Preparation of In-Situ Bimetallic CoNi Nanoparticles Suppurated on Carbon Nanotubes as Effective Catalyst for H$_2$ Generation from Sodium Borohydride

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KEYWORDS:
CoNi; In-situ reduction; Hydrogen; Sodium Borohydride.

Abstract—Multiwall carbon nanotubes (MWCNTs) enhanced Co-Ni catalysts for NaBH$_4$ hydrolysis were developed and produced in this research. The microscopes utilized was transmission electron microscope. The various species located at the surfaces of some selected catalysts has been characterized using the X-ray photoelectron spectrometer. The results reveal that even with the addition of carbon nanotubes as a promoter, the catalysts maintain an amorphous shape. In Co-Ni catalysts (NiCo@MWCNTs), however, the right amount of MWCNTs promoter results in a large specific surface area, fine dispersion of active components, more active sites, and a high electron density at active sites. Furthermore, hydrogen overflow on the catalyst is encouraged, which aids in active site regeneration and accelerates the catalytic cycle. When compared to other formulations, samples containing 5 wt% Ni and 5 wt% Co had the best catalytic activity and in this experiment, we studied the effect of different quantity of NiCo@MWCNTs (5, 10, 15, 20 mg) with keeping the other parameters are constant, different starting concentrations of SBH [NaHB$_4$] = 1, 2, 3, and 4 M (50, 100, 150 and 200mg SBH in 50ml water). and NiCo@MWCNTs towards hydrolytic dehydrogenation of SBH over a temperature range of 35-65 °C. and we have concluded that the best case to released 116 ml of hydrogen from SBH when we use 1.35 mmol at 5 mg catalyst at 12 min at 338 K and the activation energy $E = 53,54964$ kJ/mol. And the value of $\Delta G$ carries from 13.907 kJ/mol at 35 °C to 10.307 kJ/mol at 45 °C. This mean that the spontaneity of the hydrogen production increased with temperature.

I. INTRODUCTION

Hydrogen is generally recognized as one of the most promising fossil fuel alternatives in recent decades due to its reputation as a clean and efficient energy
source in the face of increasing energy demand and pollution. Given the challenges associated with storing and transporting hydrogen, chemical hydrides have been widely considered a promising storage medium. Sodium borohydride (NaBH₄) has been the subject of intense study because of its high H₂ storage capacity (10.8 wt percent), controllable hydrogen generation rate, high purity of hydrogen produced at room temperature, excellent stability in alkaline solution, recycle abilities, and nontoxic hydrolysis by-products. NaBH₄ hydrolysis may produce pure hydrogen at room temperature in the presence of suitable catalysts. For the rapid hydrolysis of NaBH₄, effective catalysts are required. It has been established that noble-metal catalysts, including Pt, Pd, Ru, and Rh, exhibit higher catalytic activity in the hydrolysis of NaBH₄ with fast hydrogen production. On the other hand, the availability of noble-metal catalysts is restricted by their prohibitive cost. Bimetallic CoNi catalysts have been widely studied for NaBH₄ hydrolysis due to their high catalytic activity and low cost. Numerous articles describe research on Co-Ni based catalysts (Bimetallic Ni-Co nanoparticles as an efficient catalyst of hydrogen generation via hydrolysis of NaBH₄ 13-39). The synergistic geometric and electrical effects of bimetallic-based transition metals nano-catalysts (such as NiMo, CuNi, CoPd, and Cu-Co), have introduced a high catalytic performance towards NaBH₄ dehydrogenation. To prevent the formation of aggregates and ensure long-term durability, Ni and Co must be distributed and stabilized in suitable materials because to their high energy surface and magnetic characteristics. During SBH hydrolysis, NaBO₂ is formed as a byproduct that binds to the catalyst surface and ultimately renders the catalyst ineffective. Foams, thin films, metal oxides, metal organic frameworks, polymers, etc. are all examples of suitable support matrices that might prevent NPs from aggregating and boost their catalytic activity. In addition, active components' mobility might be constrained by support matrices, leading to improved long-term stability. The catalyst's supporting materials are crucial to their performance and longevity. MWCNTs are one kind of supporting material that helps the composite by increasing its dispersion and specific surface area. The composites' dispersibility and specific surface area were significantly enhanced. One advantage is that the reaction area between the NaBH₄ and the active component is maximized. It is well-known that the catalytic activity of catalysts is directly affected by their production method and shape (Metal Boride-Decorated Coni Layered Double Hydroxides Supported on Muti-Walled Carbon Nanotubes as Efficient Hydrolysis Catalysts for Sodium Borohydride). Here, we look at how CoNi nanoparticles supported on MWCNTs may function as inexpensive catalysts for producing hydrogen gas from sulfuric acid brine. Chemical reduction and calcination were used to ready the introduced NiCo@MWCNTs. In order to create bimetallic CoNi NPs supported on MWCNTs, CoCl and NiCl are typically reduced in-situ with SBH at the surface of a predetermined number of MWCNTs. A methanol solution has been used for the in-situ reduction procedure. The reduction procedure results in the formation of CoNi NPs supported on MWCNTs, as shown by the physicochemical characterizations used. The produced CoNi NPs supported by MWCNTs shown brilliant catalytic activity and exceptional recycling characteristic due to the well dispersed and stabilized CoNi.

