Hydrogen generation from NaBH₄ hydrolysis using Co-B/AlPO₄ and Co-B/bentonite catalysts

Joydev Manna, Binayak Roy, Devendra Pareek and Pratibha Sharma

Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Mumbai, India

ABSTRACT
Aluminium phosphate and bentonite supported Co-B catalyst were synthesized via two step impregnation-reduction method for sodium borohydride hydrolysis. The synthesized catalysts were characterized by XRD, FTIR, XPS, FE-SEM, FE-TEM, BET, ICP-AES techniques and tested for NaBH₄ hydrolysis reaction. The results demonstrated that the synthesized supported Co-B catalysts greatly facilitate the NaBH₄ hydrolysis reaction. Highest hydrolysis rate observed for Co-B/AlPO₄ and Co-B/bentonite catalysts are 6.50 and 3.91 L min⁻¹ g⁻¹, respectively, with 2 wt% NaBH₄, 5 wt% NaOH solution at 30°C. The hydrogen generation rate was found to increase with experimental temperature. Activation energy for the hydrolysis reaction was observed to be 37 and 40.2 kJ mol⁻¹ for Co-B/AlPO₄ and Co-B/bentonite catalysts, respectively.

Introduction
One of the prime challenges faced in the recent years have been the identification of a particular material which is suitable for hydrogen storage application [1]. Complex hydrides (NaBH₄, LiBH₄, KBH₄ etc.) are the premier materials due to their light weight, high hydrogen storage capacity and ability to release hydrogen at RT through hydrolysis [2]. Sodium borohydride is the most investigated chemical hydride among them due to its high hydrogen storage capacity (10.8 wt%), stability in alkaline solution, non-toxicity and pure hydrogen production [3–5]. The hydrolysis reaction of sodium borohydride at STP proceeds as Equation (1) [6].

\[
\text{NaBH}_4 + (2 + x) \text{H}_2\text{O} \rightarrow \text{NaBO}_2 \cdot x\text{H}_2\text{O} + 4\text{H}_2 + \sim 210 \text{kJ}
\] (1)

However, this reaction is not spontaneous at room temperature and required a suitable catalyst to efficiently tailor the hydrogen generation. There have been many efforts to develop effective catalyst to improve the NaBH₄ hydrolysis reaction. Noble metals (Pt, Rh, Ru etc.) are found to be the most effective catalysts towards NaBH₄ hydrolysis but their high cost limits their wider use [7,8]. Cobalt-based catalysts, especially cobalt boride alloy (Co-B), have potential catalytic activity to replace noble metals in NaBH₄ hydrolysis [9,10]. Co-B catalysts can easily be synthesized by reduction of cobalt(II) salts but it has been observed that formed Co-B particles always prefer to be in agglomerated state due to high surface energy involved in the exothermic reduction process [11]. The agglomeration causes the surface area to decrease which in turn compromises the catalytic activity of the Co-B catalyst. The catalytic activity of Co-B can be improved by dispersing the particles in a suitable support material. Support material does not only provide space for the active materials but also render large specific surface area along with the chance...
of better dispersion in their pores. There are several reports on the effect of supported catalysts in sodium borohydride hydrolysis. Simagina et al. [12] prepared Rh/TiO₂ catalysts which showed good performance for NaBH₄ hydrolysis. Demirci et al. [13] studied the Ru promoted sulphated zirconia (ZrO₂·SO₄²⁻) catalyst and investigated the kinetics of the NaBH₄ hydrolysis. Zhao et al reported the use of carbon black (Vulcan XC 72) supported Co-B catalysts, which reduced the activation energy of reaction to 57.8 kJ mol⁻¹ [14]. Active carbon supported Co-B catalyst, prepared by Xu et al, showed activation energy of 44 kJ mol⁻¹ [15]. Co-B supported on Pd [16], SiO₂ [17], zeolites [18] has been reported to be highly effective on NaBH₄ hydrolysis.

From this perspective, the current study elaborates the application of bentonite clay and aluminium phosphate as support materials owing to their natural abundance, low cost and distinctive surface properties. The supported Co-B catalyst were prepared, characterized by various techniques. Activity of the prepared catalyst on hydrogen generation from NaBH₄ hydrolysis reaction was also observed at different reaction conditions.

**Experimental details**

**Synthesis of aluminium phosphate**

Aluminium phosphate was prepared by sol-gel method [19]. In brief, equimolar aluminium nitrate nonahydrate (375 g) and ammonium dihydrogen phosphate (115 g) was dissolved in water (60 ml) at 80 °C. Then aqueous ammonia (30%, 132.5 cc) was added to the solution drop wise and stirred for 30 min. White gel formed during this reaction was aged for 12 h, then washed several times with DI water, filtered and dried at 60 °C. The dried sample was calcined at 500 °C to obtain AlPO₄ poweder.

