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Boric acid versus boron trioxide as catalysts for green energy source H_2 production from sodium borohydride methanolysis

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ABSTRACT

Here, boric acid (H_3BO_3) and its dewatered form, boron trioxide (B_2O_3) were tested as catalysts for hydrogen (H_2) evolution in the methanolysis of sodium borohydride ($NaBH_4$) in methanol. Parameters such as catalyst types and their amounts, $NaBH_4$ concentration, and the reaction temperature affecting the hydrogen generation rate (HGR) were studied. It has been found that H_3BO_3 and B_2O_3 catalyzed methanolysis reaction of $NaBH_4$ follow up first-order kinetics relative to the concentration of $NaBH_4$. Furthermore, the conversion and activity of these catalysts were examined to determine their performance in ten consecutive use. Interestingly, H_3BO_3 and B_2O_3 have demonstrated superior catalytic performances in methanolysis of $NaBH_4$ comparing to the studies published in literature with the activation energy of respectively 22.08 $kJ.mol^{-1}$, and 23.30 $kJ.mol^{-1}$ in H_2 production. The HGR was calculated as 6481 $mL.min^{-1}.g^{-1}$ and 5163 $mL.min^{-1}.g^{-1}$ for H_3BO_3 and B_2O_3 catalyst, respectively for 50 mg catalyst at 298 K. These results are comparably better than most metal nanoparticle catalysts used for H_2 production in addition to the naturally occurring boron-based environmentally friendliness of these materials.

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1. Introduction

The energy need with the industrial development is on the rise. The environmental anxieties from fossil fuel consumption along with the pursue of cleaner and high energy density materials help to pave the roads for fast hydrogen (H_2) production systems from various new sources [1-4]. H_2 energy systems have vital importance as substitutes for fossil-based fuels due to their many superior characteristics. H_2 fueling the sun is the most abundant element in the universe and can be stored in different physical forms with their complications. For instance, H_2 storage and delivery in gas and/or in liquid forms is not easy as it requires huge volume and compressing problems [5-9]. In that respect, chemical hydrides such as sodium borohydride ($NaBH_4$) is one of the most commonly employed benign hydrides as the best known and the most studied H_2 storage material. Having a relatively high gravimetric hydrogen content of nearly 10.8% and the suitability for hydrolysis and methanolysis reactions make $NaBH_4$ a pretty attractive substrate for H_2 generation applications. The reaction of $NaBH_4$ with water and methanol can be described as follows:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \uparrow + heat\ (-300\ kJ.mol^{-1}) \quad (1)$$

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \uparrow \quad (2)$$

From the reactions in Eq (1) and Eq (2) of $NaBH_4$, methanol has some advantages over water: a) the kinetic reaction realizes faster in methanol, b) methanol offer higher catalytic activities than water at lower temperatures (subzero temperatures) owing to the low melting point of methanol (-97.6°C), c) by comparison of by-products e.g., $NaBO_2$ versus $NaB(OCH_3)_4$, there is a lesser problem in the methanolysis reactions and easy/possible to reconversion to the reactant. The use of an appropriate catalyst system plays a significant role in accelerating and/or controlling H_2 generations from hydrolysis and methanolysis reactions [10-13]. Many different types of catalyst such as metal catalyst [14-20], polymeric particles and materials [21-23], polymeric ionic liquids [24, 25], and composite catalyst [26-28] as well as acid catalyst [29-31] for $NaBH_4$ hydrolysis and methanolysis were reported. Methanolysis reaction of $NaBH_4$ is well-known for acid catalysis, directly or indirectly e.g., increasing proton numbers in the reaction media affect the H_2 generation rate positively [31, 32]. Here, boron chemicals such as boric acid and boron oxide were employed the methanolysis of $NaBH_4$ as catalysts, and their catalytic activities were determined and compared.

Boric acid (H_3BO_3) is considered as an environmentally friendly reagent used in boron oxide or boron trioxide (B_2O_3) preparation. Dewatering of boric acid starts at around 80 °C, and the first reaction is completed at around 130 °C. Reactions slow down at around 450 °C [33, 34].

$$H_3BO_3 \leftrightarrow HBO_2 + H_2O \qquad (T < 130\ ^\circ\mathrm{C}) \qquad (3)$$
$$HBO_2 \rightarrow 1/2\, B_2O_3 + 1/2\, H_2O \qquad (T > 130\ ^\circ\mathrm{C}) \qquad (4)$$

In the last decade, boric acid chemistry has shown rapid development [35]. Boric acid is a weak inorganic acid and is widely used as an effective catalyst in organic synthesis. Boric acid attracts attention and is preferred because it is perfectly soluble in water, commercially available, chemically stable, low cost, non-toxic, recyclable, light, selective and environmentally friendly [35]. In addition, its dissolution in water and alcohols makes it possible to use it as a homogeneous catalyst in different reactions, e.g., in the reaction of H_2 production from $NaBH_4$. In this study, a new catalytic pathway is presented to produce clean and sustainable energy source H_2 from the methanolysis of $NaBH_4$ using H_3BO_3 and B_2O_3 as direct catalysts. These boron-containing catalysts are environmentally benign and have been used as a green catalyst in the methanolysis of $NaBH_4$.

