized Co_3O_4 crystalline powder, the NPACs deposited by PLD showed significantly higher catalytic activity for H_2 generation by hydrolysis of $NaBH_4$. Maximum H_2 generation rate obtained by NPACs (5010 ml min^{-1} $g_{cat}{}^{-1}$) is about 5 times higher than that produced by Co_3O_4 powder (1000 ml min^{-1} $g_{cat}{}^{-1}$), which is mainly attributed to high surface area and large number of active sites provided by the Co_3O_4 NPs in the coating owing to their size and shape. By varying the O_2 pressure during PLD, two different cobalt oxide phases, namely Co_3O_4 and CoO, were formed in NPACs and found that Co_3O_4 phase is more active for hydrolysis than CoO phase with lower oxidation number. The morphology and crystallinity of Co_3O_4 NPACs were tuned by varying the laser fluence and substrate temperature respectively, and their effect on H_2 generation rate was studied. The results showed that the NPs with mixed amorphous-nanocrystalline phase on the surface act as active sites for favorable interaction and $NaBH_4$ conversion.

1. Introduction

Several growing technologies have given rise to the use of a colossal amount of hydrocarbons in a consumption-driven economy. However, the use of hydrocarbon-based energy is greatly affecting the economic, social and environmental conditions at global level [1,2]. Hydrogen (H_2) today is regarded as a clean fuel and a strategic substitute of fossil fuel in the decades ahead [3,4]. H_2 can be produced by various ways [5], but finding a cleaner route of generating hydrogen in moderate conditions is very important. Chemical hydrides are one of the best options to generate H_2 at ambient conditions through hydrolysis [6]. Among others, $NaBH_4$ has gained more attention due to its high H_2 storage capacity (volumetrically: 0.115 kg H_2 L^{-1} and gravimetrically: 10.7 wt% of H_2) [6,7]. It has the potential to be used as a synthetic fuel either in a direct borohydride fuel cell or as a hydrogen storage material for mobile applications [4,8]. Alkaline $NaBH_4$ solution is very stable and is able to produce stoichiometric amount of H_2 in the presence of an appropriate catalyst [7]. The by-product $NaBO_2$ is environmentally benign and can be potentially recycled, although the processes are still very costly [9]. Nevertheless, a catalyst is the key element to control the $NaBH_4$ hydrolysis reaction.

Although noble metals as heterogeneous catalysts are very efficient for the catalytic hydrolysis of $NaBH_4$ [7,10,11], their scarcity and cost have led to the search for low-cost catalysts as replacement to the noble metal catalysts. Alternatively, transition metal (Ni, Co) based catalysts have been found to accelerate the hydrolysis reaction [12–15]. Among the low-cost catalysts, cobalt boride (Co-B) has been widely studied for catalytic hydrolysis of boron hydrides owing to its exceptional activity, low-cost, ease of prepa-

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ration and good stability [16]. However, features like low-surface area, broadly distributed particle size and poor thermal stability against crystallization are the major drawbacks of this material. All these problems arise during the synthesis of Co-B from cobalt salt, where exothermic nature of reduction reaction reduces Co^{2+} by BH_4^- in aqueous solution to produce Co-B particles with high surface energy. These unstable particles agglomerate to form clusters and decrease the surface area. As the time progresses, the aggregation increases in the ambient atmosphere as well as during the reaction course, which further decreases the catalytic activity and the possibility to be reused. Several routes have been adopted in the current literature to improve the catalytic activity such as avoiding the agglomeration by varying the preparation parameters [17–19], by using organic templates [20,21], by doping with transition metals [22–24], or by supporting the catalyst on high surface area materials, etc. [25,26]. Though all these routes did show improvement in the performance of the Co-B catalyst, the hunt for a robust and stable catalyst still continues in order to implement it on an industrial scale.

The best way to resolve the above mentioned problems is by using precursor of cobalt in an oxidized form. The reduction reaction of cobalt oxide to form Co-B proceeds slowly with significantly lower heat release than in the case of cobalt salt. This slowness reduces the surface energy to avoid agglomeration and create high surface area. Krishnan et al. [27] first observed that cobalt oxide supports (Co_3O_4 and $LiCoO_2$) get reduced during hydrolysis of $NaBH_4$ by replacing oxygen with B to form highly active Co-B phase. This Co-B not only showed better activity than Co-B synthesized from cobalt salts, but also exhibited similar activity to that of noble metals such as PtRu, Pt/C and Ru/C. Later, the effect of crystallinity and morphology of Co_3O_4 on the activity was also studied [28]. Cobalt oxide encapsulated in C_2N polymer network displayed very high H_2 generation rate by hydrolysis of $NaBH_4$ [29]. Simagina et al. [30] investigated the mechanism of Co_3O_4 powder catalyst at various stages during the hydrolysis reaction course and established that catalytically active Co_2B phase is formed in-situ as the reaction progresses.

