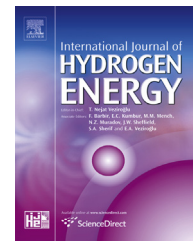




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# Mesoporous Co–B nanocatalyst for efficient hydrogen production by hydrolysis of sodium borohydride

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## ARTICLE INFO

### Article history:

Received 11 July 2013

Received in revised form

23 August 2013

Accepted 1 September 2013

Available online 1 October 2013

### Keywords:

Cobalt boride

Mesoporous structure

Sodium borohydride

Hydrogen generation

## ABSTRACT

Two types of mesoporous Co–B nanocatalysts were prepared by the reduction of cobalt chloride with Sodium Borohydride (SBH) in the presence of cationic and non-ionic surfactant templates, namely n-cetyl-trimethyl-ammonium bromide (CTAB) and Pluronic (P123) respectively. Nitrogen adsorption–desorption isotherms revealed the presence of slit-like pores on the catalyst surface which provide high effective surface area. These surface enhanced catalysts were tested for hydrogen production by hydrolysis of sodium borohydride. The mesoporous Co–B catalysts showed much higher activity (4 times) in comparison to the non-porous Co–B, which can be attributed to the higher surface area of the mesoporous structures. Co–B/P123 catalyst showed the highest hydrogen generation rate owing to the presence of wide uniform pores which facilitated easier interaction of the reactants to release hydrogen. The lack of stability in the pore structure is observed at elevated temperatures for both the mesoporous Co–B catalyst.

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## 1. Introduction

Hydrogen is considered to be an efficient energy carrier for the future, owing to its high energy content and renewability. Hydrogen, in its purest form, is utilized as a fuel in Proton Exchange Membrane Fuel Cell (PEMFC) to produce energy with zero emission of greenhouse gases [1]. Presently, the conventional methods of hydrogen production involve the steam reforming of natural gas where the final products contain various greenhouse gases (CO and CO<sub>2</sub>). For the advancement of hydrogen economy, researchers are aiming for finding ways for developing methods for hydrogen production with increased efficiency and non-polluting byproducts.

Major difficulty in the development of on-board hydrogen use for PEMFC lies in the hydrogen storage system. The

conventional means of storing hydrogen in pressurized tanks and as cryogenic liquid hydrogen are not viable for the on-board applications. Chemical hydrides (such as NaBH<sub>4</sub>, NH<sub>3</sub>BH<sub>3</sub>, LiH, KBH<sub>4</sub>, etc.), appear promising materials for storing hydrogen owing to their high volumetric and gravimetric hydrogen storage capacity as well as for their stability. Pure hydrogen can be generated from these hydrides at room temperatures and therefore they are expected to be suitable for on-board as well as off-board applications. Amongst the various chemical hydrides, Sodium Borohydride (NaBH<sub>4</sub>, SBH) has been widely accepted as a relevant hydrogen source owing to its high storage capacity (10.9 wt%). SBH has also been reported as a potential fuel for direct fuel cells [2]. Importantly, the reaction product of SBH is borax which is environmentally safe and can be recycled [3].

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To effectively control the hydrolysis of SBH, efficient catalyst is needed. Noble metal catalysts have been widely investigated and are found to be suitable for such purposes. Amendola et al. [2] and Kojima et al. [4] have effectively used Ru-based and Pt-based catalysts for hydrolysis of SBH respectively. However, the use of noble metals, Pt [5], Ru-nanoclusters [6], Pt/Ru [7], Pt/Pd [8], needs to be minimized owing to their high cost and scarcity. This has led to the search for non-noble catalysts, which are more earth-abundant and have efficiency comparable to their noble counterparts. Transition metal (Co, Ni) catalysts have been investigated in the past [9,10] and are found to be efficient in accelerating the hydrogen production rate. Cobalt boride (Co–B) is a promising candidate for hydrogen generation considering its high activity and low cost. However, during Co–B synthesis, particle agglomeration takes place which reduces the effective surface area and limits the catalytic activity. Researchers have used innovative synthesis methods to avoid agglomeration. Patel et al. [11] reported the laser ablation synthesis method to produce thin film catalyst assembled with cobalt nanoparticles in boron matrix having activity comparable to that of Pt-nanocatalyst. Embedding the catalyst into thin film matrix increases the active surface area and also prevents agglomeration. In other works, Co–B catalyst was doped with metalloid such as P [12] or metal such as Ni [13] to obtain synergic effect to provide enhanced catalytic efficiency. Doping with transition metal oxides of Cr, Cu, and Mo has been found to be helpful in avoiding agglomeration of the particles [14,15]. The oxides act as atomic barriers against agglomeration thus preserving higher surface area and enhanced catalytic activity [14,15]. Another method adopted to increase the active surface area of the catalyst and avoiding agglomeration is by supporting them on porous templates. In our recent work [16], we have reported enhanced stability and higher hydrogen generation rate by supporting Co–B catalysts on various types of mesoporous silica substrates where the activity was found to be comparable to Rh, Ru/C, and other noble metals.

