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Original Article

# HYDROGEN GENERATION FROM SODIUM BOROHYDRIDE WITH COBALT BORIDE CATALYSTS

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## Abstract

$NaBH_4$ is a promising hydrogen storage material, with its high hydrogen storage capacity (10.8 wt%), stability in alkaline solutions, mild reaction temperature, nontoxic by products and controllable hydrogen generation rates. Hydrogen generation of $NaBH_4$ was investigated with $Co_2B/TiO_2$ composite catalyst. Co catalysts are very good candidates for $NaBH_4$ hydrolysis from economical viewpoint. Composite catalysts have attracted continuous interest during the past decades and enable to give high selectivity, high activity and good stability. In this study, 1:1, 1:2, 1:3 and 1:4 molar ratio of $Co_2B/TiO_2$ composite catalysts were prepared to study hydrogen generation effects. 1:3 mole ratio composite catalysts gave the highest hydrogen generation rate. The effects of catalyst amount, NaOH and $NaBH_4$ compositions, reaction temperature on the hydrogen generation rate were investigated and kinetic rate expression was determined. The calculated activation energy was 36.50 $kJ.mol^{-1}$. These catalysts introduced perfect catalytic properties and can undertake the applications in hydrogen generation.

**Keywords:** Hydrogen generation, composite catalyst, NaBH4, ball milling, Cobalt boride catalysts.

## 1. INTRODUCTION

Hydrogen is one of the cleanest energy source with its high efficiency, zero emission, and renewability in recent years [1-5]. The wide use of hydrogen is a potential route to reduce the negative impact of the enormous carbon emissions caused by fossil fuels burning [5]. The lack of an efficient and safe medium for hydrogen storage and generation hindered the commercialization of fuel cell-based portable devices [6]. Ongoing investigations about the efficient and safe production and storage of hydrogen can improve the wide application of the hydrogen as an energy source. Chemical hydrides are one of the various hydrogen storage systems with low operation pressure, less cost and less energy losses [1, 6-8]. Additionaly, the hydrogen content existing in chemical hydrides is much higher than that of metal hydrides [7]. Sodium borohydride ($NaBH_4$) is the most promising hydrogen source because it has high hydrogen capacity (10.8 wt.%), excellent solubility, controllable hydrolysis reaction, moderate operation temperature, and is very stable in alkaline solutions, non-flammable, non-toxic in nature, environmentally friendly and renewable [1, 2, 6, 7, 9-11]. Also byproduct ($NaBO_2$) of the $NaBH_4$ hydrolysis process is nontoxic and recyclable [1, 2]. $H_2$ generation rate of this reaction is low and decreases as the reaction proceeds owing to an increase of

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the solution pH, which is due to the formation of the borates. $NaBH_4$ hydrolysis is spontaneous and in order to avoid a spontaneous reaction, the solution can be stabilized by NaOH. At the same time, first the $NaBH_4$ solution is stabilized, then $H_2$ generation needs to be catalyzed by an appropriate catalyst [12]. In addition, $NaBH_4$ is stable in air and in alkaline solutions. An empirical relationship on stability of $NaBH_4$ with pH values of solutions and storage temperature could be represented by Eqn. (1) [7].

$$\log t_{1/2} = A_{pH} - (0.034.T - 1.92) \qquad \text{Eqn. (1)}$$

where $t_{1/2}$ is the half-life of self-hydrolysis of $NaBH_4$ in minutes at a particular temperature T in K and in a solution with a pH value equal to $A_{pH}$ in the absence of catalysts. That is to say, alkaline $NaBH_4$ solution at pH 14 can be kept for 430 days from self-decaying at room temperature [7]. $NaBH_4$ can be stored for a long time as an aqueous solution stabilized by NaOH at room temperature [8].

Furthermore, hydrogen is generated by a water-based hydrolysis reaction of $NaBH_4$ with the advantage of producing half of the hydrogen from the water solvent [6]. However, the hydrolysis reaction is kinetically slow in the absence of a suitable catalyst, this reaction can be accelerated by a suitable catalyst [2]. When contacting with a given catalyst, in alkaline solutions (the alkali usually acts as a stabilizer to restrain the self-hydrolysis of $NaBH_4$ in aqueous solution) hydrogen can be released rapidly which is shown as follow reaction (1) [7]:

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_2 + 4H_2 \qquad \text{reaction (1)}$$