Although there is a report in literature in the methanolysis of $NaBH_4$ in the presence of H_3BO_3 at high concentration of H_3BO_3 (at least 0.2 M) [36], in this study, the utilization of H_3BO_3 (at low concentration, approximately 0.04 M) and B_2O_3 as catalysts in the methanolysis of $NaBH_4$ for the first time in literature is reported. In this paper, B_2O_3 was produced in a furnace via the dewatering process of H_3BO_3 at 500 °C for its potential to be used in H_2 generation as a catalyst in the methanolysis of $NaBH_4$. H_3BO_3 and B_2O_3 catalysts were characterized via Fourier Transform Infrared Radiation (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The effect of various parameters on the methanolysis reaction of $NaBH_4$ was investigated to determine reaction order. Moreover, the influence of type and amounts of catalysts, the concentration of $NaBH_4$ as well as the temperature of the reaction from 268 K to 308 K on HGR of catalysts was testified. Additionally, the reuse performance of the catalysts was investigated by employing the same catalysts in ten consecutive runs in the same reaction taking into consideration of the change in their activity and conversion%.

2. Experimental

2.1. Materials

Boric acid (H_3BO_3, ≥99.5% Sigma-Aldrich, CAS number: 10043-35-3) as the catalyst and B_2O_3 precursor, methanol (≥99.9%, Carlo Erba, CAS number: 67-56-1) as a solvent, sodium borohydride ($NaBH_4$, ≥96 %, Merck, CAS number: 16940-66-2) as H_2 source were used without further treatment.

2.2. Instrumentation

Fourier transform infrared radiation (FT-IR, NICOLET iS10, Thermo Fisher Scientific) spectra of H_3BO_3 and B_2O_3 were recorded by collecting data using ATR technique in the range of 4000-650 cm^{-1} with 4 cm^{-1} resolving power. Thermal decomposition characters of H_3BO_3 and B_2O_3 were analyzed via thermo gravimetric analysis (TGA, SII TG/DTA 6300 model) under continuous N_2 purging with the rate of 100 $mL.min^{-1}$ min gas flow and the rate of $10°C.min^{-1}$ temperature increase. For the TG analysis, approximately 4 mg of the samples were placed in ceramic TGA crucibles and the analysis was run between 50-900°C temperature ranges.

2.3. Preparation of boron trioxide catalyst

B_2O_3 was prepared by dewatering process using a furnace (Protherm, ASP series) with a temperature controller unit. Briefly, a certain amount of H_3BO_3 was weighed and transferred to the porcelain crucible and put in the furnace. The temperature program was set up as in 10 min reach the 500 °C from room temperature and the sample was kept at 500 °C temperature for 30 min. Then, the sample was cooled to room temperature and transferred to a mortar for fine grinding. Finally, the B_2O_3 was kept in a sealed bag for further use.

2.4. Determination of the catalytic activity of H_3BO_3 and B_2O_3 as catalysts in methanolysis of $NaBH_4$

The activity of H_3BO_3 and B_2O_3 as catalysts in the $NaBH_4$ methanolysis reaction was designated by recording the displacement of water volume in the course of H_2 evolution. For the experimental part, 50 mg catalyst was placed into 20 mL methanol solution containing 125 mM $NaBH_4$ in a 50 mL round-bottomed flask under continuous stirring at 1000 rpm and H_2 evolution was tracked via attached gas burette to the flask. Determination of activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$) and HGR by using H_3BO_3 and B_2O_3 catalysts was also realized by continuously measuring the released H_2 gas. Some reaction parameters on HGR in methanolysis reaction of $NaBH_4$ were assessed i.e., the catalyst type (H_3BO_3 and

B_2O_3), catalyst amount (12.5-100 mg), initial concentration of $NaBH_4$ (62.5-500 mM), and the reaction temperature (268-308 K).

2.5. Reusability of boron-based catalysts

The reuse of H_3BO_3 and B_2O_3 catalysts was tested by measuring the conversion and catalytic activity% of the catalysts after each successive use. For this objective, the same catalyst was used repeatedly in the same reaction medium by just consecutive addition of $NaBH_4$ after each H_2 elution was ended, and these cycles was continued up to ten times usage. All the reuse studies were conducted at 298 K, under 1000 rpm stirring by using 50 mg catalyst, and 20 mL 125 mM $NaBH_4$ solution in methanol. Stoichiometric ratio was used to calculate conversion%, and activity% using HGR (r_{80}) accepting the first use as 100%.

3. Results and discussion

3.1. Preparation and characterization of catalyst

Here, H_3BO_3 and B_2O_3 were exploited as a catalyst in H_2 generation reaction due to their environmentally benign and boron-containing nature. The FT-IR spectra of H_3BO_3 and B_2O_3 were given in Fig. 1. The characteristic at 3185 cm^{-1} belong to O-H bands and the bands at 1400 and 1190 cm^{-1} were assigned to symmetric stretching vibrations of B-O. The spectral peaks at 804 cm^{-1} were designated to stretching frequency of B-O-B for boron oxide. Thermal degradation patterns of H_3BO_3 and B_2O_3 were elucidated by TGA and the corresponding TG thermograms are demonstrated in Fig. 1 (b). In the thermogram, B_2O_3 seems to have better thermal stability than H_3BO_3 as anticipated from Eq (3) and (4).