II. EXPERIMENTAL

A. Materials

The multi-walled carbon nanotubes with outer diameters of 8-15 nm were supplied by Sisco Research Laboratories Pvt. Ltd. 608, B Wing, Satellite Gazedo, Andheri Ghatkopar Link Road, Andheri (E), Mumbai – 400 099, India. Sodium borohydride, 97+% (NaBH₄ = 37.8 gm/mol) Thermo Fisher (Kandel) GmbH. Erlenbachweg 2. 76870 Kandel, Germany. Cobalt Chloride (CoCl₂·6H₂O) from Chemistry Lab. Nickel Chloride (NiCl₂·6H₂O) from Chemistry Lab.

B. Catalyst Preparation

A simple in-situ chemical reduction was used to produce bimetallic CoNi catalysts that were supported on MWCNTs and promoted catalysis. In most cases, the necessary amount of CoCl₂·6H₂O and NiCl₂·6H₂O was dissolved completely in 50 ml of distilled water. After that, 0.5 grams of MWCNTs were added to the previously described solution, and it was exposed to ultrasonic waves for an hour. A 50 mL aqueous solution containing 5 weight percent NaBH₄ was utilized as a reducing agent, and this allowed for the complete reduction of CoNi on the surface of the MWCNTs. In order to prevent a violent reaction, the solution was added slowly, and the temperature of the solution was maintained at 15 °C. The solution is filtered and repeatedly washed the solution down with water. The resultant black particles were allowed to remain overnight drying in an oven set to 100 °C. After being dried, the particles were calcined at a temperature of 800 °C for two hours while a vacuum was maintained and nitrogen gas was present. The preparation of Ni-free Co has been carried out using the same methods.

C. Catalytic Hydrolysis of Sodium Borohydride

In a reaction catalysed, 1.35 mmol of NaHB₄ was dissolved into an alkaline aqueous solution that had a volume of 50 ml and was carried out in a flask with two necks. To maintain precise control over the temperature of the solution, the reaction vessel was fitted with a thermoplastic cover and wired into a water circulator bath that had a thermostat. In the glass reactor, the predetermined quantity of catalytic NiCo@MWCNTs were carried out before the addition of the SBH solution. On top of a controller magnetic stirrer, the glass reactor was brought to the desired temperature. A water-filled burette system that was manufactured at home was used for the measurement of the H₂ gas production that resulted from the SBH hydrolysis. The volume of H₂ that was generated was proportional to the amount of water that was displaced from the steadily filling cylinder. The kinetics of the hydrolysis process was investigated by varying the quantity of catalysts, the amount of SBH, as well as the temperature. Additionally, the longevity of the newly
developed NiCo@MWCNTs that went through the recycling process was investigated.