The catalyst is the key factor which affects the $H_2$ generation rate in the hydrolysis of $NaBH_4$. Pt, Ru, Pd, Rh, and other noble metal catalysts are very effective to accelerate the hydrolysis reaction of $NaBH_4$. However, these precious metals have high costs and then non-noble catalysts research is very important [2]. The general constraint of the catalysts is their deterioration, which occurs owing to processes for instance agglomeration of catalyst particles, surface oxidation of catalysts, and dissolution of the catalyst component in the alkaline $NaBH_4$ solution. The research for catalysts with excellent activity and endurance remains the current focus of research in this field [1]. Metal borides are one of the alternative catalysts, they can be synthesized in a simple way from their salt solutions and they have low cost. The perfect catalytic activity of metal borides can be based on their properties such as stability, amorphous structure, and many unsaturated sites. Cobalt boride is a leading candidate between the available metal borides owing to its outstanding catalytic properties, low cost, and easy preparation [2]. In addition to cobalt boride, cobalt borates have been also reported as the active catalysts. The boride and borate catalysts are called Co–B catalysts. In some studies, Co–B active catalysts obtained by reducing the simple salts of non-noble metals (such as $CoCl_2$ and $Co(NO_3)_2$) by $NaBH_4$ solutions [8]. The defect of the conventional Co–B solution prepared by using water is the small surface area of the alloy particles and extensively distributed particle size. All these undesirable properties result from the exothermic nature of this reaction. Besides the exothermic nature of the reduction reaction involves high surface energy causing Co–B particles to agglomerate. This particle agglomeration lowers the effective surface area of the catalyst powder thus limiting its catalytic activity [6]. Various Co-based alloys have been fabricated toward achieving improved catalytic activity by avoiding agglomeration of the alloy particles in solution, through variation of the preparation parameters [2]. The catalytic activity of these catalysts can be further developed by doping, supporting, and templating [2, 6, 8].

The support of the heterogeneous catalyst can be alumina, zeolites, carbon nanofibers, active carbon, and metal oxides, such as $TiO_2$, $La_2O_3$, $CeO_2$, $MnO_2$, and $ZrO_2$. $TiO_2$ is a recognized heterogeneous catalyst support which has tunable porous surface and distribution, high thermal stability, and mechanical strength.

In the catalyst preparation, active sites of the catalyst may be blocked by the agglomeration of the particles which contribute to instability of the catalyst. The mesoporous $TiO_2$ of pure anatase phase with sharp pore distribution and large surface area was synthesized to increase the catalyst activity and stability. The importance of an appropriate catalyst support material has been of huge interest. The idea is that the main catalyst should be dispersed on a suitable support to make the catalytic nanoparticles stable and obtain optimal performance and decrease the amount of costly metal being utilized, which accordingly decrease the total catalyst expenses. Furthermore, with porous characteristics, support materials offer a high dispersion of nanoparticle catalyst and simplify electron transfer, both of which contribute to better catalytic activities. Thus, the selection on support heterogeneous catalyst must retain its specifc properties, such as porosity, surface area, dispersion, selectivity, and activity. The morphology and pores size of the selected support materials play an important role in enhancing the heterogeneous catalyst's stability and performance. Strong interactions between the catalytic metal particles and mesoporous $TiO_2$ have been recorded. $TiO_2$ has high surface area stabilizing the catalysts in its mesoporous structure and it is an alternative support material. $TiO_2$ supported catalysts can be used at low temperature and pressures because of the high activity of $TiO_2$ nanoparticles. $TiO_2$ has strong metal support interaction, chemical stability and acid-base property and $TiO_2$ can be a good metal oxide catalyst support [13]. It is also proposed that this growth in the reaction rate might be due to the strong Co to $TiO_2$ interaction altering the catalytic properties.

The hydrogen generation rate equation is given by Eqn. (2) [14]:

$$r = Ae^{-\frac{E_a}{RT}}(Cat.amount)^x(NaOH\ conc.)^y(NaBH_4\ conc.)^z \qquad \text{Eqn. (2)}$$

In this equation Eqn. (2), r is the hydrogen generation rate, A is the pre-exponential factor, $E_a$ is the activation energy, R is the universal gas constant, T is the reaction temperature, and x, y, z are the reaction orders with respect to the amount of catalyst, the concentration of NaOH and $NaBH_4$, respectively.

In this work, hydogen generation by the hydrolysis of $NaBH_4$ investigated with prepared $Co_2B/TiO_2$ composite catalyst. The effect of $Co_2B/TiO_2$ ratio on the hydrogen generation rate was investigated. Kinetic rate equation was obtained by investigating the effects of some factors, such as catalyst amount, NaOH concentration, $NaBH_4$ concentration and reaction temperature.

## 2. EXPERIMENTAL

### 2.1 Preparation of the Catalyst

All commercial chemical reagents were used as received, $NaBH_4$ (Merck, 98 wt.%); $CoCl_2 . 6H_2O$ (Merck, 98 wt.%); NaOH (Merck, 98 wt.%); $TiO_2$ (Aldrich, 98 wt.%).

For the preparation of $Co_2B$/ $TiO_2$ catalyst, $Co_2B$ was prepared in the flask by these steps: Firstly, 2 g of $NaBH_4$ and 7 ml water were mixed to form an aqueous solution, secondly 0.2 g $CoCl_2$ was added to water to obtain $CoCl_2$ solution, and finally the $CoCl_2$ solution was added into $NaBH_4$ solution. The reaction process of solution is shown as reaction (2):

$$CoCl_2 + 2NaBH_4 + 3H_2O \rightarrow 6.25H_2 + 0.5Co_2B + 2NaCl + 1.5HBO_2 \qquad \text{reaction (2)}$$

After the reaction, the mixture in the flask was filtered and dried, then $Co_2B$ was obtained. In this study, 1:1, 1:2, 1:3 and 1:4 molar ratio of $Co_2B/TiO_2$ powders were prepared. These prepared powder mixtures were grinded in a planetary ball mill with the mass ratio of mixture and the grinding ball 1:40 for 5 minutes. Then composite $Co_2B/TiO_2$ catalysts were obtained with different mole ratios. Electron microscope views of these prepared catalysts were taken.