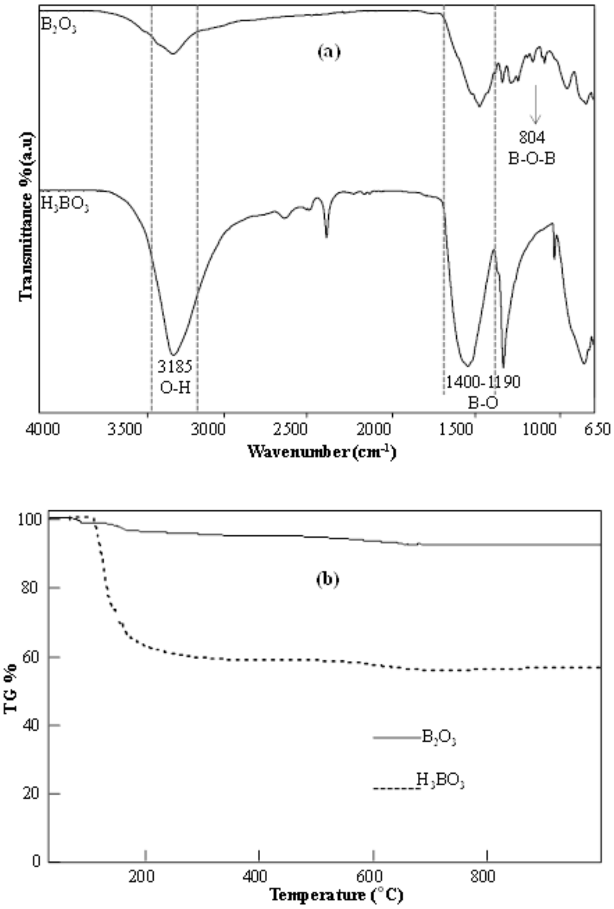


Figure 1. *The comparison of (a) FT-IR spectra of H_3BO_3 and B_2O_3, and (b) their thermal degradation curves.*

In the thermograms, the initial major decomposition temperature of H_3BO_3 was revealed from its DTG plot and determined to be around 126 °C due to removal of bounded water and upon heating up to 900°C 56% residual composition was observed with respect to the initial weight of the sample. The B_2O_3 catalyst exhibited a smoother gradual decomposition pattern and 93% of its weight was remained after heating up to 900°C.

3.2. Catalytic performance of H_3BO_3 and B_2O_3 catalysts

The rates of hydrogen generation in methanolysis of $NaBH_4$ under catalytic activities of H_3BO_3 and B_2O_3 were calculated from the constructed H_2 production plots. Rates of $NaBH_4$ methanolysis reactions were determined at the half points of conversion (r_{50}) from the H_2 generation curves recorded as a function of time ($mL.min^{-1}.g^{-1}$).

3.3. The impact of the used catalyst type on methanolysis of $NaBH_4$

It is very well-known that the methanolysis of $NaBH_4$ is an acid-catalyzed reaction and therefore elevating the number of protons in the H_2 generation medium is anticipated to have positive effects on HGR. Here, H_3BO_3 and B_2O_3 were used as acid catalysts and their catalytic performances were compared under the reaction conditions of 50 mg catalyst, and 125 mM $NaBH_4$ in 20 mL methanol at 298 K and 1000 rpm stirring.

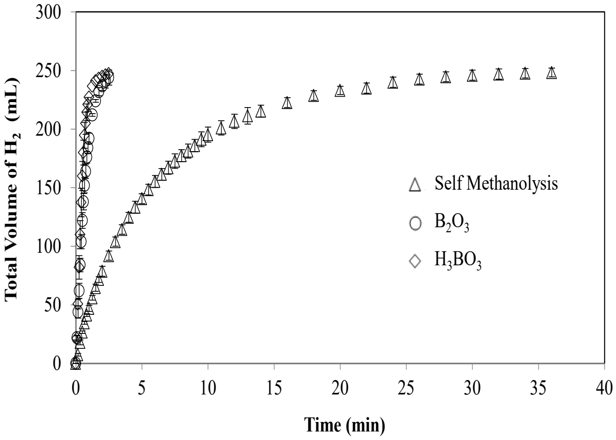


Figure 2. *Hydrogen volume vs time plots H_3BO_3 and B_2O_3 catalysts and self-methanolysis used in $NaBH_4$ methanolysis, [without catalyst or 50 mg catalyst, 125 mM $NaBH_4$ solution in 20 mL methanol, at 298 K, 1000 rpm].*

Self methanolysis was realized as a control to comprehend the catalytic activity under the same conditions with the absence of catalyst, and 100% conversions were achieved in all reactions with and without the addition of catalysts with and the same amount of H_2, ~250 mL were produced. As expected, different reaction rates were observed in self methanolysis of $NaBH_4$ and in the H_3BO_3 and B_2O_3 catalysis as plotted in Fig. 2. The HGRs H_3BO_3 and B_2O_3 were calculated as 6481, 5163 $mL.min^{-1}.g^{-1}$, respectively. So, H_3BO_3 has higher activity than B_2O_3 and it can be assumed that both catalysts possess great catalytic activity.

The suggested reaction mechanism in H_2 generation from H_3BO_3 catalyzed methanolysis of $NaBH_4$ is demonstrated in Supporting Fig. S1. A similar reaction mechanism can be considered with the exception of proton abstraction for the initial reaction of B_2O_3 as was proposed for H_3BO_3 catalyzed H_2 production.

