



Efficient hydrogen generation from sodium borohydride hydrolysis using silica sulfuric acid catalyst



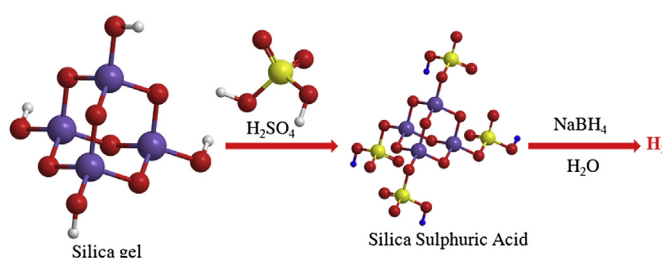
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HIGHLIGHTS

- Silica sulfuric acid is prepared successfully.
- Loading of $-\text{SO}_3\text{H}$ group is confirmed through various characterization techniques.
- Effect of this catalyst on sodium borohydride hydrolysis is studied.
- Impressive hydrolysis rate is observed in presence of this catalyst ($5.5 \text{ L min}^{-1} \text{ g}^{-1}$).
- One of the lowest activation energy is obtained for NaBH_4 hydrolysis reaction (17 kJ mol^{-1}).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 August 2014
 Received in revised form
 31 October 2014
 Accepted 9 November 2014
 Available online 11 November 2014

Keywords:

Sodium borohydride
 Hydrolysis
 Silica sulfuric acid
 Hydrogen storage
 Acid catalyst

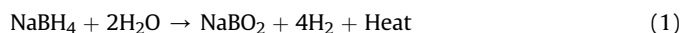
ABSTRACT

A heterogeneous acid catalyst, silica sulfuric acid, was prepared from silica gel (SiO_2) and sulfuric acid (H_2SO_4). Addition of SO_3H functional group to SiO_2 has been confirmed through various characterization techniques. The effect of this heterogeneous acid catalyst on hydrogen generation from sodium borohydride hydrolysis reaction was studied for different ratios of catalyst to NaBH_4 and at different temperatures. The catalyst exhibited high catalytic activity towards sodium borohydride hydrolysis reaction. The activation energy of the NaBH_4 hydrolysis reaction in the presence of silica sulfuric acid was calculated to be the lowest (17 kJ mol^{-1}) among reported heterogeneous catalysts till date.

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1. Introduction

Sodium borohydride (NaBH_4) is one of the mostly studied chemical hydrides used for hydrogen generation owing to its high hydrogen storage capacity (10.8 wt%), non-toxicity and purity of hydrogen product stream [1–3]. The hydrogen stored in NaBH_4 , can easily be released via hydrolysis, as described in Eq. (1) [4].



Self-hydrolysis of sodium borohydride is initiated when NaBH_4 comes into contact with water at room temperature. However, during the course of the reaction, pH of the reaction mixture increases due to formation of the by-product NaBO_2 , rendering the reaction incomplete [4]. Therefore, the primary requirement for the catalyst in this reaction is pH control of the reaction mixture to facilitate favorable hydrolysis kinetics. Several studies conducted on the catalysis of sodium borohydride hydrolysis successfully

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showed that the noble metals (Pt, Rh, Ru etc.) [5–10], and cobalt boride alloys (Co–B) [4] exhibit good catalytic effect on sodium borohydride hydrolysis. Despite advantages such as high activity and cyclic stability of noble metals, high cost and relatively less abundance of these catalysts has limited their application. Another efficient but relatively abundant catalyst, Co–B, suffers from limited cyclic stability. It is reported in literature that the activity of Co–B catalysts reduces to less than half of its initial activity after 14 cycles. This loss in activity is governed by the formation of hydrated borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boron oxide (B_2O_3) on the catalyst's surface [11].

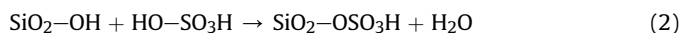
Most of the work reported in literature is focused on catalysis of NaBH_4 hydrolysis using metal or metal alloy based catalysts [12–18]. Very few literature reports are on the use of liquid acid catalysts, (e.g., HCl , H_2SO_4 , HNO_3 , carboxylic acid, CH_3COOH etc.) in NaBH_4 hydrolysis application [19–23]. Acids catalysts are a popular choice in various chemical industries like the oil refining and petrochemical industry. More than 10^8 MT/year of industrial products are produced by the use of acid catalysts [24]. Since 1940s, research has been focused on replacing liquid acid by solid acid catalysts. The advantages of safe handling, reduced reactor corrosion, eco-friendly waste disposal, simple and versatile system designing and catalyst regeneration make solid acid catalysts preferable over the liquid ones [24]. In the current work, silica sulfuric acid catalyst is employed as a heterogeneous acid catalyst to assist hydrogen production from sodium borohydride.

