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CATALYTIC HYDROGEN GENERATION FROM $NABH_4/H_2O$ SYSTEM: EFFECTS OF CATALYST AND PROMOTERS

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Abstract – A hydrogen generation system based on $NaBH_4$ hydrolysis is affected by the nature of the catalyst and catalyst promoter. Various catalyst promoters such as Al_2O_3 nanoparticles, Al_2O_3 particles, ZrO_2 sand, SiO_2, MMT clay, CNT and zeolite are compared with respect to hydrogen generation (HG) and hydrogen generation rate (HGR). The highest HG and HGR are observed with alumina nanoparticles as compared to other promoters. Cobalt chloride is found to be most efficient catalyst among the other cobalt based salts ($CoCl_2.6H_2O$, $CoSO_4.7H_2O$, $(CH_3COO)_2Co.4H_2O$, $Co(NO_3)_2.H_2O$), cadmium based salt ($CdSO_4$) and copper based salt ($CuSO_4.5H_2O$). Maximum HGR obtained is 19.47 moles/L.sec for $NaBH_4$ (1.26 moles/L)/Al_2O_3 nanoparticles (0.12 moles/L)/H_2O and $CoCl_2.6H_2O$ (0.02 moles/L) as catalyst at room temperature and atmospheric pressure. $NaBH_4$ and alumina hydrolysis reactions, hydrophilic and amphoteric nature of alumina, affinity of Co^{+2} towards BH_4^- ions and formation of aluminates are the factors that promote HGR, as illustrated in this work. Residue obtained from hydrolysis reaction is characterized for its elemental composition by the EDS technique, which confirmed a maximum percentage of boron in the residue. XRD and FTIR results concluded that adsorption of Na^+ and Co^+ ions occurred on the alumina surface and resulted in the formation of sodium aluminates and cobalt aluminates in the solution.

Keywords: Hydrogen generation, nanoparticles, alumina, sodium borohydride, cobalt chloride

INTRODUCTION

A major scientific and technical challenge to realize a hydrogen economy on a national or universal scale is wholly dependent on proficient hydrogen storage and delivery systems. Since a decade, chemical hydrogen storage has proved to be a competent approach for developing efficient hydrogen storage systems as compared to conventional storage. Sodium borohydride ($NaBH_4$) stands out as preeminent among chemical hydrides owing to its high hydrogen storage capacity (10.8 wt%) and potentially safe operational uses (Marrero et al., 2009). Similar to other hydrides, sodium borohydride undergoes a hydrolysis reaction as shown in reaction 1 and this reaction can be further activated with a suitable catalyst (Muir and Yao, 2011).

Millennium cell demonstrated the first portable hydrogen storage system based on $NaBH_4$ aqueous solutions (Amendola et al., 2000). This achievement accelerated the research in the field of $NaBH_4$-based hydrogen generation (HG) systems. The hydrolysis reaction of $NaBH_4$ is exothermic in nature, half of the hydrogen is provided by water, the generated hydrogen is highly pure and the byproduct (hydrated sodium metaborate) is environmentally safe. However, this system also suffers from some major drawbacks: variance between theoretical and practical gravimetric hydrogen storage

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2.xH_2O + 4H_2 + \Delta H\ (\text{-300 kJ/mole}) \tag{1}$$

**Corresponding author*: Arshdeep Kaur. E-mail: er.arsh87@gmail.com capacities (GHSC), excess water requirements, $NaBO_2$ solubility and the cost of $NaBH_4$ (Muir and Yao, 2011). US Department of Energy (US-DOE) in 2007 issued a No-Go recommendation for $NaBH_4$ for on-board hydrogen storage considering all the above disadvantages.

As $NaBH_4$ is a potential hydrogen storage material and considering all the drawbacks of $NaBH_4$-based hydrogen storage systems, a dual solid system is proposed combining $NaBH_4$ with other probable hydrogen storage materials that increases the overall GHSC of the system. For example, (a) Al/Li/Co/$NaBH_4$ with the water HG system gives 100% hydrogen yield at 50°C with Al (7.5 wt%) and Li (25 wt%) (Wang et al., 2013), (b) Al/$NaBH_4$ activated by lanthanum (La) metal HG system shows excellent stability with high La content (Jianbo et al., 2012), (c) Al/Li/$NaBH_4$ mixture in water activated by nickel HG system, at an optimized ratio of Al (10 wt%) and Li (10 wt%), gives 96% efficiency at 60°C (Shu et al., 2012), (d) Al/$NaBH_4$ in water with $CoCl_2$ as catalyst HG system, with an optimized composition, can achieve 90% fuel conversion within 5 min with GHSC of 5.4 wt% (Dai et al., 2011). In all the above HG systems, hydrogen storage efficiency is higher when compared to a conventional aqueous $NaBH_4$-based HG system.

Development towards $NaBH_4$-based on-board HG systems has resulted in significant research in synthesizing active catalyst. Many non-noble catalyst systems have been investigated, such as cobalt(II) chloride, nickel(II) chloride, iron(II) chloride, copper(II) chloride, and manganese(II) chloride for $NaBH_4$ hydrolysis. Cobalt(II) chloride is found to be the best active catalyst of all the above non-noble catalysts. Noble metal catalysts like platinum and ruthenium are used with different supporting materials like Pt loaded on $LiCoO_2$ or Ru loaded on TiO_2. Owing to the cost factors, it is not feasible to use noble metal catalysts for extensive applications in hydrogen storage systems (Muir and Yao, 2011).

