Research Article

Hydrogen generation from sodium borohydride via natural materials

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ABSTRACT

In this study, the catalytic activity of starch, cellulose and coffee were investigated in the dehydrogenation of sodium borohydride. The hydrogen generation rates of starch, cellulose and coffee were measured as 4.0, 6.7 and 60 ml H_2 min^{-1} g^{-1} and the activation energies of the reactions were calculated as 27.4, 17.1 and 14.5 kJ mol^{-1} for starch, cellulose and coffee respectively. The study showed that natural sources could be used directly as catalysts in the dehydrogenation of chemical hdyrides.

1. Introduction

Renewable energy has held the key for the energy crisis of the world. Energy demand could not be dependent on fossil fuels due to limited sources and environmental effects [1–3]. Among renewable energies, hydrogen energy is the most promising one due to high energy density, on demand energy providing capacity and zero emission [4,5]. It is non-toxic and environmentally friendly. Fuel cells are the most applicable hydrogen energy device that can provide electrical energy directly from chemical energy stored in hydrogen [6,7]. However, besides its positive aspects, it also has drawbacks that should be overcome. Storage is the leading problem among them since keeping hydrogen in a gas or liquefied form needs high pressure vessels. Moreover, these storage methods have low gravimetric and volumetric hydrogen storage densities. This leads to problem for its transportation and cost [8,9]. However, chemical hydrides provide a solution for these problems [10,11]. They contain high hydrogen density without the need of pressurized vessels. Also, they provide high hydrogen density, non-toxicity, efficient and safe storage and high stability. On the other hand, the hydrogen bonded in these chemicals demand a catalyst for its release and further use in fuel cells [12,13]. Various catalysts have been utilized for this purpose such as thin films, nanoparticles and acids [14–17]. Also, natural materials have been used in the synthesis of these catalyst such as coffee waste, cellulose, starch [18–21]. However, to the best of our knowledge, they have not been utilized as catalysts and their catalytic properties have not been investigated in the dehydrogenation of chemical hydrides. In other words, they were not directly used in the dehydrogenation of chemical hydrides.

In this study, the catalytic activity of natural sources such as starch, cellulose and coffee were analyzed directly in the dehydrogenation of sodium borohydride (NaBH4). Moreover, the effects of their utilized weights, sodium borohydride concentration and temperature on the hydrogen generation rates were investigated. With the direct usage of these natural materials, the synthesis steps and costs were aimed to reduce in the utilization of catalysts.

2. Material and Methods

$NaBH_4$ and cellulose were bought from Sigma-Aldrich. The starch and coffe (robusta, mocha pot grinded) were obtained from local shops. Hydrogen generation tests were carried by water displacement method. A water filled graduated glass tube was attached to the glass reaction flask. 2.5 mmol $NaBH_4$ was dissolved in 30 deionized water and 1 g catalyst (cellulose, coffee or starch) was dispersed in 20 ml deionized water. Aqueous $NaBH_4$ and catalyst solutions were added to the reaction flask and stirred at 500 rpm with a magnetic stirrer. The hydrogen production rate was calculated by the displaced water volume within the time interval of the reaction. The initial hydrogen generation rates were reported and they were given in the unit of ml H_2 min^{-1} $g^{-1}_{catalyst}$.

3. Results and Disscussion

Natural materials have been used for the catalyst production in the hydrogen generation from chemical hydrides. They were utilized as supporting layer for nanoparticles in order to enhance their catalytic activities. In this study, natural materials were used directly in the hydrogen generation process and their catalytic behaviors were investigated. It was known that proton can catalyze the dehydrogenation of chemical hydrides.

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Therefore if proton donor group was introduced into their solutions, the dehydrogenation process would be catalyzed and the hydrogen production rate would increase. With this aim, we utilized starch, cellulose and coffee as natural catalysts in this study.

Figure 1 shows the catalytic activity of all three catalysts in the dehydrogenation reaction of $NaBH_4$. The reactions were conducted at 20ºC and $NaBH_4$ did not display any self-dehydrogenation. Firstly, starch demonstrated the lowest hydrogen generation rate with 4.0 ml H_2 min^{-1} g^{-1}_{starch} among them. Secondly, cellulose displayed a higher dehydrogenation rate than starch and it was measured as 6.7 ml H_2 min^{-1} $g^{-1}_{cellulose}$. Lastly, coffee showed the highest rate among them which is 60.0 ml H_2 min^{-1} g^{-1}_{coffee}.