**Synthesis of Co-B/AlPO₄ and Co-B/bentonite**

Co-B catalyst was impregnated on the supports (AlPO₄ and bentonite) by two step impregnation-reduction method. To prepare Co-B/AlPO₄, 1 g of AlPO₄ powder was added to 50 ml cobalt chloride (0.34 g CoCl₂·6H₂O) solution and stirred for 24 h at 300 rpm. This mixture was dried at 90 °C and the obtained dry powder was dispersed in 50 ml water followed by ultrasonication for 10 min. The dispersed solution was reduced by adding 10 ml sodium borohydride solution ([BH₄⁻]/[Co²⁺] = 5) dropwise. The obtained black precipitate was washed several times by DI water and filtered followed by drying at 60 °C under vacuum. Co-B supported on bentonite (Co-B/bentonite) catalyst was prepared by similar procedure using bentonite clay instead of AlPO₄.

**Characterization**

Crystalline nature of the catalysts was determined with Philips X-ray Diffractometer using Cu K-α radiation of wavelength 1.54 Å within the 20 range of 10°–80°. FTIR spectra were recorded on a Perkin Elmer spectrophotometer over the range of 350–4000 cm⁻¹. Elemental composition of the materials were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) in a spectrometer model ARCO5 from M/s. Spectro. Morphology analysis was done by Jeol JSM-7600F FEG-SEM. FEG-TEM images were obtained from a Philips CM200 FEG-TEM machine. Surface composition and oxidation state of elements in all the catalysts were determined by Thermo VG scientific MultiLab ESCA2000 XPS machine. A monochromatic radiation of Al Ka (1486.6 eV) was used to obtain the spectra. Specific surface area was analyzed by N₂-adsorption isotherm at −196 °C using a Micromeritics ASAP (Accelerated Surface Area and Porosimetry System) 2020 model. Before each N₂ adsorption experiments, samples were outgassed at 300 °C.

**Hydrolysis test**

Hydrolysis tests were performed in a three neck round bottom (RB) flask reactor and the hydrogen release was measured by water displacement method [11]. The reactor was kept inside a water bath to maintain the reaction temperature within ±1 °C range of the set value. The stabilised alkaline borohydride solution was introduced from a separating funnel into the RB flask containing catalyst. Hydrogen evolution starts as soon as solution comes in contact with the catalyst. The evolved hydrogen gas was then passed through a silicone tube and collected in an inverted cylinder by water displacement method. The volume of the generated hydrogen was measured from the change in height of the water level in cylinder with respect to time.

**Results and discussion**

**Characterization of Co-B/AlPO₄**

Figure 1(a) shows the XRD patterns for synthesized AlPO₄ and Co-B/AlPO₄. Absence of any distinctive peaks in the figure confirms the amorphous nature of the synthesized AlPO₄ support and Co-B/AlPO₄ catalyst. Amorphous nature of the cobalt boride (Co-B) is reported throughout the literature [20–22]. SAED patterns (Figure S1, see ESI) obtained from FEG to TEM analysis also confirms the amorphous nature of the obtained catalyst.

FTIR spectra for AlPO₄ and Co-B/AlPO₄ are denoted in the Figure 1(b). In AlPO₄ transmittance peaks for Al-O-P vibrations were assigned at 500 and 730 cm⁻¹ [23]. P–O stretching frequency was observed in the range of 1000–1500 cm⁻¹. The P=O stretching peak is assigned around 1650 cm⁻¹. In the FTIR spectra of Co-B/AlPO₄, four additional transmittance peaks were observed at 800, 2070, 2843, 2917 cm⁻¹ corresponding to boron lattice vibration along with the peaks observed for
AlPO₄. One peak in Co-B/AlPO₄ spectra near 1621 cm⁻¹ appearing due to the B-O stretching vibration may be corroborated to the surface oxidation of the catalysts.

Morphology of the synthesized support and catalyst was observed by FEG-SEM analysis. The as synthesized AlPO₄ particles were found to consist of micron scale rounder agglomerates having much smaller (~100 nm) primary particles (Figure 1(c)). As prepared catalyst, Co-B/AlPO₄ was also observed to be in agglomerated state (Figure 1(d)). However size of the primary particles in Co-B/AlPO₄ were comparatively smaller (10–50 nm) than the primary particles of the support materials. The formation of lower particle sizes may be occurred during the formation of Co-B particles via vigorous reduction of the cobalt salt by NaBH₄.