3.3. The effect of H_3BO_3 amount as a catalyst in $NaBH_4$ methanolysis

The activity and amount catalysts are of paramount importance for scale up H_2 generation applications in terms of financial concerns, therefore, five different amounts of catalyst, 12.5, 25, 50, 75, and 100 mg of H_3BO_3 were chosen and the other parameters were held constant in $NaBH_4$ methanolysis reactions. It was demonstrated in Fig. 3(a) that, the total volume of generated H_2 is independent of the amount of catalyst. The kinetic rates of performed reactions were calculated based on the half points in the conversion (r_{50}) of $NaBH_4$ from the graphs constructed as the volume of H_2 production versus time. In other words, from the H_2 production curve with time, the curves up to 125 mL H_2 production with time are considered. For the catalytic activity that is the rate of hydrogen generation per gram catalyst, HGR is constructed by calculating the reaction rates from the slope released H_2 versus time graphs for different weights (gram) of used catalysts. Besides, the figure inset in Fig. 3(a) demonstrates that increasing the amount of H_3BO_3 from 12.5 mg to 100 mg proportionally increased the rate of the methanolysis reaction from 152 $mL.min^{-1}$to 424 $mL.min^{-1}$, and the catalytic activity (HGR) of the H_3BO_3 catalyst was calculated to reduce to 4243 from 12145 $mL.min^{-1}.g^{-1}$. As shown in the inset, the rate of H_2 release reaction versus the amount of used catalyst was constructed, and the value of 2623 $mL.min^{-1}$ was obtained from the slope of the plot. This result states the dependence of catalyst weight on the rate of H_2 release reaction in the weight range of 12.5 mg and 100 mg catalyst that results in an HGR value of 2623 $mL.min^{-1}$ weight average H_2 production rate.

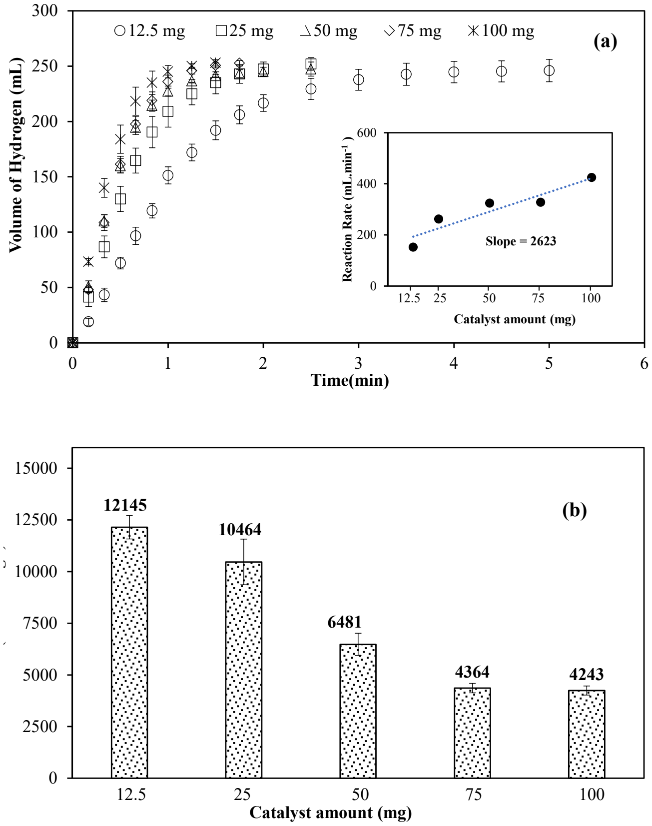


Figure 3. *Effect of H_3BO_3 catalyst amount on the methanolysis of $NaBH_4$, (a) H_2 production volume as a function of time, and reaction rate versus catalyst amount in the inset figure and, (b) the effect of catalyst amount on HGR. [catalyst: 12.5-100 mg H_3BO_3; 125 mM $NaBH_4$ solution in 20 mL methanol, at 298 K 1000 rpm].*

As can be readily understood from Fig. 3(b) that regardless of the amount of H_3BO_3 catalyst, the same volume of H_2 was produced, increasing weight of the catalyst from 12.5 mg to 100 mg shortens the H_2 production time, HGR which was respectively decreased from 12145 to 4243 $mL.min^{-1}.g^{-1}$, Moreover, ln(rate) vs ln(catalyst concentration) graph was plotted to evaluate the impact of the amount of H_3BO_3 catalyst on reaction order which in turn shows an almost linear relationship with the slope of 0.44 that is less than 1.

The same experiments were carried out for B_2O_3 and corresponding graphs were given in Fig. 4. Again, the same amount of H_2 was produced in the course of H_2 generation and only the time got shortened to produce the same amounts of H_2 upon increasing the weight of catalyst from 12.5 mg to 100 mg. On the other hand, the rate of the reaction was increased from 161 mL.min^{-1} to 305 mL.min^{-1} for B_2O_3 catalyst, and the HGR value of 1569 mL.min^{-1} weight average H_2 production rate was calculated from the slope of the plot given in the inset figure as the rate of the reaction with respect to the mass of the catalyst (Fig. 4(a)).