Unfortunately, all these catalysts were developed in the form of powder where separating the catalyst for their reuse is difficult, and is a major hurdle to overcome. On the other hand, -catalyst in the form of coatings or thin film, which can serve as an environmentally friendly "*green catalyst*" for easy recovery, reuse and can function as ON/OFF switch for the reaction, has not yet been studied. Mainly nanoparticle assembled coatings (NPACs) are best suited catalyst providing high surface area and good stability against aggregation as a result of immobilized and adherent nature of NPs on the suitable substrate. Amongst various synthesis techniques, Pulsed Laser Deposition (PLD) has emerged as a viable method for the production of NPACs, in a single step, with desired properties [31–33] by simply tuning the deposition parameters. Cobalt NPs embedded in boron matrix thin film catalyst synthesized by PLD showed similar activity to that of Pt/C for hydrolysis of $NaBH_4$ and NH_3BH_3 [34]. In our recent work [35], reactive PLD was used to synthesize Co_3O_4 NPs assembled coating with narrow size distribution. These NPs produced by PLD are definitely more efficient for photocatalysis reaction as compared to NPs synthesized by various other chemical and physical methods [36].

The present work mainly focuses on the use of inexpensive Co_3O_4 catalyst NPACs synthesized on glass substrates, by using PLD technique, for H_2 production from hydrolysis of Sodium Borohydride. The Co_3O_4 NPACs showed enhanced H_2 generation rate as compared to the bulk Co_3O_4 powder, the causes of which have been investigated and reported in the present work. The laser deposition parameters are varied to study the effect of crystallinity, morphology and chemical states of Co_3O_4 NPs on the catalytic activity.

2. Experimental methods

2.1. Catalyst preparation

2.1.1. Co_3O_4 powder

Co_3O_4 powder was prepared by the co-precipitation (CP) method as per the procedures reported in the literature [36]. Dilute ammonia solution (25%) was added as a precipitator to the homogeneous 0.04 M aqueous solution of $CoCl_2$ under continuous stirring. After stirring at room temperature, the obtained cobalt hydroxide ($Co(OH)_2$) precipitate was filtered and subsequently washed with distilled water and ethanol for several times. Finally, the $Co(OH)_2$ precipitate was vacuum dried and later thermally treated at 400 °C for 2 h to obtain the Co_3O_4 powder.

2.1.2. Co_3O_4 coating

NPACs of Co_3O_4 were deposited by PLD using KrF excimer laser (Lambda Physik) with an operating wavelength of 248 nm, pulse duration of 25 ns, and repetition rate of 20 Hz. Details of the deposition apparatus and mechanisms involved are well reported in the literature [37]. Laser ablation was carried out by using a pure metallic Co target under oxygen atmosphere. Prior to the deposition, the PLD chamber was evacuated up to a base pressure of 10^{-6} mbar. Co_3O_4 NPACs (see technical details in Ref. [36]) were deposited on Si and glass substrates by maintaining target to substrate distance at 5.5 cm, with substrate position parallel to the target, or normal to the flow velocity of the plume expansion. Several samples were deposited by varying O_2 gas pressure (3×10^{-3}, 8×10^{-3}, 4.5×10^{-2} and 8×10^{-2} mbar), substrate temperature (25, 200, 250 and 300 °C) and different laser fluences (1, 3, 5 and 7 J/cm^2). Out of the three parameters, two were kept constant and the third was varied during each deposition of the coating.

2.2. Catalyst characterization

The surface morphology of all samples was studied by scanning electron microscope (SEM-FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy analysis (EDS, INCA PentaFET-x3) to determine the composition of the samples. Transmission Electron Microscopy (TEM) analysis was performed with a field emission FEI TECNAI F20 SuperTwin FEG (S) TEM microscope operating at 200 kV. Raman spectra were recorded by using HORIBA JobinYvon Lab RAM Aramis Raman spectrometer with diode pumped solid state laser at 634 nm. Structural characterization of the deposited samples was carried out by conventional X-ray diffraction (XRD) (Regaku Ultima IV), Cu Kα radiation (λ = 1.5414 Å), in Bragg–Brentano (θ–2θ) configuration. X-ray photoelectron spectra (XPS) were acquired with a monochromatic Al Kα (1486.6 eV) X-ray source and a hemispherical analyzer using a PHI 5000 Versa Probe II instrument. Appropriate electrical charge compensation was employed to perform the analysis and binding energy was referenced to the C 1s peak.

2.3. Hydrolysis measurements

For catalytic activity measurements, an alkaline stabilized solution of $NaBH_4$ (0.025 ± 0.001 M, pH 14) (Sigma Aldrich) was prepared. Gas volumetric method was used to measure the hydrogen volume generated by hydrolysis reaction. Detailed description of the measurement apparatus can be found elsewhere [38]. In the present experiment, 150 ml of the above $NaBH_4$ solution was used and maintained at 30 °C before adding the catalyst to the solution. In each experiment, weight of catalyst deposited in the form of coatings was close to 1 mg, whereas the amount of catalyst used as powder was 10 mg. H_2 production rate was calculated by measuring the weight of the water displaced which can be eas-