The presence of cobalt and boron in the XPS survey analysis (Figure S2, see ESI) of Co-B/AlPO₄ confirms the doping of Co-B onto the AlPO₄ support. The XPS spectra of Co₂p and B₁s electronic levels for Co-B/AlPO₄ are shown in Figure 1(e) and (f), respectively. For Co₂p, one major peak appears at the binding energies (BE) in a range of 780–785.3 eV attributed to the Co2p₃/2 level, along with a 3d → 4s satellite peak in the range 785.5–792.5 eV [24]. One peak for 2p₁/₂ also appears

**Figure 1.** (a) Powder XRD patterns and (b) FTIR spectra of AlPO₄ and Co-B/AlPO₄; (c) FE-SEM images of AlPO₄ and (d) FE-SEM images of Co-B/AlPO₄; (e) XPS spectra of Co₂p and (f) B₁s of Co-B/AlPO₄ catalyst.
Characterization of Co-B/bentonite

X-ray diffraction patterns of bentonite and Co-B/bentonite is shown in Figure 2(a). From the figure, it can be observed that bentonite is a crystalline material with distinct diffraction pattern. XRD pattern of bentonite matches with the JCPDS reference code 00-003-0019 of sodium aluminium silicate hydroxide hydrate. After Co-B loading onto the bentonite surface, peaks corresponding to bentonite diffraction pattern is overshadowed by Co-B amorphous broad peak [11].

FTIR spectrum of bentonite and Co-B/bentonite is shown in Figure 2(b). The FTIR band at 3632 cm$^{-1}$ was attributed to stretching vibrations of structural O–H groups of bentonite [26]. The bands observed at 918 cm$^{-1}$ is corresponding to Al–OH–Al bending vibrations. A complex broad band at 1048 cm$^{-1}$ is appeared due to the stretching vibrations of Si–O groups, while the bands near 525 and 468 cm$^{-1}$ are due to Al–O–Si and Si–O–Si bending vibrations, respectively [27]. For Co-B/bentonite, all bands corresponds to bentonite along with band near 680 cm$^{-1}$ corresponds to B lattice vibration of Co-B is observed. Another band corresponds to B–O stretching vibration observed at 1380 cm$^{-1}$ [28].

Figure 2. (a) Powder XRD patterns and (b) FTIR spectra of bentonite and Co-B/bentonite; (c) FE-SEM images of bentonite and (d) FE-SEM images of Co-B/bentonite.
Hydrolysis of NaBH₄ in the presence of Co-B/AlPO₄

It is a general practice to use alkaline stabilized NaBH₄ solution as feed stock for hydrogen generation [11]. Otherwise fuel loss will occur due to the self-hydrolysis of NaBH₄ in the presence of water. Self-hydrolysis of NaBH₄ can be averted by adding alkali (e.g. NaOH, KOH etc.) in the solution. It has also been reported that the NaOH concentration controls the hydrogen generation rate (HGR) from NaBH₄ hydrolysis reaction [29]. In order to understand the effect of NaOH concentration on the NaBH₄ hydrolysis, tests were performed with 2 wt% NaBH₄ solution stabilised by NaOH at five different concentrations (1, 2, 3, 4 and 5 wt%) at 30 °C in the presence of 0.1 g Co-B/AlPO₄ catalyst. The results so obtained are reported in Figure 3(a). It has been observed that with increase in NaOH concentration, HGR was increased. Average HGR was found to be 1.41 L min⁻¹ g⁻¹ in the presence of 1 wt% NaOH, which increased to 6.50 L min⁻¹ g⁻¹ when NaOH concentration increased to 5 wt%. Similar observation is reported in literature for Co and Ni based catalysts [30]. It has been suggested that at higher pH, desorption of $\text{B(OH)}_{4}^-$ from the surface of catalysts increases and consequently renewal of the active site for hydrolysis reactions enhanced [11].

In Figure 3(b), hydrogen generation volume obtained through hydrolysis of alkaline (5 wt%) NaBH₄ (2 wt%)
solution using Co-B/AlPO₄ catalyst are reported as a function of time at different solution temperature (30, 40, 50 and 60 °C). It has been observed that hydrolysis rate increases with increase in the solution temperature. From the Arrhenius plot (Figure 3(c)) of the NaBH₄ hydrolysis reaction in the presence of Co-B/AlPO₄ catalyst, the activation energy of the reaction is calculated to be ca. 37 kJ mol⁻¹, which is much lower compared to the other reported catalyst like, Co-B supported on carbon (57.8 kJ mol⁻¹) [14] and multiwall carbon nanotubes (40.4 kJ mol⁻¹) [31], structured Co₃B (45 kJ mol⁻¹) [32], Raney Co (53.7 kJ mol⁻¹) [33], Co supported on activated carbon (44 kJ mol⁻¹) [15], Co-B thin film (44.47 kJ mol⁻¹) [34].