## 2.2 Hydrogen Generation Experiments

NaOH was added (2 %wt, 7 %wt, 12 %wt) into a flask which was filled with water to prepare alkali NaOH solution, and then $NaBH_4$ (1 wt%, 4 wt%, 9 wt%) was added into the NaOH solution. This solution was filled to the flask with two openings placed into the constant temperature water bath at 25-30-35 °C. The composite catalyst $Co_2B/TiO_2$ was added into this flask. Water-displacement method was used to measure the volume and the rate of hydrogen generated in the presence of the composite catalyst $Co_2B/TiO_2$. Then the hydrogen generation experiments were performed by using different proportion and the amount of composite catalysts of $Co_2B/TiO_2$. The suitable catalyst ratio and catalyst addition amounts were investigated. 1:1, 1:2, 1:3 and 1:4 molar ratio of $Co_2B/TiO_2$ were used in the preparation of catalysts. The investigated amounts of $Co_2B/TiO_2$ composite catalysts in the experiments were 0.1, 0.2 and 0.3 g. $NaBH_4$ concentration (1 wt%, 4 wt%, 9 wt%), and NaOH concentration (2 wt%, 7 wt%, 12 wt%) also varied to investigate their effects for this reaction rate. Kinetic rate equation was determined according to, catalyst amount, $NaBH_4$ conc., and NaOH conc. and reaction temperature.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Effects of Catalyst Properties on Hydrogen Generation Rate

Figure 1 shows the micrographs of the prepared composite catalysts. From these figures we can see the similar particles and surfaces, but as the $TiO_2$ ratio increased then the smaller particles formed by ball milling. Catalyst surfaces were increased when the smaller particles were obtained and the pores and cavities increased by the addition of $TiO_2$ and applying ball milling. As the reaction surface increased on the catalysts then the reaction rate was increased and 1:3 ratio of $Co_2B/TiO_2$ gave the highest reaction rate. When the ratio was 1:4 then the reaction rate decreased by the decrease of the active components in the catalyst and also the decrease of the surface of the catalyst when compared to 1:3 ratio catalyst.

Figure 2 shows the relation between hydrogen generation volume and time for $Co_2B/TiO_2$ composite catalyst with the different ratios of 1:1, 1:2, 1:3 and 1:4. The catalytic activities of the different ratio catalysts were assessed by the hydrogen generation during the hydrolysis of $NaBH_4$ (9 wt%) at 35 °C and with 2 wt% NaOH concentration. The same amount of catalyst (0.3 g) was used in all the different cases. Hydrogen was instantaneously produced when the $NaBH_4$ was in contact with the composite catalysts. However the hydrogen generation rates of the different ratio catalysts decreased in the following order:
1:3 ratio > 1:2 ratio > 1:4 ratio > 1:1 ratio respectively with the hydrogen generation rates of 364.58> 347.22 > 313.73 > 106.06 mL $min^{-1}\cdot g^{-1}$. $Co_2B/TiO_2$ ratio significantly affects the catalytic activity as can be seen from these results. The reaction completed at a shorter time and the hydrogen generation rate is the biggest with the samples with 1:3 $Co_2B/TiO_2$ ratio composite catalyst. The reaction completed at a longer time with 1:1 $Co_2B/TiO_2$ ratio and the reaction rate with this ratio is 106.06 mL $min^{-1}$ $g^{-1}$ which is lower than the 1:3 ratio result of 364.58 mL $min^{-1}\cdot g^{-1}$.

