

Catalytic effects in generation of hydrogen from NaBH₄

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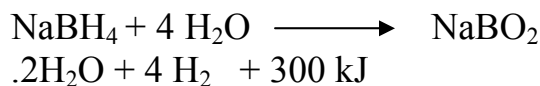
Abstract: NaBH₄ is a hydrogen storage material. Hydrolysis of NaBH₄ generates high-purity humidified hydrogen suitable for use in PEM fuel cells. Sodium borohydride can be stabilized in alkaline solution without hydrogen generation. Catalysts are used to generate hydrogen from stabilized solution (theoretical hydrogen content 10.8 wt. %). In this study cobalt based catalysts (Co, Co-Ni, Co-Cr, Co-Mo) have been prepared by reduction of metal ions in alcoholic solution by using NaBH₄. These catalysts were employed for the hydrolysis of alkaline solution of NaBH₄ and the activity was compared with that of commercial Co powder. Among the examined catalysts Co-Mo system is found to be active for the hydrolysis of sodium borohydride.

Introduction

In the pursuit of alternative energy sources, hydrogen has been identified as one of the energy carriers. Hydrogen appears as the choice because of its uniqueness in terms of renewability, high energy density and environmental benignity. The technical challenges in achieving hydrogen driven society include cost effective hydrogen production, storage and distribution. Chemical storage of hydrogen in the form of metal hydrides represents an attractive alternative, which has been the subject of a large number of investigations in the past. The group VIII metals have their own affinity for hydrogen and most of these metals have been used as components of intermetallic systems, which are examined for hydrogen storage purposes. There are a variety of intermetallics that have been examined for hydrogen storage purposes [1]

The group I, II and III light elements, e.g. Li, Na, Mg, B, and Al form a large variety of metal hydrogen complexes. They are interesting especially because of their light weight and high hydrogen

storage content. The hydrides of Boron, tetra hydroborates M(BH₄)_x and the tetra hydro aluminates are interesting materials. Chemical hydrides are reactive with water which results in the release of H₂ [2]. Among these chemical hydrides, sodium borohydride is safe and practical system suited for storing hydrogen. But it is unstable and sensitive to moisture. Sodium borohydride in alkali medium is stable under ordinary conditions and liberates hydrogen in the presence of catalyst in a safe and controlled manner [3].



This hydrolysis reaction occurs at different rates depending on the catalyst used and its preparation method. Hua et al. (4) and Kaufman and Sen (5) investigated nickel and cobalt borides as catalysts for practical, controlled generation of H₂ from NaBH₄ solutions. Amendola et al [6] reported the application of Ru-catalyzed hydrolysis of aqueous borohydride solution as hydrogen generator for proton exchange

membrane fuel cells (PEMFC). The reaction product can be rehydrogenated to NaBH_4 with saline hydrides like MgH_2 , CaH_2 . Even though alkali solution adds more weight to the system since water is another source of hydrogen still it reaches the storage capacity 7.3 wt%, which is well above the required amount, 6.5 wt% (DOE standard). Hence aqueous NaBH_4 seems to be one of the acceptable hydrogen storage medium. The catalytic effect of Cobalt based catalysts (Co, Co-Ni, Co-Cr, Co-Mo, and Co-Sn) on the kinetics of hydrolysis reaction is reported in this present study.

Experimental

Preparation of catalysts:

Cobalt based catalysts were prepared by the chemical reaction of Cobalt chloride and metal precursor (NiCl_2 for Ni, CrCl_3 for Cr, SnCl_2 for Sn and Na_2MoO_4 for Mo) with the sodium borohydride. In a typical procedure Cobalt and metal precursors were dissolved in methanol (1:1 mole ratio) and the solution was cooled in ice water bath under constant stirring for 30 min, and then slowly an alkaline solution of NaBH_4 was added. Metal to borohydride ratio was taken as 1:4 in order to achieve complete reduction. The reaction temperature was maintained at 283 K. The precipitate was filtered and washed with distilled water several times then dried in vacuum at 343 K and finally annealed in hydrogen atmosphere for 3 hrs at 623 K. The powder samples were characterized by X-ray diffractometry (Rigaku D/max 2400) with $\text{Cu K}\alpha$ radiation

Hydrogen generation:

The prepared catalysts and Co catalysts were used for the hydrolysis of alkaline NaBH_4 solution and the catalytic activity was compared.