**D. Characterization**

Electron microscopic examinations of representative NiCo@MWCNTs catalysts have been performed in order to study the morphology and the particle size of these materials. The microscopes utilized was transmission electron microscope (TEM, model JEOL JEMTH-100 II). The various species located at the surfaces of some selected catalysts has been characterized using the X-ray photoelectron spectrometer (SPECS GmbH).

**III. RESULTS AND DISCUSSION**

TEM images of the resulting NiCo/MWCNT composite after in-situ reduction in SBH and calcination in argon atmosphere at 800 °C are shown in Fig. 1. Composites demonstrated that metal nanoparticles were uniformly decorated and distributed on the MWCNTs surfaces. The average size of MWCNTs and NiCo NPs are 19 and 21 nm, respectively. NiCo/MWCNT XRD patterns are shown in Fig. 2. The distinctive carbon peak of MWCNTs appears at 26°. Nickel and cobalt are found to be dispersed in the same way in the examined sample. Think about this: Nickel and cobalt can form a substitutional alloy because (i) they are chemically similar, (ii) their atomic weights are close to each other (Ni: 58.7, Co: 58.9), (iii) their crystal structures have face-centered cubic (FCC) symmetry with nearly identical cell parameters (Co: 3.544, Ni: 3.523), and (iv) they share the same valence. This means that the FCC cobalt crystal may be modified by exchanging nickel atoms for cobalt atoms, or vice versa. As expected, three peaks arise at 44.5°, 51.8°, and 76.9°, all of which are consistent with a face-centered cubic structure and hence indicate the presence of Co and/or Ni.

**A. H₂ Production from The Hydrolytic Dehydrogenation of SBH by NiCo@MWCnts.**

1) Effect of Ni@MWCNTs and NiCo@MWCNTs catalysts in H₂ production from SBH.

The unique properties of SBH make it the most practical boron-hydrides for H₂ generation (e.g. stability in air, non-flammability and toxicity, commercially availability, high H₂ storage efficiency and side product recyclability). Hydrolytic dehydrogenation from SBH often makes use of high-priced catalysts. In this work, we developed NiCo@MWCNTs as a readily accessible, simple to manufacture, and inexpensive catalyst. An initial control experiment demonstrated that the MWCNTs-free catalyst exhibited no catalytic activity in the hydrolysis process at ambient temperature and 40 °C, necessitating further investigation into the catalytic performance of NiCo@MWCNTs in hydrogen generation from the SBH dehydrogenation. This shows that MWCNTs lack catalytic activity for hydrolytic dehydrogenation of SBH, since their production of H₂ was mostly comparable to that of the self-hydrolysis process. The hydrolytic dehydrogenation reaction of H₂ gas evolved per mol of SBH vs time in the presence of Ni@MWCNTs and NiCo@MWCNTs catalyst and 1.35 mmol (50 ml of 1 mol) NaBH₄ at room temperature is shown in Fig. 3b. Regardless of the catalyst utilized, hydrolytic dehydrogenation of SBH commenced very immediately. In the presence of Ni@MWCNTs and NiCo@MWCNTs, hydrolytic dehydrogenation of SBH takes 60 minutes and yields 2.3 and 3.95 mmol H₂/mmol of SBH, respectively. When compared with Ni@MWCNTs, the catalytic characteristics of NiCo@MWCNTs are superior. Fig. 3a shows that the maximum rate of mass transfer achieved by NiCo@MWCNTs is 1600 mL/min, which is much higher than the rate of 1300 mL/min achieved by Ni@MWCNTs. The Synergistic action of Ni and Co may explain why Ni@MWCNTs show less catalytic activity than NiCo@MWCNTs. In addition, MWCNTs geometrically maximized action dilutes the aggregated Ni and Co sites on the catalyst surface and fractures massive metallic Ni and Co ensembles active for hydrolytic dehydrogenation of SBH. It has been shown that using MWCNTs as a support improves the chemical stability of Ni and Co NPs in addition to boosting the adsorption of SBH.

2) Effect of NiCo@MWCNTs catalyst concentration in H₂ production from SBH.