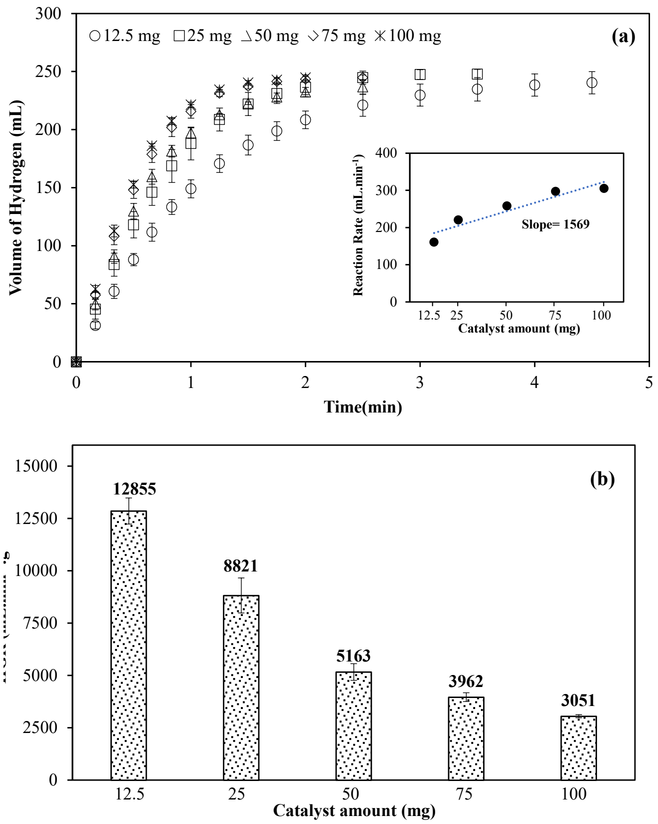


Figure 4. *The impact of B_2O_3 catalyst amounts on methanolysis of $NaBH_4$, (a) H_2 production volume as a function of time, and reaction rate versus catalyst amount was given in the inset figure and, (b) the effect of catalyst amount on HGR. [catalyst: 12.5-100 mg B_2O_3; 125 mM $NaBH_4$ solution in 20 mL methanol, at 298 K 1000 rpm].*

As shown in Fig. 4(b), weights of the used B_2O_3 catalyst were increased from 12.5 mg to 100 mg and a corresponding decrease in HGR values were observed respectively from 12855 mL.min^{-1}.g^{-1} to 3051 mL.min^{-1}.g^{-1}. The impact of B_2O_3 catalyst weight on reaction order was also evaluated from the slope of ln(rate) vs ln(catalyst concentration) plot and the slope of 0.29 with a straight line was obtained which was also less than 1. Customarily, the amount of catalyst in literature is chosen as 50 mg for these types of reactions [21]. Here 50 mg of the catalyst was therefore used for comparative purposes with those of the formerly reported catalyst systems.

3.4. The impact of used $NaBH_4$ concentration

The change in HGR with respect to altered $NaBH_4$ concentrations was investigated by using five $NaBH_4$ concentrations such as 62.5, 125, 250, 375, 500 mM of $NaBH_4$, and only the $NaBH_4$ concentration was changed by keeping other parameters constant as in the following: weight of B_2O_3 catalyst, 50 mg; a volume of methanol, 20 mL; temperature of the reaction, 298 K; rate of stirring, 1000 rpm. The H_2 production plot given in Fig. 5(a) was generated as a function of time under different $NaBH_4$ concentrations and demonstrates that volume of H_2 production proportionally increases with the increased concentration of $NaBH_4$. Similarly, in Fig. 5(b), HGR was evidenced to show a linear increase with increased $NaBH_4$ concentration. The slope of ln(reaction rate) versus ln($NaBH_4$ concentration) plot was calculated to be 1.10, hence indicating the reaction follows first-order kinetics according to $NaBH_4$ concentration.

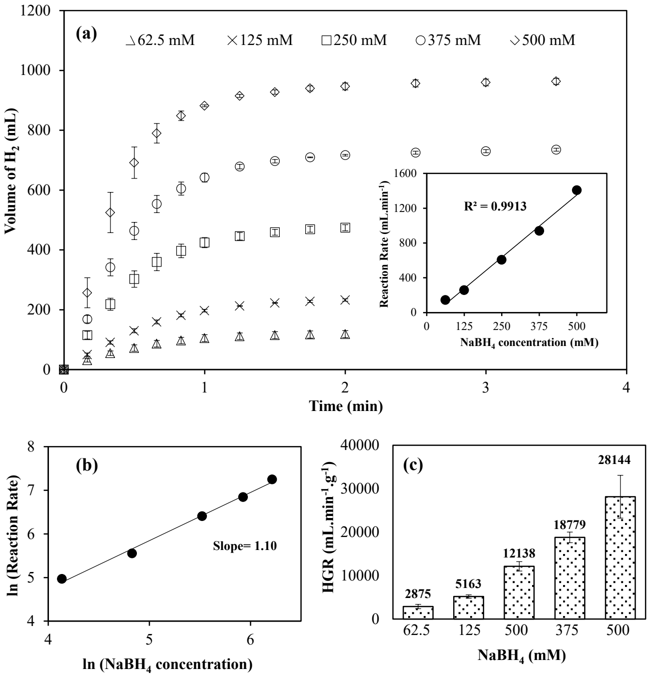


Figure 5. *The impact of $NaBH_4$ concentration on the B_2O_3 catalyzed methanolysis of $NaBH_4$, (a) H_2 production volume as function of time, and reaction rate versus amount of $NaBH_4$ was given in the inset, (b) ln(reaction rate) vs ln($NaBH_4$ concentration), and (c) effect of $NaBH_4$ concentration on HGR [catalyst: 50 mg B_2O_3; 20 mL 62.5-500 mM $NaBH_4$ at 298 K, 1000 rpm].*

As shown in Fig. 5(c), by increasing the concentration of $NaBH_4$ from 62.5 mM to 500 mM, HGR increases from 2875 mL.min^{-1}.g^{-1} to 28144 mL.min^{-1}.g^{-1}. This particular increase might be mainly due to the inadequacy of the initial $NaBH_4$/catalyst ratio to reach the dynamic saturation point of the used catalyst with the present hydride.

3.5. The impact of temperature

The impact of temperature on H_3BO_3 and B_2O_3 catalyzed methanolysis of $NaBH_4$ has been investigated at five different temperatures (268, 278, 288, 298, 308). Using 50 mg H_3BO_3 catalyst at different reaction temperatures in $NaBH_4$ methanolysis, volumes of produced H_2 were graphed against increasing temperature and presented in Fig. 6(a).