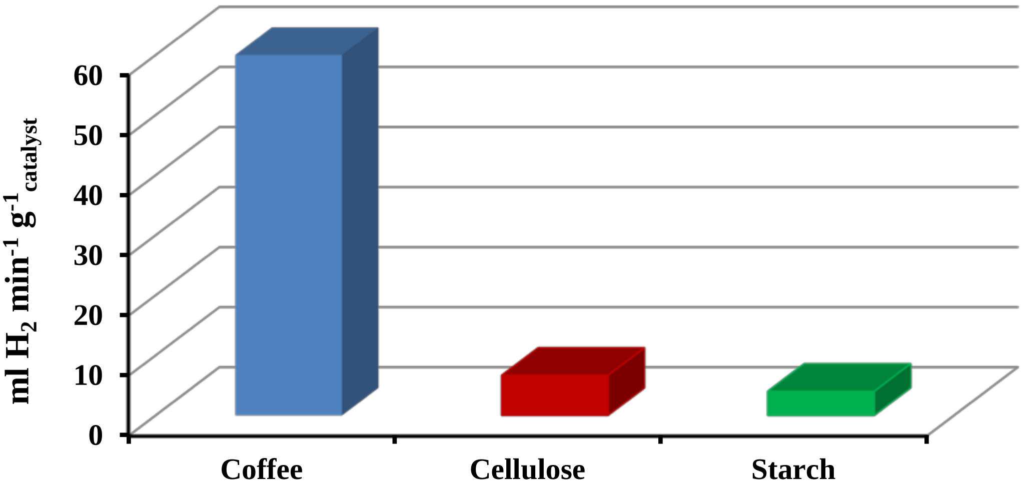

Fig. 1. Hydrogen generation rates of starch, cellulose and coffee

The hydrogen generation rate increased with increasing catalyst amount. This result was expected since more catalyst would react with more $NaBH_4$ molecules within a time interval. Therefore, more reaction took place and the hydrogen generation rate would increase. On the other hand, the dependency of the hydrogen generation rate on the catalyst amount was important in order to find the increment rate with the utilized catalyst weight. In order to analyze the effect of catalyst amount on the dehydrogenation rate of $NaBH_4$, the utilized catalyst weights were varied from 250 mg to 5 g and the measured hydrogen generation rates were plotted against catalyst amount. It could be seen that there is a linear relation between catalyst amount and dehydrogenation rate of $NaBH_4$ with the power of 0.9036, 0.9552 and 0.9389 with respect to the starch, cellulose and coffee weights, respectively (Figure 2).