Fig. 4a indicates the plots of volume of H₂ gas released per versus duration time for the hydrolytic dehydrogenation process with different concentration of NiCo@MWCNTs (5, 10, 15, 20 mg) with keeping the other parameters are constant (e.g. concentration of SBH 1.35 mmol (50 ml of 1 mol). As can be observed in the Fig.4a, the SBH with completely conversion as the stoichiometric H₂ was evolved and the duration time decrease with increase the amount of catalyst. The rate of H₂ generation appears to be directly proportional to the amount of the catalysts. Fig. 4b demonstrates the plot of logarithmic rate of H₂ generation was obtained from the linear portion versus the logarithmic concentration values of NiCo@MWCNTs, which shows a straight line with a slope of 0.96 demonstrating that the hydrolytic dehydrogenation SBH is in accordance with the first order kinetics regard to the NiCo@MWCNTs concentration.

3) Effect of SBH concentration in H₂ production from SBH.

It was also possible to determine how much of an impact SBH concentration had on the rate at which H₂ was produced. Several tests were run with different starting concentrations of SBH [NaBH₄ = 1, 2, 3, and 4 M (50, 100, 150 and 200 mg SBH in 50 mL water)]. Both the catalyst concentration ([NiCo@MWCNTs] = 5 mg) and temperature (318 K) were held constant. Increasing the SBH concentration had little effect on H₂ production, as shown in Fig. 5b. The logarithmic curve of H₂ production rate is shown in Fig. 5a. A straight line with a slope of 0.4 was generated by plotting the linear component of each graph against the logarithmic values of [NaBH₄]. It follows zero-order kinetics with regard to [NaBH₄] for SBH to undergo hydrolytic dehydrogenation. At low [NaBH₄], the
reaction proceeded according to a first order reaction, whereas at high [NaHB₄] it proceeded according to a zero order reaction. The production of NaBO₂ at large concentrations slows reactions, which may explain this phenomenon.

4) Effect of reaction temperature in H₂ production from SBH.

As-synthesized NiCo@MWCNTs 5mg and 1.35 mmol SBH were used in order to calculate the activation energy (Ea) of NiCo@MWCNTs towards hydrolytic dehydrogenation of SBH over a temperature range of 308-338 K. Higher reaction temperatures resulted in more hydrogen being released (Fig. 6c). The Arrhenius plot (shown in Fig. 6a) is made by reversing the temperature axis and plotting the logarithm of the rate constant K for hydrogen generation, which is derived from the linear part of each plot in the Fig. 6b, with inverse of absolute temperature.

B. Figures, Tables and Schemes

Fig. 1: Low and high magnifications TEM images of NiCo@MWCNTs after in-situ reduction in SBH and calcination in argon atmosphere at 800 °C.

Fig. 2: The XRD results showed that the crystalline size of Co–Ni is related to the heat-treatment temperature.

Fig. 3: (a) Rate of H₂ of NiCo@MWCNTs and Ni@MWCNTs. (b) H₂ released from alkaline aqueous SBH solution in the presence of NiCo@MWCNTs, Ni@MWCNTs and without catalyst.

Fig. 4: (a) Effect of NiCo@MWCNTs on H₂ release from alkaline aqueous SBH; (b) logarithmic plot of rate vs. [NiCo@MWCNTs] at 45°C and 1.35 mmol of SBH.

Fig. 5: (a) logarithmic plot of reaction rate vs. [NaBH₄], at 45°C and 5 mg Catalyst; (b) Analysis of the effect of NaBH₄ concentration
C. Formatting of Mathematical Components

The value of $E_\text{a}^\circ$ was determined to be 20 using the slope and Arrhenius equation based on the findings of the impacts of catalyst concentration, SBH concentration, and reaction temperatures.

$$r = -d[SBH]dt = k[HFB - 40]^{0.9466} [SBH^{-0.1}]$$  \hspace{1cm} (1)

$$k = Ae^{-\frac{E_\text{a}^\circ}{RT}} \rightarrow \ln k = \ln 15.602 - \frac{36432}{8.3147}$$  \hspace{1cm} (2)

$$r = -d[SBH]dt = 15.602e^{-\frac{43.82}{R}T}[HFB - 40]^{0.9466}[SBH^{-0.1}]$$  \hspace{1cm} (3)