Cobalt chloride is also investigated along with $NiCl_2$ and $CuCl_2$ and is found to be more reactive (Schlesinger et al., 1953). Comparing with other Co(II) salts like $Co(CH_3COO)_2$, $CoSO_4$, CoF_2, $Co(NO_3)_2$, $CoCl_2$ is found to be 4 times more reactive (Demirci et al., 2010; Liu et al., 2006 and Liu et al., 2008). This is essentially due to the electrophilic and strong positive charge of Co^{+2} that attract BH_4^- ions (Akdim et al., 2009 a). To increase the activity of catalyst and to gain high reactivity, catalysts are supported with different materials, for example Co or $CoCl_2$ supported with aluminium oxide (Al_2O_3) (Cakanyildirim and Guru, 2010), zeolite (Rakap and Ozkar, 2009) and carbon nanotubes etc. (Huang et al., 2008). Co-B catalyst is also doped with metal additives like Ni, Fe, Cu, Cr, and Mo (Muir and Yao, 2011).

Based on the above literature study and the problems related to $NaBH_4$-based hydrolysis systems, the present study gives the novel concept of addition of alumina (Al_2O_3) nanoparticles with $NaBH_4$ and $CoCl_2$ as catalyst. In this paper, a comparative study is performed among $CoCl_2$ and other cobalt based salts and among different promoters for $NaBH_4$ hydrolysis. Residual material left after the hydrolysis reaction is characterized using different analytical methods.

EXPERIMENTAL

Materials

Sodium borohydride ($NaBH_4$) (97% purity) and cobalt chloride hexahydrate ($CoCl_2.6H_2O$) (98% purity) were procured from M/s Loba Chemie Ltd., sodium hydroxide pellets (NaOH) (97% purity) and cobalt acetate tetrahydrate ($(CH_3COO)_2Co.4H_2O$) were purchased from Central Drug House Pvt. Ltd., γ-alumina (Al_2O_3) (20nm, 99% purity), γ-alumina (Al_2O_3) (100-200μm, 99% purity) and montmorillonite (MMT) clay were obtained from M/s Sigma Aldrich Chemicals Pvt. Ltd., copper sulphate pentahydrate ($CuSO_4.5H_2O$) (99% purity) and zeolite 13X (99% purity) were obtained from Merck Ltd., carbon nanotubes (CNT) were purchased from Nanoshell Ltd. Chemicals like cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) (99% purity), silicon oxide (SiO_2) (99% purity), cobalt trinitrate ($Co(NO_3)_2.3H_2O$) (97% purity), cadmium sulphate ($CdSO_4$) (99% purity) and zirconium sand (ZrO_2 66.90 %, SiO_2 32.54 %, Al_2O_3 1.15 %, TiO_2 0.27 %, Fe_2O_3 0.04 %) were purchased from SD Fine Chemicals Ltd.

Methods

The equipment used in the H_2 generation experiments is described in Figure 1. Reagents were added to the 250 mL three neck glass reactor in predetermined amounts in powdered form. The concentration of $NaBH_4$ and NaOH added is fixed as 1.26 moles/L and 0.93 moles/L, respectively. Concentrations of chemicals selected as catalysts and promoters were fixed as 0.02 moles/L and 0.12 moles/L, respectively while performing comparative studies. 10 mL solution of NaOH was added by a pressure equalizing funnel connected to the middle port of the reactor. H_2 was collected in an inverted cylinder through a plastic tube attached to the right hand port of reactor.

The amount of hydrogen generation was measured (at 298 K and 1 atm) by the change in water level by the downward displacement of water in cylinder. This system is described as water replacement system. The left hand port is attached to a thermowell to observe the change in reaction temperature. To maintain the system in isothermal conditions a water bath is used. All the experiments were carried out in similar conditions as described above.

Residue analysis

Black colored residue left after the reaction finished was dried and kept overnight in incubator at 50 to