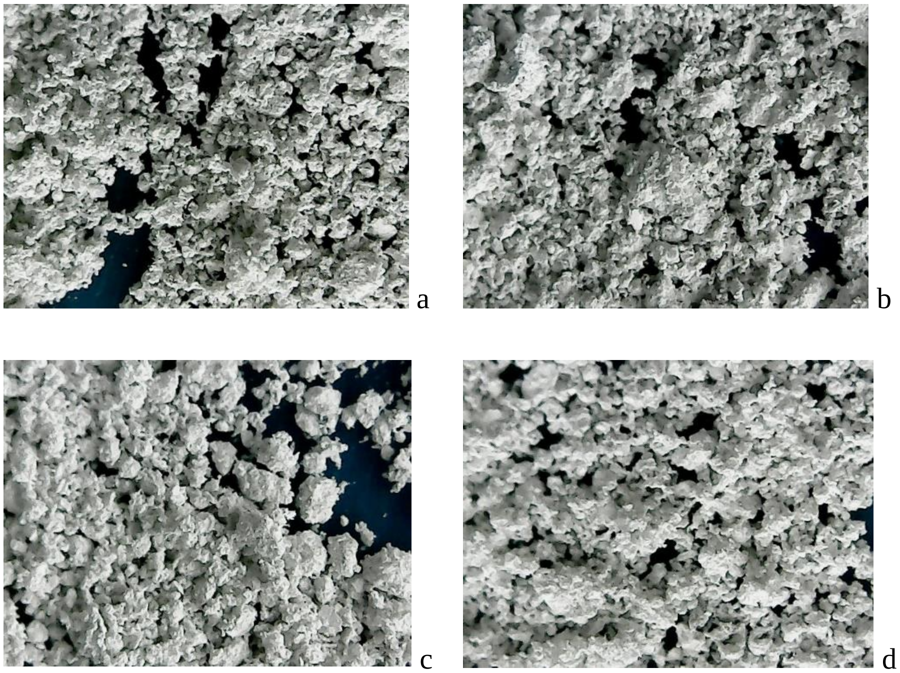

**Figure 1**. Micrographs of catalysts prepared with different ratios, a) 1:1, b) 1:2, c) 1:3 and d) 1:4, respectively.

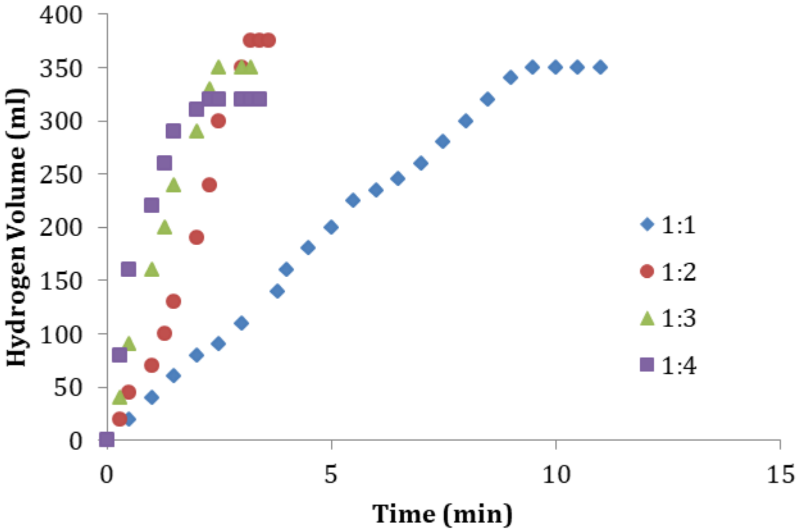

**Figure 2:** The relation between hydrogen generation volume and time for $Co_2B/TiO_2$ catalyst with the different ratios of 1:1, 1:2, 1:3 and 1:4 with 0.3 g catalyst, 9 wt% $NaBH_4$, 2 wt% NaOH, at 35 °C.

### 3.2 Effects of Experimental Factors on Hydrogen Generation Rate

The effects of some experimental factors on the hydrogen generation rate can be found by the investigation of kinetics of $NaBH_4$ with the prepared composite catalyst. These factors are; catalyst amount, NaOH concentration, $NaBH_4$ concentration, reaction temperature and these factors determine the reaction rate.

The effect of catalyst amount on the hydrogen generation rate was investigated by $Co_2B/TiO_2$ ratio of 1:3, 9 wt% $NaBH_4$ , 2 wt% NaOH concentrations at 35°C (Figure 3). It is clear from the Figure 3 that the hydrogen generation volume and hydrogen generation rate increases with increasing amount of the composite catalyst used. The hydrogen production process took longer when the catalyst amounts were 0.1 and 0.2 g. When the amount of the catalyst increased to 0.3 g, the average hydrogen generation rate increased gradually from 312.5 to 480.77 mL $min^{-1}$ $g^{-1}$. As a result, the hydrogen generation rate can be controlled by adjusting the catalyst amount used in the hydrolysis reaction. Figure 4, shows that ln (hyd. gen. rate) changed linearly with the ln (catalyst amount), and the slope of the straight line, which determined the order of reaction (x), was 1.39.

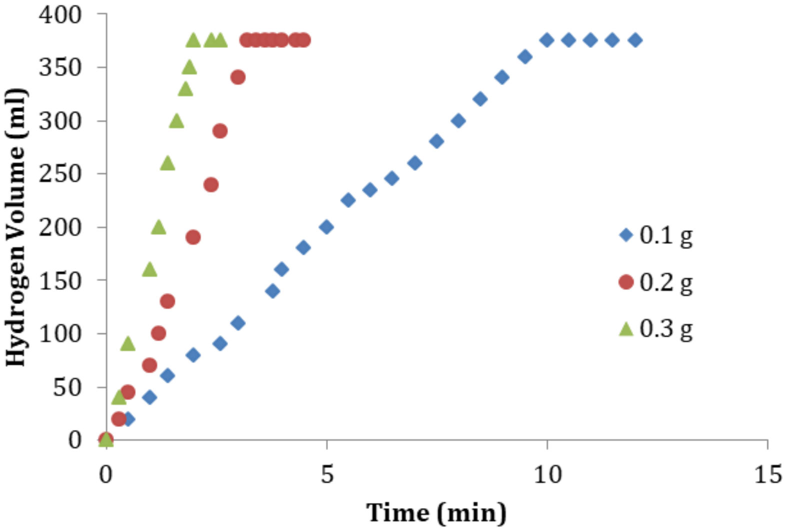

**Figure 3:** The relation between hydrogen generation volume and time for $Co_2B/TiO_2$ catalyst with the different amounts of 0.1, 0.2 and 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3, 9 wt% $NaBH_4$ concentration, and 2 wt% NaOH concentration, at 35 °C.