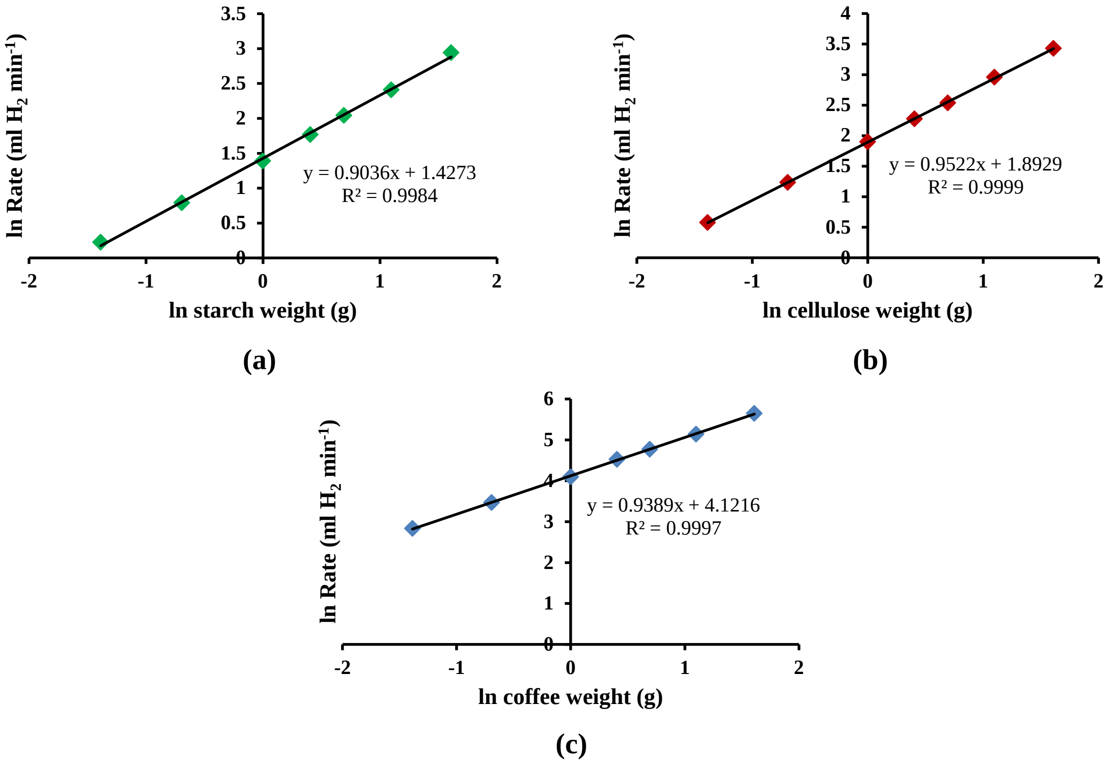

Fig. 2. The weight effect of starch (a), cellulose (b) and coffee (c) on the hydrogen generation rate

Beside the catalyst weight, $NaBH_4$ concentration was also an important parameter that affected the hydrogen generation rate. In order to analyze the dependency of rate on $NaBH_4$ concentration, the concentration was varied from 0.01 M to 0.3 M. As shown in Figure 3., there is a linear relation between them. The dehydrogenation rate of $NaBH_4$ increased with the power of 0.8496, 0.8685 and 0.8066 with respect to $NaBH_4$ concentration for starch, cellulose and coffee, respectively.