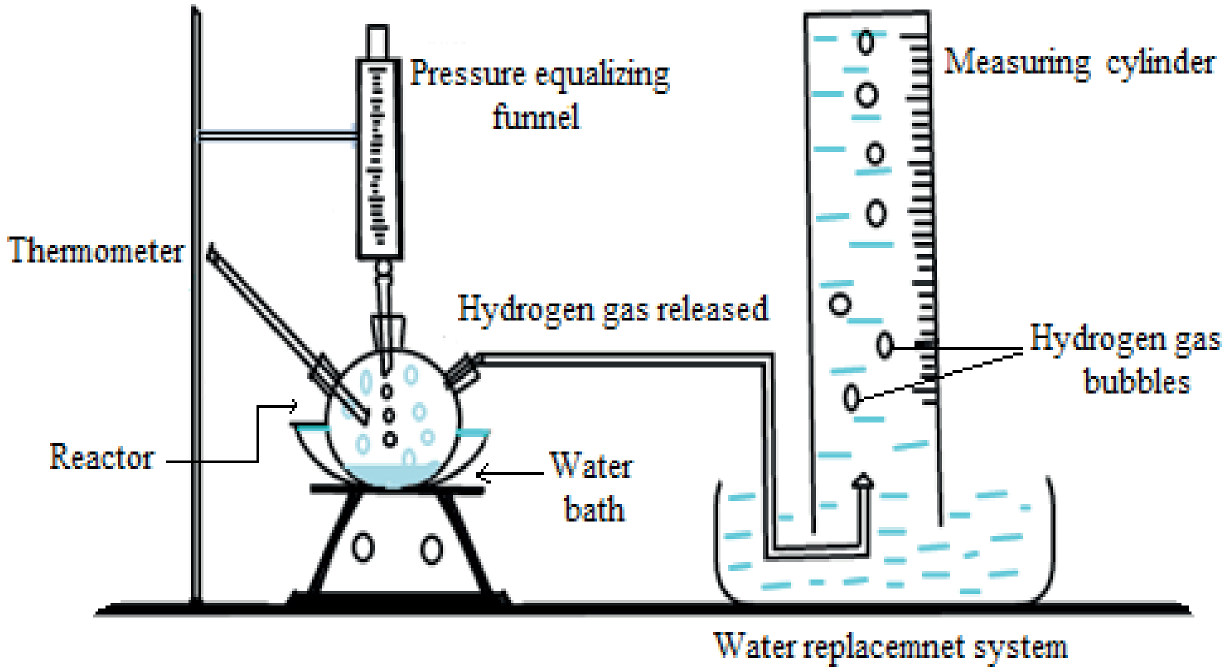

Figure 1. Experimental set up (Kaur et al., 2015)

70°C. The dried residue was crushed and prepared for characterization. To know the elemental composition of the residue it was characterized by EDS (Energy dispersive electron microscopy). FTIR (Fourier transform infrared spectroscopy) could further predict the functional groups present in the residue and XRD (X-Ray diffraction) gives the estimated final products formed in the residue. Residue was observed on a scanning electron microscope (JEOL JSM 6510 LV) equipped with integrated silicon drift detector (SDD) technology to carry out EDS analysis. The specimen was coated with 50 µm thick gold film in an automatic sputter coater (Polaron) to avoid charging under the electron beam prior to EDS. Fourier transform infrared (FTIR) spectra of the residue was recorded on an Agilent Cary 6610 FTIR spectrometer fitted with universal ATR sampling accessories. The spectra were recorded in the range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1}. XRD was carried out by recording X-ray diffraction patterns using a PANalytical X'Pert Pro Diffractometer, operated at 45 kV and 40 mA with monochromatic Cu-Kα radiation (λ=1.5406 Å), in the 2θ range of 20-80°.

RESULTS AND DISCUSSION

Comparison among different promoters

Different promoters such as γ-Al_2O_3 nanoparticles, γ-Al_2O_3 particles, ZrO_2 sand, SiO_2, MMT clay, CNT and zeolite were evaluated for HG using $CoCl_2$ as catalyst as shown in Figure 2. It is observed that Al_2O_3 nanoparticles give higher HG than other promoters. Comparison among different promoters with respect to maximum HGR is shown in Table 1. With respect to maximum HGR the following order is observed for promoters: γ-Al_2O_3 nanoparticles > zeolite > MMT clay > CNT > zirconia sand > γ-Al_2O_3 particles > silica.

The promoter increases the catalytic sites on catalyst surface that helps in decreasing its cost. As shown in Figure 2, HG is maximum for γ-Al_2O_3 nanoparticles that could be due to better reactivity of reactants, which in turn is caused by the high surface area and hydrophilic and amorphous nature of γ-Al_2O_3 nanoparticles.

According to Demirci et al. (2010), although γ-Al_2O_3 and active carbon have high surface area, Al_2O_3 is reported to exhibit higher HGR than active carbon on account of its hydrophilic character as compared to the hydrophobic nature of carbon. Due to the hydrophilic nature of Al_2O_3, the top oxide layer of the Al_2O_3 surface forms hydroxide after chemisorption of H_2O molecules, as shown in reaction 2. These hydroxyl groups adsorb cations and result in the formation of aluminates (Sposito, 1996; Soler et al., 2009).

$$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3 \quad (2)$$

Additionally, as alumina is amphoteric in nature, the surface hydroxyl groups show either acidic or basic behavior depending on the pH of the solution (Marx et al., 2010). The pH of the present system is greater than 9. This could cause the adsorption of metal ions on the alumina surface and cationic adsorption of Co^{+2} or Na^{+} could occur on the hydroxide layer of alumina according to reaction 3 (Fan et al., 2013; Brunelle, 1978; Grenmam et al., 2010).

Table1. HGR using different promoters

S. No.	Promoter	Maximum HGR (moles/L.sec)
1.	Alumina (nanoparticles)	19.47 ± 0.57
2.	Alumina particles	8.46 ± 0.44
3.	CNT	9.97 ± 0.47
4.	MMT clay	11.24 ± 0.43
5.	Silica	7.01 ± 0.50
6.	Zeolite	12.57 ± 0.61
7.	Zirconia sand	9.81 ± 0.53

$$Al(OH)_3 + NaOH \; f \quad NaAl(OH)_4 \qquad (3)$$

The presence of the hydroxide layer also causes passivation on the aluminum surface and prevents interaction of H_2O molecules with Al. Sodium aluminate ($NaAlO_2$) ions or polymeric aluminate ions act as crystallization nuclei for the aluminium hydroxide layer and cause direct interaction of water molecules with metal (Al) and help in the release of protons in the solution. This process promotes reaction 4, which affects the HGR of the system (Li et al., 2005; Buchner et al., 1999; Kanturk et al., 2008).