The experimental setup used, consisted of a reaction vessel, a 20.0 ml syringe and a water trap to measure the volume of hydrogen. The reaction vessel consisted of 100 ml conical flask sealed with rubber septum. The syringe was inserted through the septum and was used to introduce measured amount of alkaline NaBH_4 solution into flask. A calibrated burette of 1000 ml capacity was filled with water, is connected to the water bulb by a flexible tube. The top outlet of the reaction vessel was connected to the gas burette. The volume of hydrogen generated from the solution was measured by the displacement of water in the burette.

Results and discussion

The X-ray diffraction patterns of the prepared catalysts after annealing at 623 K in hydrogen atmosphere are shown in Fig. 1. As shown in figure various diffractive peaks indicative of metallic Co, MoO_3 appeared on the XRD pattern of the Co-Mo catalyst. However, no diffractive peaks indicative of metallic Mo or the crystalline Co-Mo alloys were identified. The Mo-dopant in Co-Mo catalysts was mainly present in the form of MoO_3 . For the Co-Ni catalysts diffraction peaks correspond to the metallic Co and Ni. In the case of Co-Sn system, peaks corresponding to the CoSn alloy were identified.

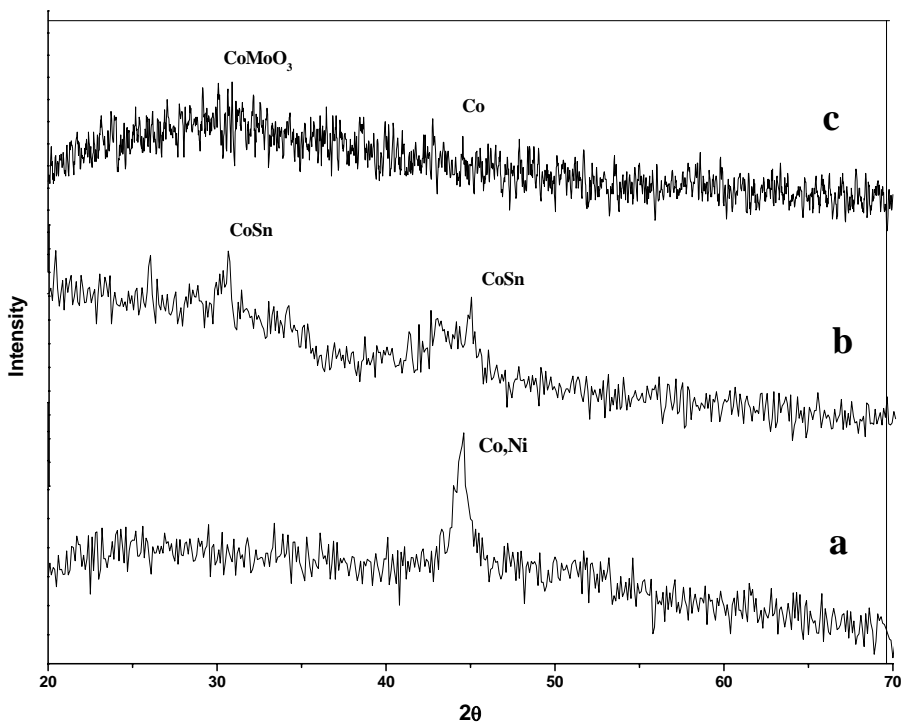


Fig. 1. X-ray diffraction pattern of prepared catalysts (a) Co-Ni (b) Co-Mo (c) Co-Sn

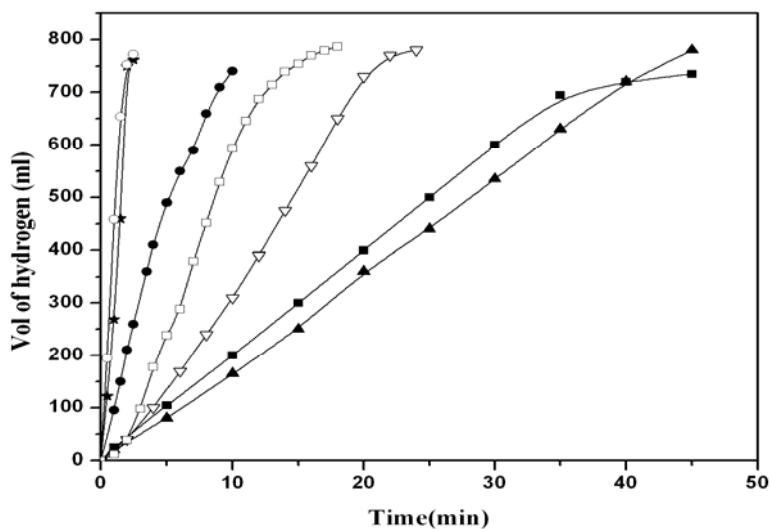


Fig. 2. Catalytic performance of cobalt based catalysts (■) Co- commercial (▲) NiCo-commercial (▽) Co (●) NiCo (□) CoSn (★) CoCrO₃ (○) CoMO₃ and (20 ml of 1.5 wt% NaBH₄ + 4 wt% NaOH).