**Hydrolysis of NaBH₄ in the presence of Co-B/bentonite**

To observe the effect of NaOH concentration for Co-B/bentonite catalyst the NaBH₄ hydrolysis reactions were performed with 2 wt% NaBH₄ solution stabilised by NaOH at five different concentrations (1, 2, 3, 4 and 5 wt%) at 30 °C in the presence of 0.1 g Co-B/bentonite catalyst. The obtained results are reported in Figure 4(a). From Figure 4(a), it is apparent that, hydrolysis rate increased with increase in alkalinity as observed in case of Co-B/AlPO₄. The average HGR was increased from 0.8 to 3.91 L min⁻¹ g⁻¹ when concentration of NaOH was increased from 1 to 5 wt%.

Hydrogen generation plot of Co-B doped bentonite at different temperatures and corresponding Arrhenius plot for calculating Eₐ are shown in Figure 4((b) and (c)). It is evident from the Figure 4(b) that HGR increases with increase in the temperature of the reaction. Activation energy for catalysed hydrolysis reaction calculated from Arrhenius plot was found to be 40.2 kJ mol⁻¹. The obtained activation energy is less than the reported 65–69 kJ mol⁻¹ for unsupported powder Co-B catalyst [35,36].

The hydrolysis reaction of sodium borohydride in presence of boride catalysts proceed via five-step reaction mechanism (Equations (2)–(6)) [37]. The first step (Equation (2)) of the reaction is reversible surface adsorption and dissociation of borohydride ion to form MH and MBH₃⁻ [where M is the active catalysts surface]. In second step (Equation (3)) charge associated with MBH₃⁻ became reversible with catalyst surface (M) and borane (BH₃). This step is referred as the anodic step of the hydrolysis reaction. In the step 4 (Equation (5)), where an electron is transferred with water and catalyst surface. In third step (Equation (4)) borane reacts with the OH⁻ anion to form comparatively stable...
intermediate (BH$_3$OH$^-$). The produced intermediate ion is assumed to have same reactivity as borohydride ion and goes through similar steps as Equations (2)–(4) to form BH$_4^-$ (OH$^-$_2) which further repeats the same steps to produce BH(OH)$_3$ and finally B(OH)$_4$$. In the last step (Equation (6)), the formed MH in Equations (2) and (5), react to produce a mole of hydrogen (H$_2$) and regenerate the catalyst.

\[
\begin{align*}
2M + BH_4^- &\leftrightarrow MBH_3^- + MH \\
MBH_3^- &\leftrightarrow BH_3^- + M + e^- \\
BH_3^- + OH^- &\rightarrow BH_2(OH)_2^- \\
M + e^- + H_2O &\rightarrow MH + OH^- \\
MH + MH &\rightarrow 2M + H_2
\end{align*}
\]

Similar reaction pathway of borohydride hydrolysis is followed in presence of the synthesized supported Co-B catalysts. The support materials (AlPO$_4$ and bentonite) have helped to improve the kinetics of the boride catalyst. The observed improvement in NaBH$_4$ hydrolysis kinetics in the presence of the synthesized catalysts is mainly due to the increase in the amount of active species (Co-B) by increasing surface area after loading the catalysts on the surfaces of AlPO$_4$ and bentonite. Also, as found from XPS, decrease in binding energy of Co$^0$ in supported Co-B catalyst indicates an increase in electron density after supporting on the AlPO$_4$ surfaces. Thus, high dispersion of Co-B, distinctive surface properties of the support materials and the higher metallic cobalt content in the supported Co-B catalyst helped to improve the hydrogen generation rate.

**Conclusion**

Hydrolysis rate in the presence of the supported Co-B catalysts (Co-B/AlPO$_4$ and Co-B/bentonite) are observed to be high compared to the other reported catalysts. Co-B/AlPO$_4$ catalyst is found to be more active than the Co-B/bentonite catalyst. Highest hydrolysis rate observed for Co-B/AlPO$_4$ catalyst is 6.50 L min$^{-1}$ g$^{-1}$ at 5 wt% NaOH concentration and 30 °C. For Co-B/bentonite catalyst, highest HGR observed is 3.91 L min$^{-1}$ g$^{-1}$ at same condition. The hydrogen generation rate was found to increase with experimental temperature. Activation energy for the hydrolysis reaction was observed to be 37 and 40.2 kJ mol$^{-1}$ for Co-B/AlPO$_4$ and Co-B/bentonite catalysts, respectively.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

**ORCID**

Binayak Roy [http://orcid.org/0000-0003-1204-9808](http://orcid.org/0000-0003-1204-9808)

Devendra Pareek [http://orcid.org/0000-0001-7231-6686](http://orcid.org/0000-0001-7231-6686)

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