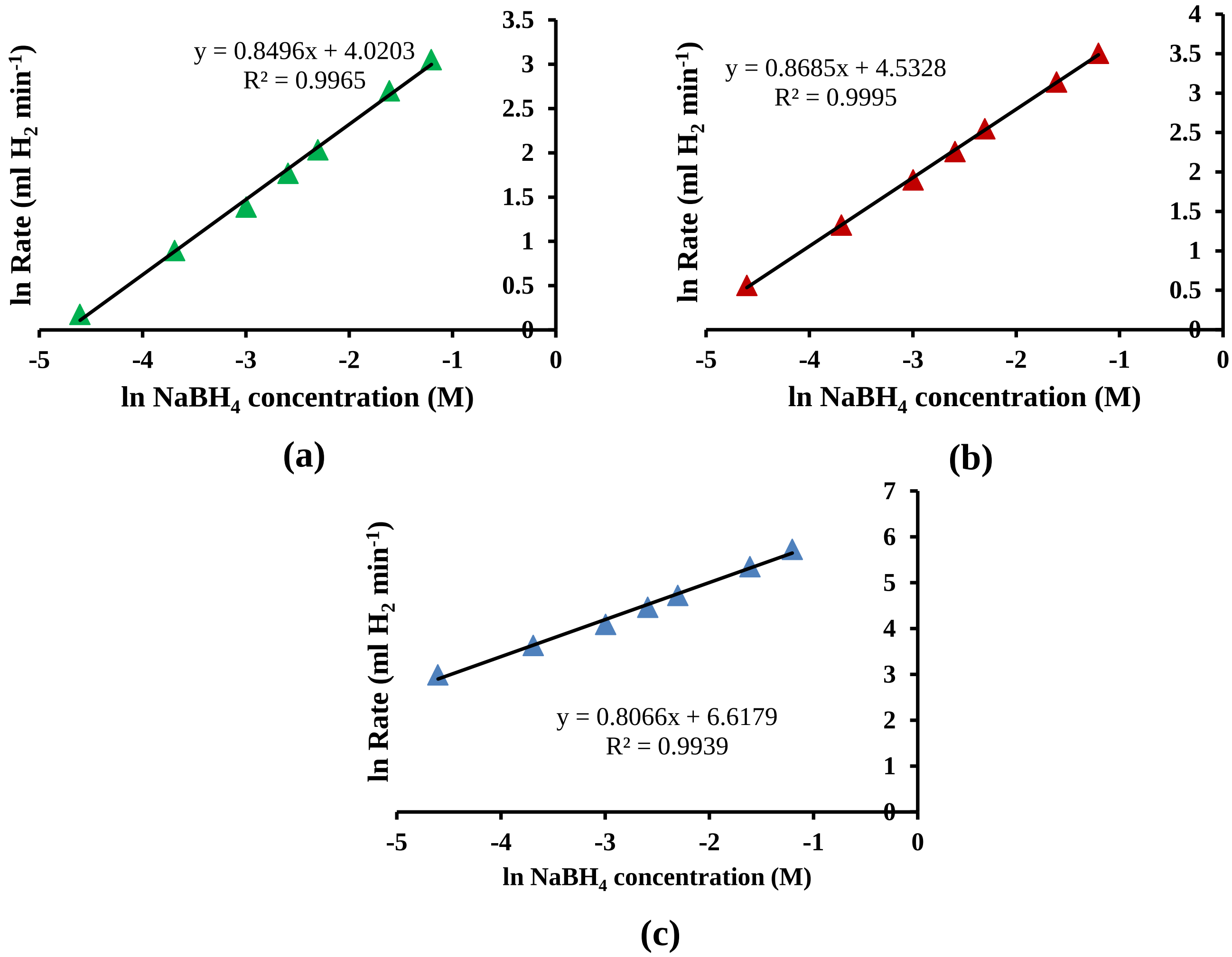

Fig. 3. The concentration effect of $NaBH_4$ on the hydrogen generation rate for starch (a), cellulose (b) and coffee (c)

Although the particle size of coffee particles was higher than both starch and cellulose, it provided a much higher hydrogen generation rate than starch and cellulose. This may be associated with activation energies of reactions for these catalysts. In order to calculate the activation energy, hydrogen generation rates at various temperatures were investigated (Table 1). Arrhenius equation ($k = Ae^{-E_a/RT}$) was utilized for the calculation. and ln(rate) was plotted against T^{-1}. The slope of the graph gave the $-E_a.R^{-1}.T^{-1}$ where E_a and R were the activation energy and universal gas constant, respectively. From the slope, activation energies were calculated and they were found as 14.5, 17.1 and 27.4 kJ mol^{-1} for coffee, cellulose and starch, respectively. It could be seen that the highest hydrogen generation rate was observed with the lowest activation energy (Figure 4).

Table 1. Hydrogen generation rates at various temperatures

	Hydrogen Generation Rate (ml H_2 min^{-1} $g^{-1}_{catalyst}$)		
Temperature (°C)	Starch	Cellulose	Coffee
20	4.0	6.7	60
25	4.6	7.2	63
30	5.6	8.0	69
35	6.6	8.8	75
40	8.0	10.0	84