Measurement of catalytic activity:

In all the measurements, 0.1g of catalyst was taken in the reaction vessel then the reactor was introduced in the thermostatic bath for about 15 min, after that 20 ml of 1.5 wt% NaBH₄ + 4 wt% NaOH solution was rapidly injected with 20 ml syringe.

The liberated hydrogen was measured with respect to time from the volume of water displaced in the gas burette. Hydrogen gas was generated from sodium borohydride solution with rapid rate. Among the examined catalysts Co-Mo has shown higher catalytic activity compared to other catalysts. Moreover, Co-M systems (M=Mo, Cr and Ni) are more active than Co alone. The effect of temperature and concentration of NaOH on the hydrogen generation rate was studied.

Effect of NaOH concentration on hydrogen generation rate:

The results of the study on the dependence of the hydrolysis reaction rate on NaOH concentration is given in the Fig. 3. The reaction rate is enhanced by the increase of NaOH concentration. The reaction rate increases with increasing NaOH concentration up to 12-wt% then decreases. More over as shown in Fig. 4, as the sodium hydroxide concentration increases total hydrogen released decreases. The optimum value of NaOH has around 8 – 12 wt% of NaOH. The extent of hydrogen release can be achieved upto 6.8 wt% in 8 wt% NaOH solution and 6.65 wt% in 10 wt% NaOH solution.

It is very difficult to explain the role of NaOH on the hydrolysis reaction at this stage. In the absence of catalyst it inhibits the reaction and stabilizes the borohydride ions while in

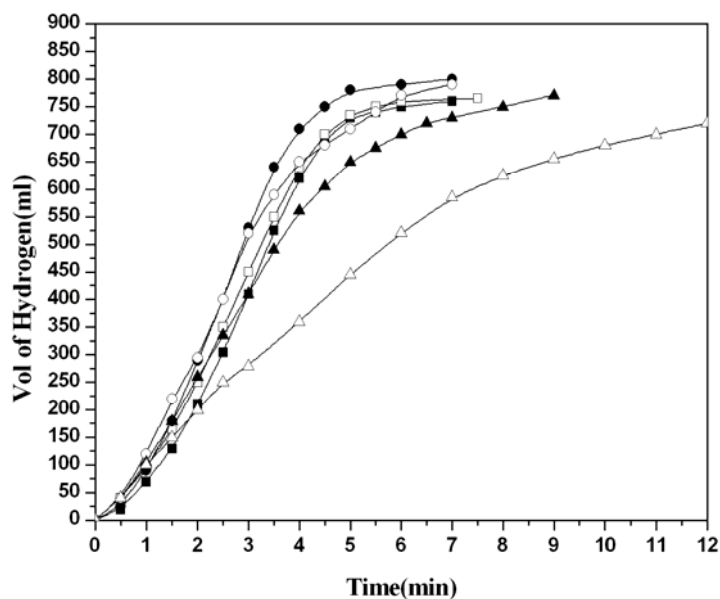


Figure 3: Effects of NaOH concentration on the hydrogen generation rate measured using 20 ml of x wt% NaOH + 1.5 wt% NaBH₄ solutions ($x = 4, 8, 12, 16, 20, 24$) at room temperature using 0.1 g of Co-Ni catalyst.

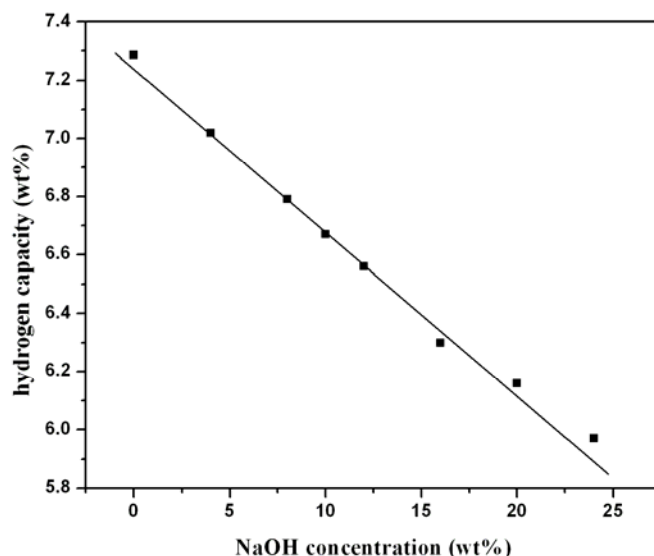


Figure 4: Maximum H₂ storage capacity of the NaBH₄ + NaOH solution system as a function of the NaOH concentration

the presence of catalyst it accelerates the rate of hydrolysis. As the concentration increases, solution becomes viscous, the water molecules gets solvated with the hydroxide ions thus the reaction rate decreases at the higher concentrations of sodium hydroxide