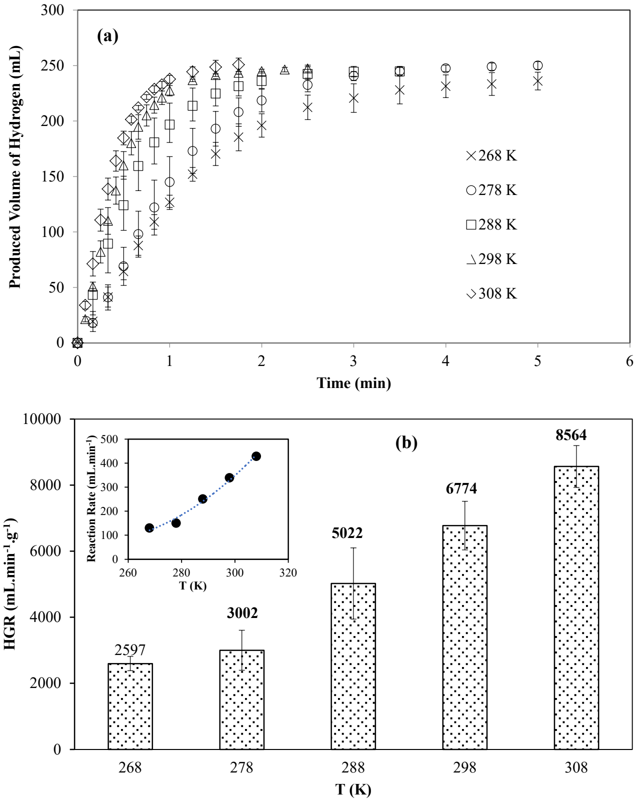


Figure 6. *The impact of temperature on H_3BO_3 catalyzed methanolysis of $NaBH_4$, (a) H_2 production volume as a function of time, and (b) effect of temperature on HGR and, inset figure is the reaction rate versus temperature [catalyst: 50 mg H_3BO_3; 125 mM $NaBH_4$ solution in 20 mL methanol, temperature range 268-308 K, 1000 rpm].*

All of the methanolysis reactions performed at different temperatures produced an average volume of 250 mL H_2. Based on the presented graph in Fig. 6(b), HGR of the H_3BO_3 was increased from 2597 $mL.min^{-1}.g^{-1}$ to 8564 $mL.min^{-1}.g^{-1}$ as the temperature of the reaction was raised from 268 K to 308 K. The reaction rate is given in the inset of Fig. 6(b) clearly illustrates that almost an exponential increase was occurred from 130 $mL.min^{-1}$ to 428 $mL.min^{-1}$ upon increasing the temperature of the reaction from 268 K to 308 K. The HGR value of 2597 $mL.min^{-1}.g^{-1}$ even at -5 ºC offers great advantages for these systems.

The catalytic performance of B_2O_3 was also examined at the range of 268 K-308 K and the rate of H_2 generation in response to changing temperatures was demonstrated in Fig. 7(a).

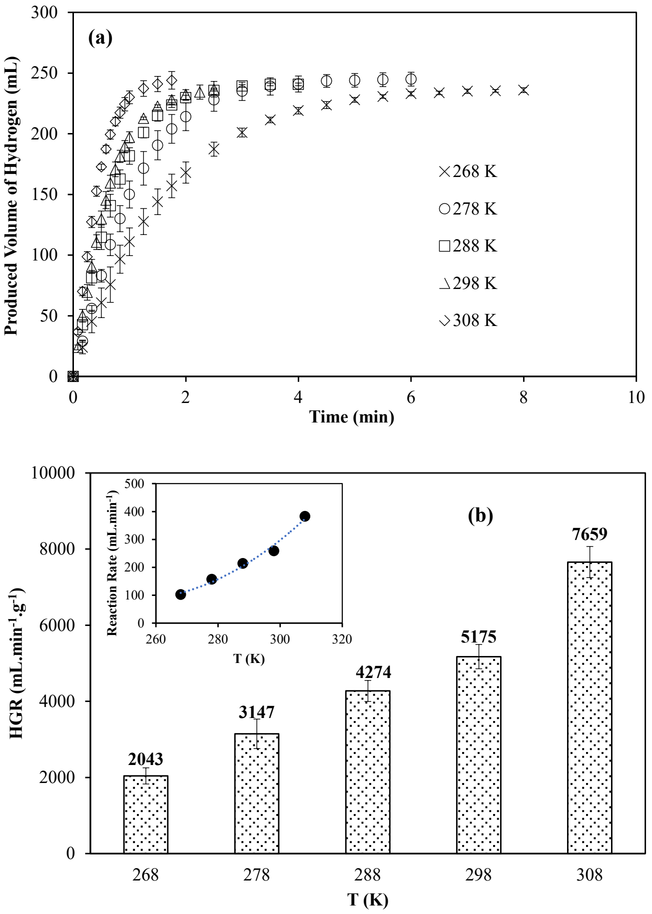


Figure 7. *The impact of temperature on methanolysis of $NaBH_4$, (a) H_2 production volume as a function of time, and (b) effect of temperature on HGR and, inset figure is the reaction rate versus temperature [catalyst: 50 mg B_2O_3; 125 mM $NaBH_4$ solution in 20 mL methanol, temperature range 268-308 K, 1000 rpm].*

Again, 250 mL of average H_2 volume was recorded for all reactions of $NaBH_4$ conducted at varying temperatures. The HGR graph of the B_2O_3 catalyzed methanolysis reaction was depicted in Fig. 7(b) as can be noticed wherefrom the HGR has experienced an increase from 2043 $mL.min^{-1}.g^{-1}$ to 7659 $mL.min^{-1}.g^{-1}$ upon raising temperature of the reaction from 268 K to 308 K. and the figure given in the inset of Fig. 7(b) apparently reveals an increment in the rate of H_2 evolution from 102 $mL.min^{-1}$ to 383 $mL.min^{-1}$ after boosting the temperature from 268 K to 308 K. Therefore, even natural B_2O_3 can be used as a benign catalyst to generate H_2 from chemical hydrides offer unprecedented alternatives to the existent metal nanoparticle, polymeric IL, and IL molecule-based catalyst.