$$2Al + 6H_2O2 \rightarrow Al(OH)_3 + 3H_2 \qquad (4)$$

Furthermore, aluminate concentration boosts the deposition process of $Al(OH)_3$ on Co particles and speed up the formation of a highly activated Co/Al complex. This complex enhances HGR by promoting reaction 5. Hence, $Al(OH)_3$ acts as a catalyst carrier and promotes the catalytic activity of Co_xB species formed during the $NaBH_4$ hydrolysis reaction with $CoCl_2$ as catalyst, as shown in reaction 6. There exists a synergistic catalytic effect between Co and Al for $NaBH_4$ hydrolysis that improves the overall HGR (Fan et al., 2013; Soler et al., 2007),

$$NaBH_4 + 4H_2O \xrightarrow{Catalyst} NaBO_2.2H_2O + 4H_2 \quad (5)$$

Formation of byproduct ($NaBO_2.2H_2O$) in reaction 5 significantly affects Al hydrolysis due to its alkaline nature, as the increase in alkalinity increases NaOH based reactions (reaction 7 and 8). This leads to the promotion of reaction 3 and eventually reaction 4 (Liu et al., 2006; Soler et al., 2009).

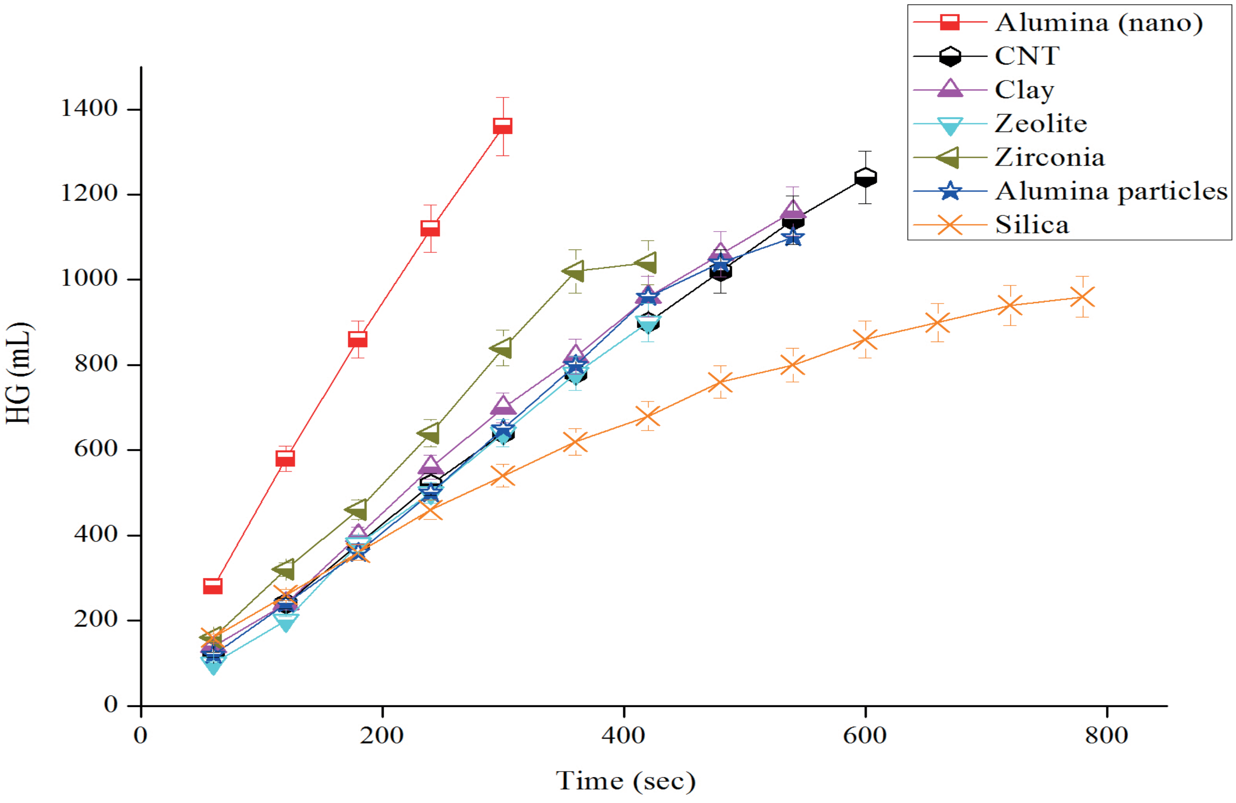

Figure 2. HG using different promoters with $CoCl_2.6H_2O$ as catalyst

$$CoCl_2 + 2NaBH_4 + 3H_2O \rightarrow 0.5Co_2B \downarrow + 2\mathrm{NaCl} + 1.5\mathrm{HBO_2} + 6.25\mathrm{H_2} \uparrow \qquad (6)$$

$$NaBO_2.2H_2O\ f \quad NaB(OH)_4 \qquad (7)$$

$$NaB(OH)_4\ f \quad H_3BO_3 + NaOH \qquad (8)$$

The above chemical reactions describe that Al_2O_3 (nanoparticles) enhances the kinetics of the $NaBH_4$ hydrolysis reaction. The presence of Al_2O_3 nanoparticles in the solution improves the catalytic activity of $CoCl_2$ as a catalyst and significantly promotes the overall HGR of the system.

Comparison among different catalysts

After the selection of the catalyst promoter, different catalysts, namely $CoCl_2.6H_2O$, $CoSO_4.7H_2O$, $(CH_3COO)_2Co.4H_2O$, $Co(NO_3)_2.H_2O$, $CdSO_4$, and $CuSO_4.5H_2O$, were evaluated. As shown in Figure 3, $CoCl_2.6H_2O$ shows maximum HG. Not much hydrogen is evolved with $CdSO_4$ and $CuSO_4.5H_2O$. Comparison of the HGR using different cobalt-based salts as catalyst with alumina nanoparticles as promoter is given in Table 2.