Effect of temperature hydrogen generation rate:

The catalysts are active even at lower temperature (283 K). Reaction begins immediately after adding the solution to the catalyst. The influence of temperature on the rate of the hydrogen generation for the Co-Mo catalyst is shown in Fig. 5. The reaction rate is sensitive to this variable. As expected, the rate increases with increase in temperature. The influence of temperature is clearly shown by the increasing slope values on the linear region of the plots, for increasing values of the reaction temperature. Activation energies for the sodium borohydride hydrolysis with different catalysts are shown in Table 1. The activation energies are comparatively low for CoNi and CoSn catalysts than for CoCrO₃ and

CoMoO₃ and Co but the reaction rates were inverse. This indicates that the hydrolysis reaction follows different path in CoMoO₃ and CoCrO₃ catalysts. Kojima et al. [7] reported catalytic activity of metal catalyst coated on metal oxide and the catalytic activity was attributed to the acid functional groups of metal oxide. MoO₃ in CoMoO₃ system acts as oxygen source; it induces the surface hydroxyl groups and these hydroxyl groups further reacts with the borohydride anion which is adsorbed on the Cobalt metal surface. The hydroxyl groups are weakly bound to the surface of MoO₃ where as strongly adsorbed in the case of metals hence the reaction rate will be faster for CoMoO₃ compared to CoNi or CoSn catalysts.

To study the reusability of the catalyst, the catalyst used in the particular reaction was removed from the reaction mixture by filtration and then washed dried. The catalyst was regenerated by heating in hydrogen atmosphere at 573 K for 3h before its reuse in the reaction. The CoMoO₃ catalyst can be recovered and reused in further reaction without a significant degradation in activity.

Although the catalytic activity was gradually diminished, a conversion of over 90% was still achieved after 100 h.

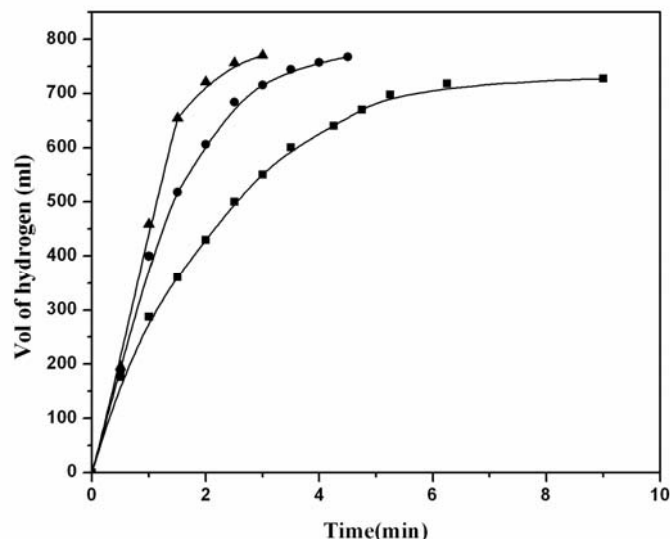


Figure 5: Effects of solution temperature on the hydrogen generation rate measured from 1.5 wt% NaBH₄ + 10 wt% NaOH solutions using 0.1 g of Co-Mo catalyst.

Table 1: Activation energies and borohydride hydrolysis rate for Cobalt based catalysts.

Catalyst	Activation energy (kJ/mol)	Hydrogen evolution rate at 301 K (ml/min)
Co	60	100
Co-Ni	36.4	205
Co-Cr	61.19	370.6
Co-Mo	74.2	458.2
Co-Sn	57.68	72.6

Conclusion

The hydrolysis of NaBH₄ using cobalt based catalysts was studied. The effect of temperature and NaOH concentration on the hydrogen generation rate was studied. The main conclusions drawn from the investigation are:

- (i) The prepared catalyst presents good activity for the hydrogen generation;
- (ii) The catalyst is capable for practical application as a hydrogen generator coupled to fuel cells. The reaction rate increases with an increase in temperature and NaOH concentration up to 12 wt%.

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