The parameters of activation energy Ea, enthalpy ΔH, and entropy ΔS were determined for H_3BO_3 and B_2O_3 catalyzed methanolysis of $NaBH_4$, and the rate constants between 268 - 308 K reaction temperature range, graphs of ln(k) vs T^{-1} plots and $\ln(k.T^{-1})$ vs $(1.T^{-1})$ were plotted based on well-established Arrhenius (Eq. (5)) and Eyring (Eq. (6)) equations, respectively.

$$lnk = ln\,A - (\frac{Ea}{RT}) \tag{5}$$

$$ln\left(\frac{k}{T}\right) = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{R}\left(\frac{1}{T}\right) \tag{6}$$

Where, k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 $J.K^{-1}.mol^{-1}$), T is temperature, k_B is Boltzmann constant (1.381 x 10^{-23} $J.K^{-1}$), h is Planck constant (6.626 x 10^{-34} J.s), $\Delta S^{\#}$ is the entropy of activation, and $\Delta H^{\#}$ is the activation enthalpy.

The results show very well fitness with the Arrhenius and Eyring equations and respective plots for H_3BO_3 and B_2O_3 catalysts were respectively shown in Supporting Fig. S2 (a) and Supporting Fig. S2 (b), and used to calculate activation parameters. The comparison of activation energies was given in Supporting Fig. S2 (c). The activation parameters for H_3BO_3 and B_2O_3 catalyzed $NaBH_4$ methanolysis and rate constants were summarized in Table 1.

Table 1. *The rate constants calculated at different temperatures, and activation parameters for H_3BO_3 and B_2O_3 catalyzed $NaBH_4$ methanolysis.*

Catalyst	T (K)	k (min^{-1})	E_a ($kJ.mol^{-1}$)	$\Delta H^{\#}$ ($kJ.mol^{-1}$)	$\Delta S^{\#}$ ($J.mol^{-1}.K^{-1}$)
H_3BO_3	268	0.8422	22.08	19.70	-171.93
	278	1.2281			
	288	1.7401			
	298	2.3297			
	308	3.0068			
B_2O_3	268	0.5863	23.30	20.91	-169.54
	278	1.1273			
	288	1.3931			
	298	1.6765			
	308	2.5924			

Reaction conditions: 50 mg catalyst; 125 mM $NaBH_4$ solution in 20 mL methanol at 298 K, 1000 rpm.

The E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ were designated as 22.08 $kJ.mol^{-1}$, 19.70 $kJ.mol^{-1}$ and -171.93 $J.mol^{-1}.K^{-1}$, respectively for H_3BO_3 and as 23.30 $kJ.mol^{-1}$, 20.91 $kJ.mol^{-1}$and -169.64 $J.mol^{-1}.K^{-1}$, for B_2O_3 catalyzed methanolysis reactions, respectively. Interestingly, both boron-based catalysts demonstrated one of the best ones or the lowest E_a amongst the different catalysts used for the same purpose of H_2 generation from methanolysis of $NaBH_4$ as presented in Table 2. As can be seen wherefrom the E_a values of 22.08 and 23.30 $kJ.mol^{-1}$ for H_3BO_3 and B_2O_3 catalysts calculated in the range of 268-308 K is considerably lower than those of the previously reported metal-based catalyst, polymeric nanoparticles, etc. as compared in Table 2. As a result, H_3BO_3 and B_2O_3 catalysts may have great potential for an environmentally benign H_2 generation system with the capability of working even relatively lower temperature e.g., subzero temperatures from the methanolysis of $NaBH_4$ for real industrial applications.

Table 2. *The comparison of activation energies of some of the different catalysts used in literature in catalytic hydrolysis and methanolysis reactions of hydrides for H_2 generation.*

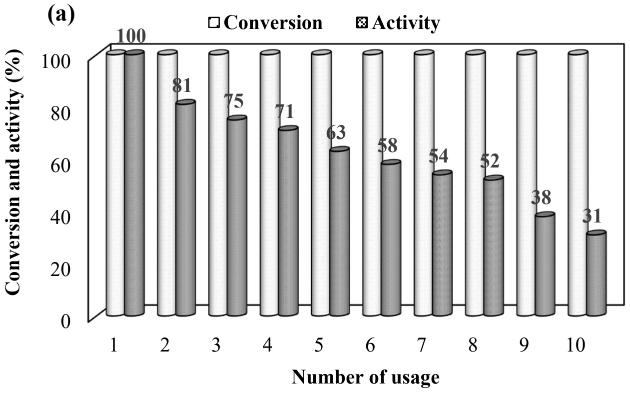
Catalyst	Temperature (K)	Activation energy ($kJ.mol^{-1}$)	HGR ($mL.g^{-1}.min^{-1}$)	References
$Co\text{-}TiO_2$ (methanolysis)	273-298	20.4	-	[8]
1 M Phosphoric acid (KBH_4 ethanolysis)	303-333	2.98	6423	[12]
Cu/Co catalyst (hydrolysis)	293-333	42.66	-	[14]
Ni_2P-sol-gel (methanolysis)	273-313	24.9	3700	[15]
Ni_2-P-TPR (methanolysis)		44.5	7140	
$CoCI_2$ (methanolysis)	253-323	25-29	-	[16]
Ru/Al_2O_3 (hydrolysis)	273-308	14.8	204.3	[17]
Ru–Co/C (methanolysis)	298-333	36.83	9360	[18]
Co-P/CNTs-Ni foam (methanolysis)	298-313	49.94	2430	[19]
Fe-B NPs (methanolysis)	293-323	7.02	5487	[20]