The following order for maximum and overall HGR is observed: $CoCl_2.6H_2O > CoSO_4.7H_2O > (CH_3COO)_2Co.4H_2O > Co(NO_3)_2.H_2O$. Catalytic activity of Co-based metal salts is dependent on Co^{+2} cation due to its electrophilic nature that is strongly attracted towards BH_4^- ions from $NaBH_4$, thus enhancing the hydrolysis of $NaBH_4$ (Demirci et al., 2010).

As the cation Co^{+2} is similar among all salts studied in the present work and $CoCl_2$ exhibits high HGR, the anions CH_3COO^-, Cl^-, SO_4^{2-}, NO_3^- could be another factor that affects the catalytic activity of metal catalysts. Maximum solubility of anions in solution, defined by coefficient of diffusivity, is higher for Cl^- ions as compared with anions of other salts (Akdim et al., 2009 b). This could be the reason behind high HGR with $CoCl_2$. Similar results were observed by Akdim et al. (2009 c), where Co was tested among different cobalt based salts; it was reported that $CoCl_2$ is 4 times more reactive than $Co(CH_3COO)_2$, $CoSO_4$, CoF_2 and $Co(NO_3)_2$ in catalyzing the $NaBH_4$ hydrolysis reaction.

Additionally, $CoCl_2$ was also compared with $CdSO_4$ and $CuSO_4$ salts and it was observed that no hydrogen was released with $CdSO_4$, while the reaction terminated with $CuSO_4$ after 10 seconds only. The reason could be the lower affinity of Cu^{+2}, Cd^{+3} towards BH_4^- ions. The present system is studied in detail by performing analysis of the residue, to predict the possible reactions that could occur between different reactants. The residue, formed after the reaction terminated, could explain the reactivity among all the reactants in the system.

Analysis of the residue

The residue obtained from the optimum system consisting of $NaBH_4$ (1.26 moles/L), Al_2O_3 (0.12 moles/L), NaOH (0.93 moles/L), and $CoCl_2$ (0.02 moles/L) was analyzed. The residue was a grey coloured solid powder and was characterized using EDS, XRD and FTIR. Elemental composition is determined by the quantitative analysis of the surface by EDS. The elemental composition of one section (Figure 4) is estimated as B (72.19 wt%), Na (4.47 wt%), Al (0.07 wt%), Cl (0.06 wt%), O (23.14 wt%) and Co (0.07 wt%).

Similar results were observed earlier for a section of the EDS as B (74.24 wt%), Na (4.26 wt%), Al (0.12 wt%), Cl (0.09 wt%), O (21 wt%) and Co (0.04 wt%) (Kaur et al., 2015). As shown in Table 3, the residue consists of boron in maximum percentage followed by oxygen and aluminium and with the least percentage of cobalt and chlorine.

The XRD pattern of the residue is shown in Figure 5. The major components of the residue from XRD are polymeric sodium aluminates; $NaAl_{11}O_{17}$ (Ref. code 01-079-2288) and $Na_2Al_{22}O_{34}$ (Ref. code 072-1406). This is in confirmation with chemical reaction 4 as formation of sodium aluminates enhances hydrolysis of Al in the solution and eventually increases overall HGR of the system. Prediction of $CoAl_2O_4$ (Ref. code 082-2251) in the solution signifies the formation of activated Co/Al complex that could promote reaction 5. It is confirmed from XRD that Na/Al and Co/Al species are formed, which play additional roles in hydrogen generation in the solution as discussed in the previous section.

The XRD pattern also shows the presence of $Na_2BO_2(OH)$ (Ref. code 037-0173) which is formed as a result of formation of $NaBH_4$ hydrolysis byproduct $NaBO_2.H_2O$ (Soler et al., 2009). This observation indicates that NaOH-based reactions (7 and 8) occur in the solution that enhance Al and $NaBH_4$ hydrolysis.

NaCl (Ref. code 01-071-3742) is formed due to the reaction of cobalt chloride with borohydride ions as shown in reaction

Table 2. HGR using different cobalt-based salts as catalyst (with alumina nanoparticles as promoter)

S. No.	Catalyst	Maximum HGR (moles/L.sec)	Overall HGR (moles/L.sec)
1.	$(CH_3COO)_2Co.4H_2O$	15.49 ± 0.54	14.54 ± 0.50
2.	$CoCl_2.6H_2O$	19.47 ± 0.57	17.89 ± 0.59
3.	$Co(NO_3)_2.6H_2O$	11.27 ± 0.57	9.66 ± 0.52
4.	$CoSO_4.7H_2O$	16.93 ± 0.65	16.06 ± 0.61