When the pH value of the solution is lower than 9, then the $NaBH_4$ solution can hydrolyze spontaneously. NaOH is usually added to the solution as a stabilizer in order to keep the $NaBH_4$ solution stable at room temperature. In addition to this, the concentration of NaOH crucially affects the hydrogen generation rate. As shown in Fig. 5, when NaOH concentration varied from 2 wt% to 12 wt% in the presence of 9 wt% $NaBH_4$ solution and 0.3 g of catalyst at 35 °C, the hydrogen generation rate decreased gradually with increasing NaOH concentrations. At low NaOH concentration of 2 wt%, the reaction rate was quite fast, and the hydrogen production process completed within 2.4 min. When the NaOH concentration increased to 12 wt%, the hydrogen production rate reduced severely, extending the whole reaction process to 10.5 min, which is longer time than when 2 wt% NaOH was used. Figure 6 shows that the slope of the straight line was -0.80 which is the order of reaction, (y). As a result, NaOH had a negative effect on the hydrogen generation rate. By the increase of NaOH concentration, $OH^-$ is considered to be a competitive adsorbate with $BH_4^-$ for the catalyst surface. In conclusion, hydrogen generation rate decreases with more $OH^-$ which would occupy the adsorption sites, and it is less likely for $BH_4^-$ to contact with the active components on the composite catalyst.

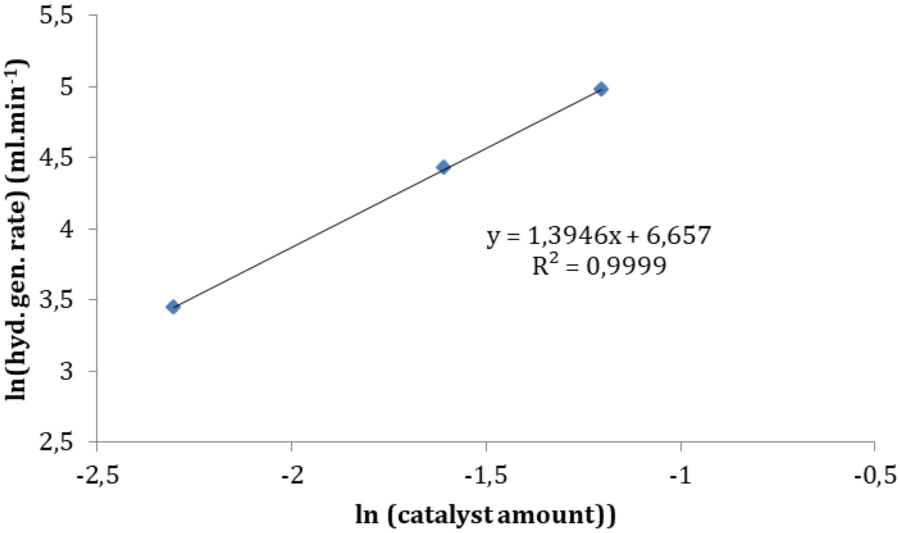

**Figure 4:** The relation between ln (hydrogen generation rate) and ln (cat. amount) with the 2 wt% of NaOH conc., with 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3 and 9 wt% $NaBH_4$ concentration.

$NaBH_4$ concentration is the important factor because of the being a hydrogen source in this reaction and determines the kinetics of the reaction. Therefore, the effect of $NaBH_4$ concentration on the hydrogen generation rate was further studied using $NaBH_4$ with different concentrations (1, 4, and 9 wt%) and 2 wt% NaOH at 35 °C. Figure 7 shows the hydrogen generation volume as a function of time with the catalyst amount of 0.3 g. The hydrogen generation rate increased significantly when the concentration of $NaBH_4$ increased from 1 wt% to 9 wt%. In the study of [14] with Zr/Co/C catalyst, when the $NaBH_4$ concentration further increased to 20 wt%, the hydrogen gen. rate dropped remarkably. In that study, when the concentration of $NaBH_4$ was below 20 wt%, the solution viscosity obtained was relatively low, and the mass transfer limitation was relatively weak, so the hydrogen generation rate was mainly controlled by heat transfer.