Cell-EPC-DETA-HCl (methanolysis)	263- 313	30.80	2015	[21]
P(MTMA) (methanolysis)	258-318	24.10	4838±126	[23]
SSA (hydrolysis)	298-343	17	3900	[29]
H_3BO_3 (hydrolysis)	293-313	20.31	-	[30]
Hydrochloric acid (semi-methanolysis)	293-323	5.84	4875	[31]
Acetic acid (semi-methanolysis)		2.81	3960	
Self methanolysis	273-313	62.99	-	[37]
H_3BO_3 (methanolysis)	268-308	22.08	6481	This study
B_2O_3 (methanolysis)		23.30	5163	

As presented in Table 2, systems catalyzed by H_3BO_3 and B_2O_3 exhibit better catalytic performance than most of the methanolysis reactions reported in the literature [14, 16, 18, 19, 21, 23].

3.6. Reuse of H_3BO_3 and B_2O_3 catalyst

The reuse of a catalyst and its performance is the foremost important parameters for the industrial success of any catalyst system. To determine the reusability, the H_3BO_3 and B_2O_3 catalysts were used repetitively in the same setting by calculating the conversation and catalytic activities and comparing their values after each use. The conversion is calculated based on stoichiometry of the reaction in accord with Eq (2), and activity is calculated presuming the initial catalytic activity as 100% for the first use by considering its reaction rate as base taking its' ratio to each consecutive use. The conversion and activity % of H_3BO_3 and B_2O_3 as a catalyst for H_2 generation from methanolysis reaction is illustrated in Fig. 8 (a) and (b), respectively.



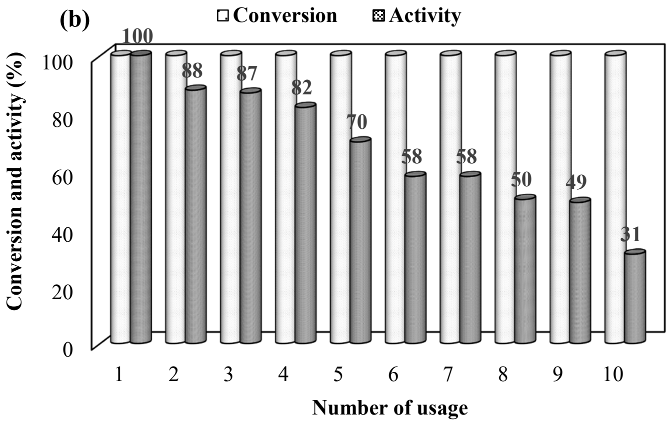


Figure 8. *The reuse of (a) H_3BO_3 and (b) B_2O_3 catalyst in methanolysis of $NaBH_4$ in terms of conversion and % catalytic activity [catalyst: 50 mg; 125 mM $NaBH_4$ solution in 20 mL methanol at 298 K, 1000 rpm].*

Regardless of catalysts types, both of the catalysts provided 100 % conversion up to 10 successive runs. The catalytic activity on the other hand reduced after each for both of the catalysts. For example, 100 % catalytic activity of H_3BO_3 catalyst decreased to 81% at 2nd use and continued to decrease to 31% at 10th use. The same reduction trend is also seen for the B_2O_3 catalyst as the 100% catalytic activity is decreased to 88% at 2nd use and continues to decrease afterward reaching 31% at 10th use as shown in Fig. 8b. Although the reduction in catalytic activity% of B_2O_3 catalyst is not as sharp as H_3BO_3 catalyst, both catalysts can keep over 50% activity up to 8th cycles. Therefore, both of these catalysts can be safely used as green catalysts for the generation of green energy carrier, H_2 generation from hydride methanolysis reactions.

4. Conclusions

In conclusion, the utilization of boron containing environmentally benign catalysts such as H_3BO_3 (~ 0.04 M) and B_2O_3 in the methanolysis of $NaBH_4$ were reported for the first time in this study. The H_3BO_3 and B_2O_3 as catalysts afforded relatively low Ea values, 22.08 $kJ.mol^{-1}$, and 23.30

kJ.mol^{-1}, respectively in methanolysis of $NaBH_4$ in comparison to the conventional catalysts reported for the same reaction as given in Table 2. These values are better than most of the reported noble metal-based catalysts in the literature make these boron-based natural catalysts better suited of feasible than most of those reported expensive and toxic ones e.g., metal nanoparticle-based catalysts and/or IL-based catalysts employed in methanolysis of $NaBH_4$ for H_2 generation. Besides, these environmentally friendly boron based catalysts also provided higher hydrogen generation rates (HGR) e.g., 6481 mL.min^{-1}.g^{-1} and 5163 mL.min^{-1}.g^{-1} in comparison to the many metal nanoparticle based catalysts reported in the literature. Furthermore, the reusability studies revealed that both H_3BO_3 and B_2O_3 catalysts can be used up to 8 repeated reuse cycles at 298 K, retaining 50% of their catalytic activity by providing 100% substrate ($NaBH_4$) conversion for every single use. Consequentially, the acid-based catalysts reported here with laborless, cost-effective preparation and environmentally benign natures bestow outstanding candidacy for the displacement of mostly toxic and/or costly counterparts used in industrial and environmental implementations.

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