Mesoporous supports provide a better way of increasing the active surface area but the quantity of catalyst that can be supported is very small as compared to that of the template itself. Thus it is important to find the means of increasing the active surface area of the Co–B catalyst itself without supporting them on other substrates or introducing other elements. This can be achieved by forming nanostructure on the Co–B catalyst surface. Tong et al. [17] and Li et al. [18] reported the synthesis of amorphous Co–B catalyst with mesoporous structures which provide high surface area for improved hydrogenation. In another work by the same authors, Co–B flowers with mesoporous structures were synthesized and tested for hydrogen production from hydrolysis of  $\text{KBH}_4$  [19].

In this work, we have studied the catalytic activity of mesoporous (MSP) Co–B catalysts for  $\text{H}_2$  production by means of hydrolysis of alkaline  $\text{NaBH}_4$  solution. For this purpose, two types of MSP Co–B catalysts were synthesized using two different surfactants and compared with non-porous Co–B powder for the same reaction. Enhanced catalytic activity of MSP Co–B is correlated to the high surface area and the typical pore structures. Activation energy barriers and stability of the

mesoporous catalysts are also investigated for hydrolysis reaction.

## 2. Experimental

### 2.1. Catalyst preparation

Two types of mesoporous (MSP) Co–B nanoparticles were synthesized by using two different surfactants namely, *n*-cetyl-trimethyl-ammonium bromide (CTAB) and Pluronic (P123). All the chemicals used for the synthesis were acquired from Sigma Aldrich. The methods used for the synthesis are described below:

#### 2.1.1. CoB/CTAB

This type of MSP Co–B was synthesized as per the procedure described by Tong et al. [17] using CTAB as the surfactant template. 0.362 mg of CTAB (0.032 M) was added to aqueous solution (0.05 M) of cobalt chloride ( $\text{CoCl}_2$ ) and stirred for 60 min at around 318 K. After cooling at room temperature, sodium borohydride ( $\text{NaBH}_4$ ) (0.24 g), as a reducing agent, was added to the mixture under continuous stirring. When bubble generation ceased, the remnant solution was filtered and the resulting black powder was washed extensively with distilled water for several times followed by ethanol for two times. Later the catalyst powder was transferred into 100 ml of ethanol and the combined mixture was refluxed at 353 K for 24 h. The refluxed solution was then collected and washed with ethanol for three times followed by drying in vacuum.

#### 2.1.2. CoB/P123

Pluronic (P123) was used as the surfactant template to synthesize this type of MSP Co–B. The synthesis was carried out exactly by the same method as that with CTAB, just by replacing CTAB with P123 as the templating material.

Non-porous Co–B was also synthesized for comparison by reduction of cobalt chloride solution.

### 2.2. Catalyst characterization

The BET surface area and adsorption–desorption isotherms of all the catalyst powders were determined using surface area and porosity analyzer (Micromeritics ASAP 2020) by nitrogen adsorption at 77 K after degassing at 413 K for 3 h. The surface morphology and microstructure of all the catalyst powders were studied using scanning electron microscopy (SEM-FEG, JSM 7001F, JEOL) and Transmission Electron Microscopy (TEM, JEOL). Structural characterization of all the catalyst powders was performed by X-Ray Diffractometer (XRD) using the  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5414 \text{ \AA}$ ) in Bragg–Brentano ( $\theta$ – $2\theta$ ) configuration.

For catalytic activity measurements, an alkaline-stabilized solution of sodium borohydride (pH 13,  $0.025 \pm 0.001 \text{ M}$ ) (Rohm and Haas) was prepared by the addition of NaOH. The volume of hydrogen gas generated during the reaction was measured by gas volumetric method in an appropriate glass reaction chamber. The reaction chamber was maintained at a constant temperature within accuracy of  $\pm 0.1 \text{ K}$  by using a thermostatic bath. The chamber was equipped with a catalyst insertion

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