The activation enthalpy ($\Delta H$, (kJ.mol$^{-1}$)) and the activation entropy ($\Delta S$, (J.mol$^{-1}$. K$^{-1}$)) may be used to get the Gibbs free energy of activation ($\Delta G$, (kJ.mol$^{-1}$)) using Eqs. (4) and (5).

$$\ln k_D = \ln \frac{k_D}{h} + \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (4)

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (5)

Where $k_D = (k/T)$, $K_B$ and $h$ are the Boltzmann constant $(1.381 \times 10^{-23} \text{ J.K}^{-1})$ and the Planck constant $(6.626 \times 10^{-34} \text{ J.s}^{-1})$, respectively.

$\Delta G$ equation can be summarized as follows:

$$\ln k_D = 14.455 - 6118.2 \text{ [1/T]}$$

$$\Delta S^\circ = 8.314 \times 14.455 = 120.2 J/\text{mol.K}$$

$$\Delta H^\circ = (8.314 \times 6118.2) = 50866 J/\text{mol} = 50.866 kJ/\text{mol}$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ = \begin{cases} 13.907 \text{ (13.907 kJ/mol)} \\ 12.707 \text{ (12.707 kJ/mol)} \\ 11.507 \text{ (11.507 kJ/mol)} \\ 10.307 \text{ (10.307 kJ/mol)} \end{cases}$$

IV. CONCLUSIONS

For catalytic hydrolysis of NaBH$_4$ solution, Co-Ni/MWCNT catalysts were produced by chemical reduction of aqueous sodium borohydride with cobalt chloride and nickel chloride. The use of MWCNTs as support is favorable to the catalytic reaction.

The author did not receive any financial support of the research authorship and publication of this article.
DECLARATION OF CONFLICTING INTERESTS STATEMENT:

The author declared that there are no potential conflicts of interest with respect to the research authorship or publication of this article.

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Arabic Title

تحضير جزيئات النانوية ثنائيات المعدن على مادة الكربونات النانوية كمحفز قullet لاستهلاك الهيدروجين من بوروهيدريد الصوديوم

Arabic Abstract

في هذا البحث تم تطوير ونتائج المواد النانوية الكربونية متعددة الجدران المحسنة مع معدن النانو纹理 الكروي على النانوية إعادة التجميع كميات كافية من هيدروجين بهدف تحسين كفاءة عملية إعادة التجميع. تم استخدام التجربة الأرضية لإنتاج نانو纹理 الكروي متعدد الجدران المحسنة. كتبت النتائج أنه مع زيادة الظروف التشغيلية لوضح الأنابيب الكربونية، التحالفات مع富裕 نوع من معدن اللاند VATHICالنيكل والكوبلت، ينتج عن النقص في الكمية المناسبة من متعدد الجدران النانوية يمكن تحليلها بشكل تفصيلي، وتشابه كتلة التكثيف والذروة النشطة مع تركيز الضغط في النتيجة. برامج تحليل متعددة النانو纹理 لخصوصية الحفاز مع التركيبات الأخرى، فإن العينات المتنوعة من النانو纹理 النانوية تتسم بنشاط التحفيز. تتم رفع درجة حرارة المحفز، مما يساعد في تجديد الموقع النشط وسرع الدورة التحفيزية. بالإضافة إلى ذلك، تبين أن تغير درجات الحرارة في المحفز المحسنة مع معدن النيكل والكوبلت كان لها تأثير ضئيل على النتائج. في النهاية، تم التوصل إلى أن أفضل نسب التركيب النانو纹理 الكربونية متعددة الجدران المحسنة مع معدن النيكل والكوبلت هي (11/3) والذي يتكون من 11٪ من النانو纹理 الكربونية المتعددة الجدران ضمت 3٪ من الكوبلت. بناءً على النتائج، يمكن استخدام هذه الناجحات في تحسين أداء نظام إنتاج الهيدروجين من بوروهيدريد الصوديوم.