Silica sulfuric acid (SSA) catalyst has been mainly reported in catalysis of organic reactions [25–27]. SSA catalyst is a solid heterogeneous alternative to sulfuric acid. The high catalytic activity of this catalyst is attributed to the higher surface acidity caused by intense dispersion of SO_3H group on the surface of silica. The low cost of silica together with the advantages as a solid acid catalyst establishes this catalyst as a very promising candidate.

2. Experimental

2.1. Preparation of catalyst

Silica sulfuric acid catalyst was prepared by the soak and dry method [27]. Silica gel (230–240 mesh, Merck, India) was dispersed in diethyl ether. Concentrated sulfuric acid (98%) was added drop wise to the silica gel dispersed in diethyl ether. This mixture was stirred for 10 min and dried in a hot air oven (at 60°C) for 18 h. The dry powder thus obtained was heated at 120°C for 3 h in order to obtain the catalyst. Silica sulfuric acid is formed according to the reaction pathway (2), finally leading to formation of the brown colored catalyst. The as prepared catalyst was stored inside an argon-filled glovebox (MBraun), characterized and finally used for hydrolysis.



2.2. Characterization of catalyst

The morphology, physical properties and phase structure of silica gel (SG) and silica sulfuric acid (SSA) catalyst were characterized by various analytical techniques. The phase structures were determined with a Philips X-ray Diffractometer using $\text{Cu K}\alpha$ radiation having wavelength 1.54 \AA within the 2θ range of $15^\circ\text{--}60^\circ$. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer spectrophotometer over the range of $300\text{--}4000 \text{ cm}^{-1}$. Surface morphology was examined by Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) using Zeiss Ultra 55 model and

Field Emission Gun-Transmission Electron Microscope (FEG-TEM) using PHILIPS CM200 model. BET surface area was analyzed using a Micromeritics ASAP 2020 model. N_2 -adsorption isotherm was recorded at -196°C . Specific surface area, pore size and pore volume of all samples were calculated from BET, Langmuir, t -plot, BJH modelizations. Before each adsorption cycle, samples were out-gassed at 150°C .

2.3. Hydrolysis tests

Hydrogen evolution from hydrolysis of sodium borohydride was measured by water displacement method, using a hydrolysis set-up as reported elsewhere [28]. In a three-neck RB (round-bottom) flask, 0.02 g of solid sodium borohydride and an appropriate amount of catalyst were placed together and a constant volume of water (25 ml) was introduced to the RB flask using a pressure-equalizing separating funnel. The RB flask was kept inside a water bath to maintain the reaction temperature within the set value $\pm 1^\circ\text{C}$. The evolved hydrogen was passed through a silicone tube into an inverted cylinder, where the volume of hydrogen generated was measured with respect to time. The pH of the reaction and temperature were recorded by a digital pH meter and a thermocouple inserted through the neck of the RB flask.

3. Results and discussion

3.1. Characterization

XRD patterns obtained for silica gel and silica sulfuric acid are shown in Fig. 1. Both the patterns contain a broad peak in the range

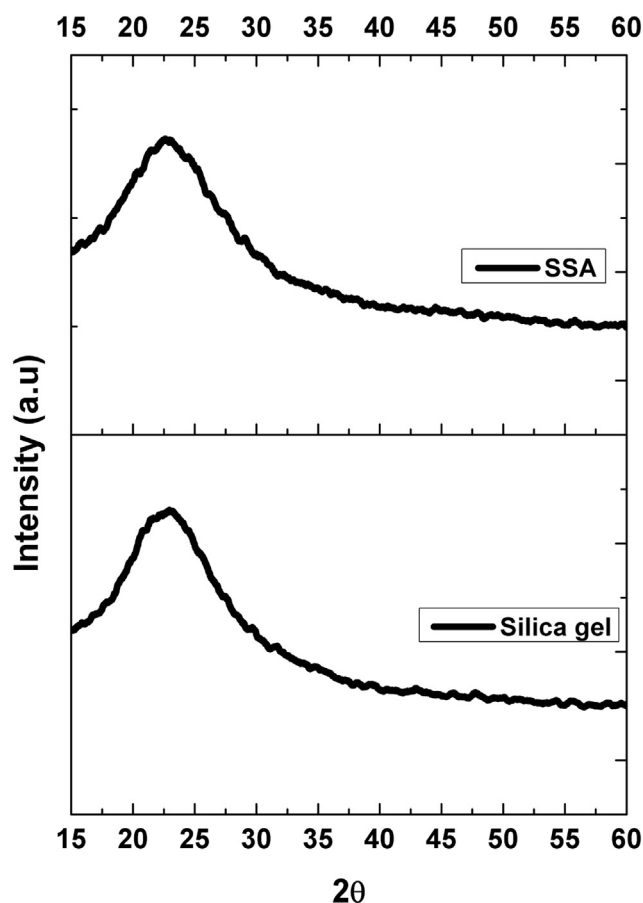


Fig. 1. XRD pattern of silica gel and SSA.

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