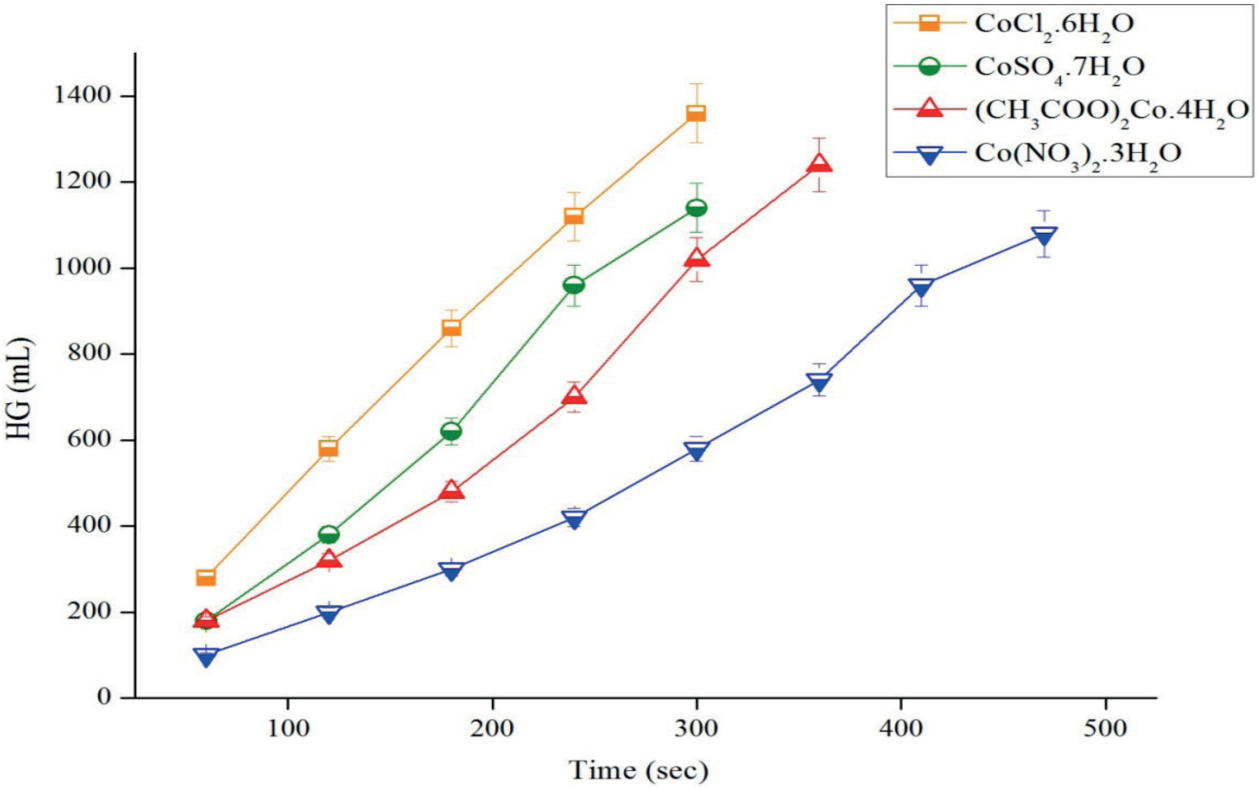

Figure 3. HG using different cobalt based salts as catalysts

6 and formation of Co_3BO_5 (Ref. code 085-1736) is the result of Co^{2+} ions reacting with $NaBO_2$ (George et al., 1993). Inset graph in Figure 5 gives the peak around $2\theta = 45^o$; the diffracted peaks indicate the amorphous structure of the material and presence of Co_xB compounds (Demirci and Miele, 2010).

The residue analysis by FTIR (Figure 6) shows B-O deformation (669, 735 and 846 cm^{-1}) of Co_3BO_5 as also indicated by XRD. Peaks due to Al-O stretching (914 cm^{-1}), B-O stretching (1084 cm^{-1}) and B-O-H (1169 and 1282 cm^{-1}) are indicative of the formation of aluminates and sodium metaborate based byproducts (Hannauer et al., 2011). Deformation and adsorption bands in the range of 3200-3700 cm^{-1} are related to O-H stretching that reveals the formation of aluminium hydroxides (Xuelian et al., 2009). Therefore, FTIR analysis indicates the formation of aluminates and sodium metaborate based byproducts and the same is predicted by XRD analysis.

The B-H stretching band region of 2000-2300 cm^{-1} has almost completely disappeared; it can be inferred that complete conversion of $NaBH_4$ occurs due to the presence of Al_2O_3 nanoparticles in the system (Dai et al., 2011). Thus, results from XRD and FTIR are in agreement with the chemical reactions reported.

The factors that promote overall HG in the present system are $NaBH_4$ hydrolysis, Al_2O_3 hydrolysis, formation of Co/Al species, Na/Al species, and formation of byproducts like $Al(OH)_3$ and $NaBO_2.2H_2O$ in solution.

Table 3. EDS analysis of residual material

Element	Analysis of residue in sectioned area in Figure 4		Analysis of residue (reported by Kaur et al., 2015)	
	Weight (%)	Atomic (wt%)	Weight (%)	Atomic (wt%)
B	72.19	80.22	74.24	81.8
Na	4.47	2.34	4.26	2.21
Al	0.07	0.03	0.12	0.05
Cl	0.06	0.02	0.09	0.03
Co	0.07	0.01	0.04	0.01
O	23.14	17.32	21.25	15.82