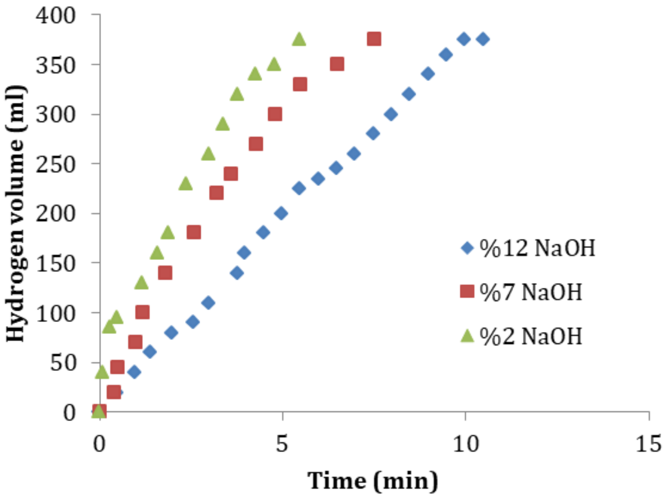

**Figure 5:** The relation between hydrogen generation volume and time for composite catalyst with the different wt% of NaOH concentration, with 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3, and 9 % $NaBH_4$ conc., at 35 °C.

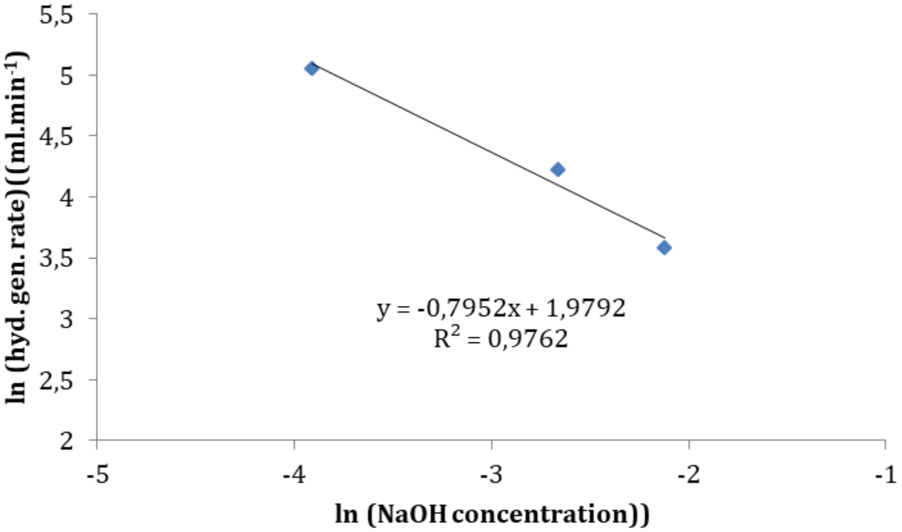

**Figure 6:** The relation between ln (hydrogen generation rate) and ln (NaOH conc.) for composite catalyst with the 9 wt% of $NaBH_4$ concentration, with 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3.

As the $NaBH_4$ hydrolysis reaction is exothermic, the more heat will be produced by the hydrolysis reaction by the higher $NaBH_4$ concentration. The heat inside the reaction system leads to the increase of reaction temperature, which accelerates the hydrogen generation rate by fast hydrolysis of $NaBH_4$ in the system. However, when the concentration of $NaBH_4$ increases to 20 wt%, the concentration of the produced $NaBO_2$ would also rise remarkably, which gives rise to the increase of the solution viscosity. The increase of viscosity limits the mass transfer of $NaBH_4$ from the solution to the inner surface of the catalyst, and also prevents the diffusion of $NaBO_2$ (sodium metaborate) from the catalyst to the reaction solution. As a result, the hydrogen generation rate is mainly controlled by mass transfer rather than heat transfer, and a relatively low hydrogen generation rate is finally obtained. [15] also found a similar observation on carbon-supported cobalt catalyst. They determined that increased viscosity of the reaction solution resulted the mass transportation limitations and hydrogen generation rate decreased. Concentrations higher than 20 wt% $NaBH_4$ was not preferred and (1, 4, and 9 wt%) $NaBH_4$ solutions were investigated in this study. Figure 8 shows, only for the $NaBH_4$ concentrations less than 20 wt% were adopted to determine the reaction order with respect to $NaBH_4$ concentration. From this figure the slope was 0.32, which is the order of the reaction, (z).

The effect of temperature on the $NaBH_4$ hydrolysis was investigated at a temperature range of 25-35 °C with 0.3 g of composite catalyst with $Co_2B/TiO_2$ ratio of 1:3 ratio, 9 wt% $NaBH_4$, 2 wt% NaOH. As illustrated in Fig. 9, the hydrogen volume and hydrogen generation rate increased gradually with the solution temperature increasing from 25 to 35 °C. Figure 10 shows Arrhenius plot and from the slope of the straight line the activation energy was calculated to be 36.50 $kJ.mol^{-1}$ which was similar to the other studies; [14] 34.84 $kJ.mol^{-1}$ with Zr/Co/C catalyst, [16] 57.8 $kJ.mol^{-1}$ with Co–B/C catalyst, [17] 43.1 $kJ.mol^{-1}$ with Co-B catalyst, [2] 33.3 $kJ.mol^{-1}$ with Co–B prepared in acetone solvent, [18] 45.5 $kJ.mol^{-1}$ with Co-B hollow sphere catalysts. The activation energy 36.50 $kJ.mol^{-1}$ which was a much lower value than some of these previously reported cobalt-based catalysts. The favorable activation energy, together with the high catalytic activity and low cost of $Co_2B/TiO_2$ catalyst makes it a very promising catalyst in future studies for developing hydrogen generation and applications.