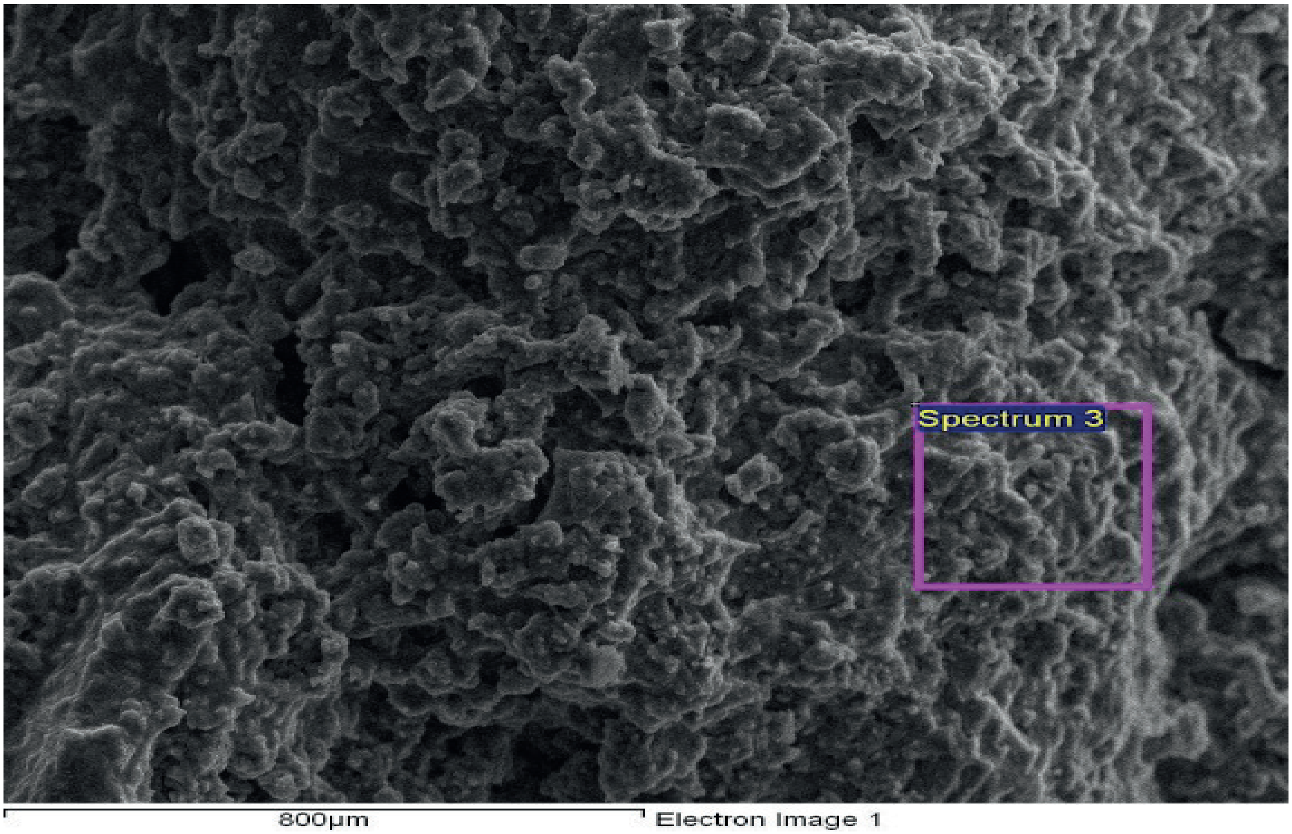

Figure 4. Sectioned area of residual material for EDS analysis

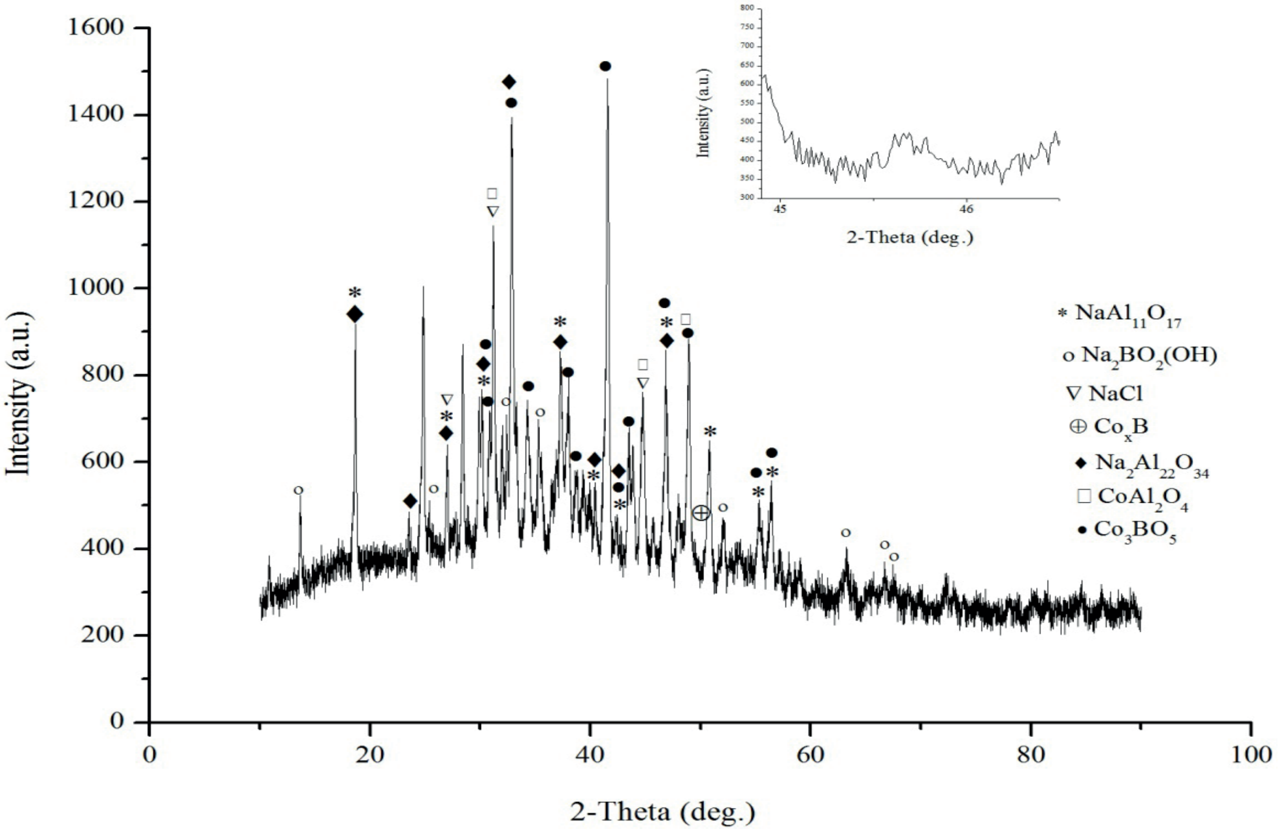

Figure 5. XRD analysis of the residue

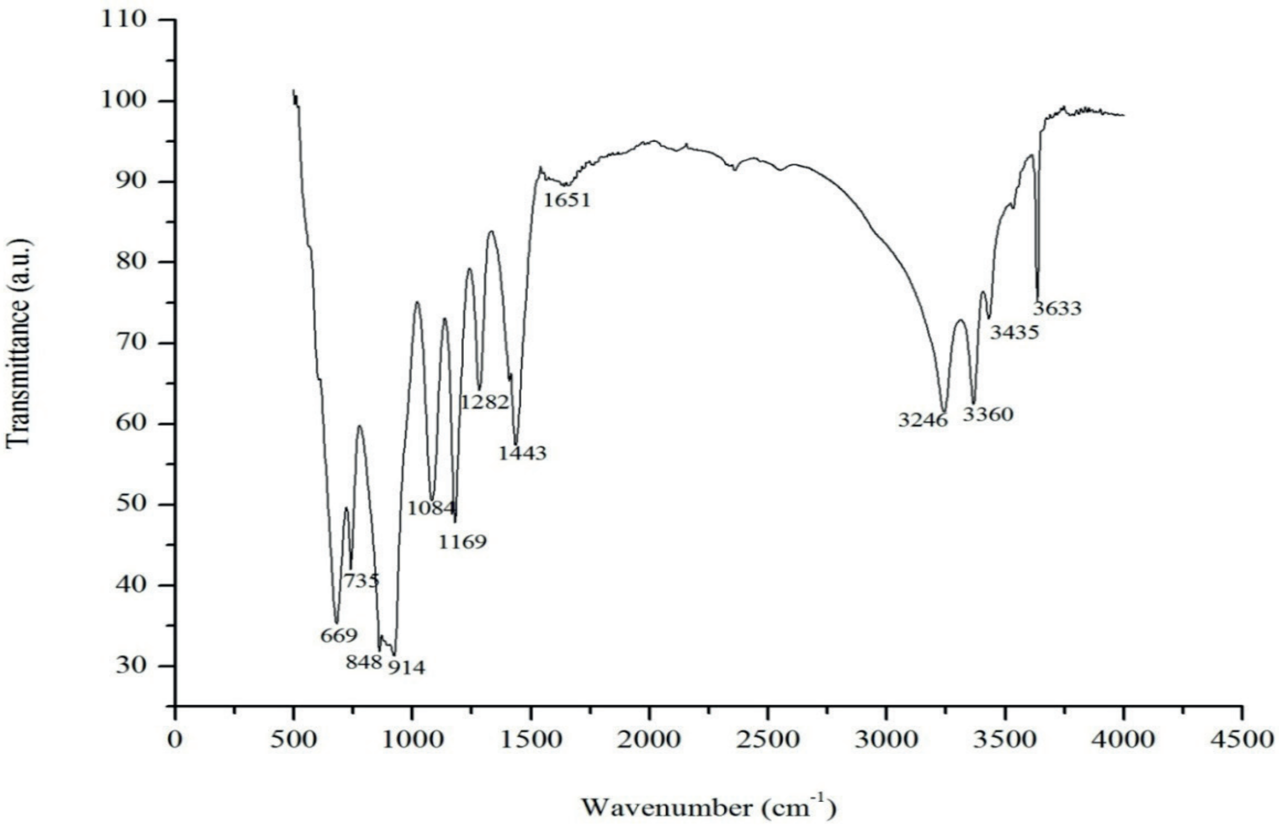

Figure 6. FTIR analysis of the residue

CONCLUSIONS

From these experiments it can be concluded that

- γ-Al_2O_3 nanoparticles are the best catalyst promoter and $CoCl_2.5H_2O$ is the best catalyst found among all the promoters and catalysts studied in this system with maximum HGR of 19.47 moles/L.sec.
- Boron is present in maximum percentage in the residue as expected. Aluminates like $NaAl_{11}O_{17}$, $Na_2Al_{22}O_{34}$ and $CoAl_2O_4$ are formed during hydrolysis of $NaBH_4$ in the present system.
- The factors that promote HGR are (a) hydrophilic, amphoteric nature and large specific surface area of γ-Al_2O_3 nanoparticles, (b) strong affinity of Co^{+2} towards BH_4^- ions and (c) formation of aluminates and sodium metaborate based byproducts.
- $NaBH_4$/γ-Al_2O_3 nanoparticles/H_2O with $CoCl_2$ as catalyst are a potential source of hydrogen generation and this system can be applied to fuel cell applications due to its high hydrogen storage density when compared with other conventional $NaBH_4$/H_2O based hydrogen storage systems.

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