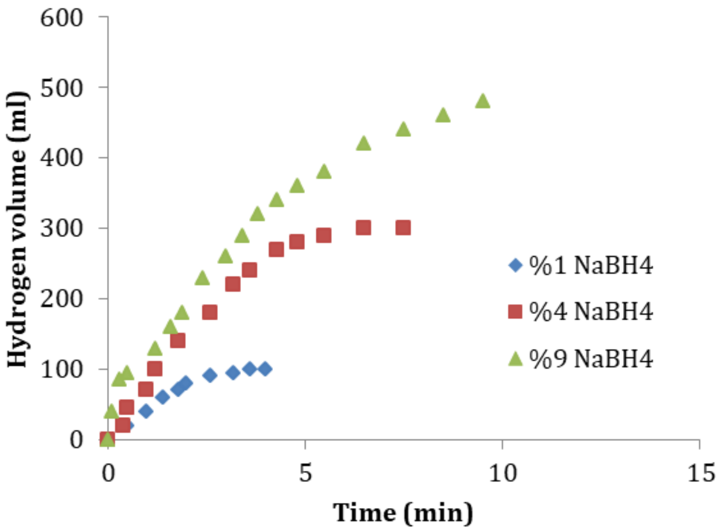

**Figure 7:** The relation between hydrogen generation volume and time for composite catalyst with the different wt% of NaBH4 concentration, with 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3, and 2 wt% NaOH conc., at 35 °C.

Figure 10 shows the Arrhenius plot of the composite catalyst with $Co_2B/TiO_2$ ratio of 1:3. The activation energy of the hydrolysis reaction was determined to be 41.2, 39.4, 36.5, and 40.8 kJ/mol when using the composite catalysts prepared with the ratio of 1:1, 1:2, 1:3 and 1:4 respectively. The catalyst prepared with ratio of 1:3 produced the lowest activation energy of the $NaBH_4$ hydrolysis reaction, this indicates the catalytic superiority of the catalyst prepared with this ratio.

The activation energy and x, y and z factors for this reaction with the prepared composite catalyst were found and the final overall kinetic equation with the concentration of $NaBH_4$ less than 20 wt% can be expressed as Eqn. (3) which is similar to Eqn. (2):

$$r = Ae^{36500/(RT)}(cat.amount)^{1.39}(NaOH\ conc.)^{-0.80}(NaBH_4\ conc.)^{0.32} \qquad \text{Eqn.(3)}$$

This kinetic expression can give useful information when the $Co_2B/TiO_2$ composite catalyst is used for developing hydrogen generation and hydrogen-based studies.

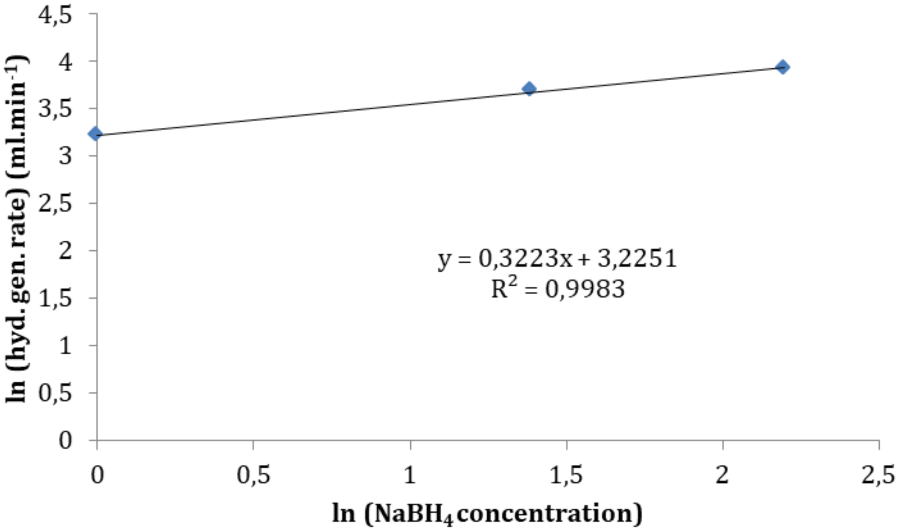

**Figure 8:** The relation between ln (hydrogen generation rate) and ln (NaBH$_4$ concentration) for composite catalyst with the 2 wt% of NaOH concentration, with 0.3 g catalyst with Co$_2$B/TiO$_2$ ratio of 1:3.

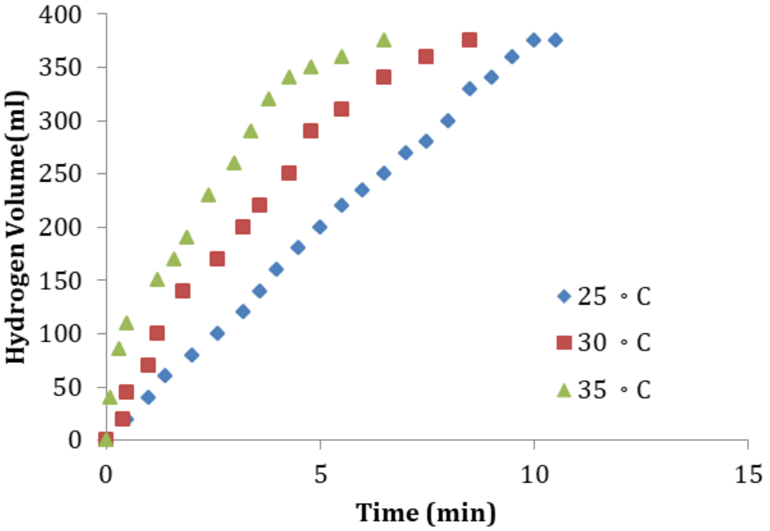

**Figure 9:** The relation between hydrogen generation volume and time for composite catalyst with the different reaction temperatures, 9 wt% of NaBH4 conc., with 0.3 g catalyst with Co$_2$B/TiO$_2$ ratio of 1:3, and 2 wt % NaOH conc.

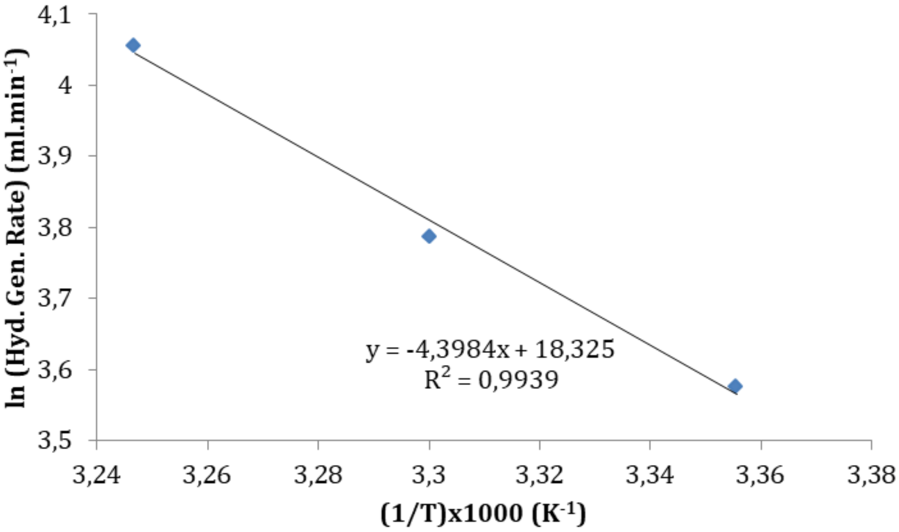

**Figure 10:** Arrhenius plot for $Co_2B/TiO_2$ catalyst with the 0.3 g catalyst with $Co_2B/TiO_2$ ratio of 1:3, 9 wt% of $NaBH_4$ conc., and 2 wt % NaOH conc.

## 4. CONCLUSIONS

$Co_2B/TiO_2$ composite catalysts with 1:1, 1:2, 1:3 and 1:4 mole ratio were prepared and investigated in the $NaBH_4$ experiments. These catalysts prepared by reduction of $CoCl_2$ with $NaBH_4$. The rapid mixing leads to formation of $Co_2B$ particles. The use of $TiO_2$ as catalyst support material and use of ball milling in the preparation of composite catalyst provided high specific surface area and high surface roughness on the catalyst surface. The larger the surface roughness, the more the number of the defects, which can provide more active sites on the catalyst surface. The porous structure is favorable for the diffusion of the reaction products. These characteristics are beneficial for enhancing catalytic activity. 1:3 mole ratio composite catalysts gave the highest hydrogen generation rate as 364.58 $ml.g^{-1}.min^{-1}$ with 0.3 g catalyst amount, 2 wt% NaOH concentration, 9 wt% $NaBH_4$ concentration and at 35 °C.

Catalyst amount, NaOH and $NaBH_4$ concentrations and reaction temperature effects the hydrogen generation rate. By the investigation of these factors on the hydrogen generation rate, the kinetic rate equation was developed. This kinetic expression can give useful information when the $Co_2B/TiO_2$ composite catalyst is used for developing hydrogen generation and hydrogen-based studies. Adjusting the concentration of the alkaline $NaBH_4$ solution the catalytic activity of the catalysts increased.

The catalytic activity was determined through investigation of hydrogen release kinetics. From the calculated activation energy of 36.50 $kJ.mol^{-1}$ for 1:3 mole ratio $Co_2B/TiO_2$ composite catalysts, as this value is low when compared to previous studies, then we can conclude that, the prepared composite catalyst shows superior catalytic activity for the hydrolysis of $NaBH_4$. $Co_2B/TiO_2$ composite catalysts can be potential to be used as a cost-effective and sustainable catalyst in the future hydrogen generation and applications studies. Further improvement in kinetic properties and catalytic activity for the catalysts is being carried out.

## 5. ACKNOWLEDGEMENTS

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