45	9.6	11.7	96

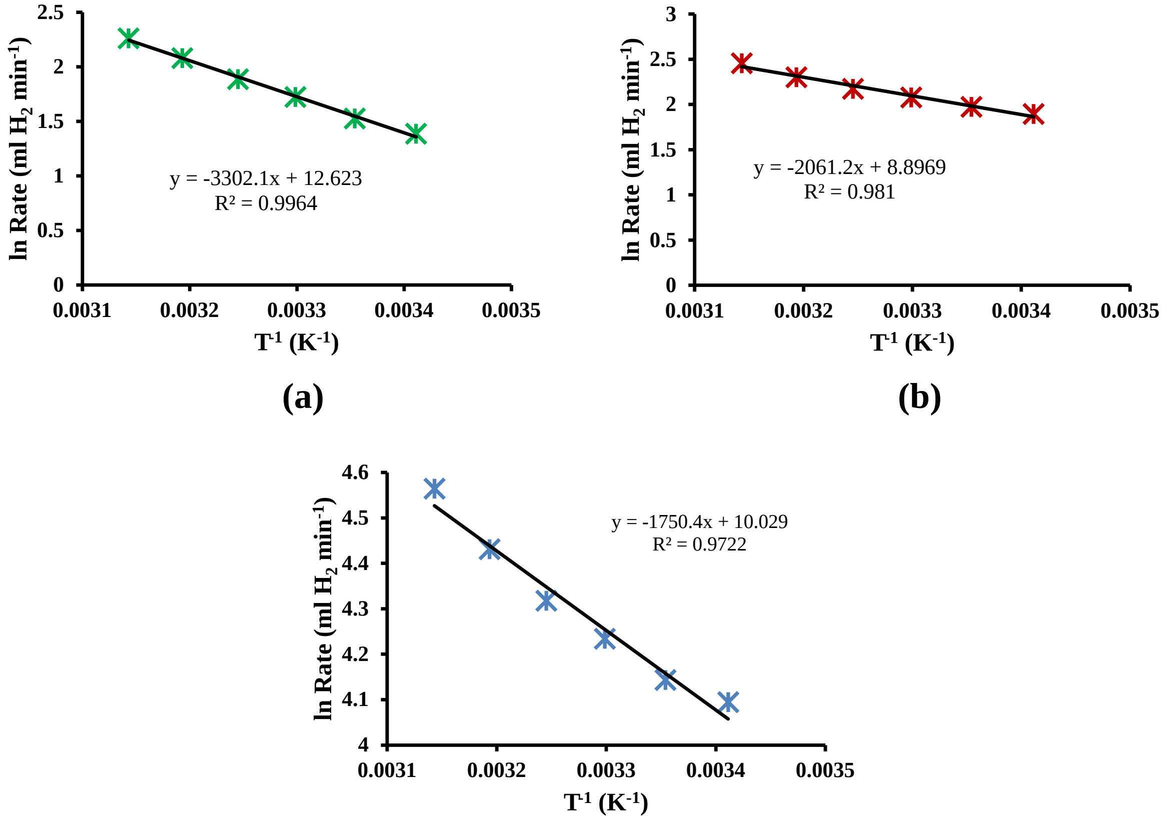

Fig. 4. Hydrogen generation rates of starch (a), cellulose (b) and coffee (c) at various temperature

Durability was another important parameter for the utilization of the catalyst. Since, it was hard to recollect starch after hydrogen generation tests, durability tests were conducted with cellulose and coffee. Prior to durability tests, both catalysts were treated with sulfuric acid beforehand and washed with water in order to avoid excess acid residues. Coffee showed the higher hydrogen generation rate when compared to cellulose. After 6 runs, its rate was also higher than cellulose. On the other hand, the decrease in the hydrogen generation rate was much higher for coffee than cellulose. Thus, cellulose provided higher durability than coffee (Figure 5).

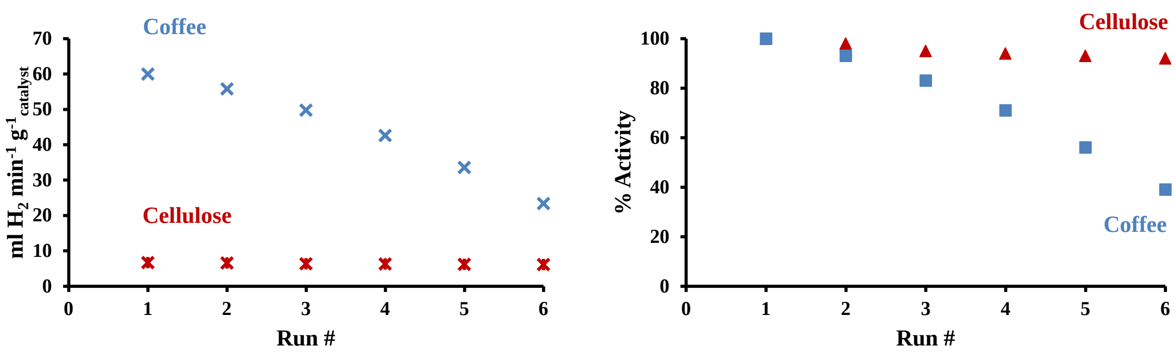

Fig. 5. Reusability of cellulose and coffee

4. Conclusion

In the study, starch, cellulose and coffee were tested in the dehydrogenation of $NaBH_4$. They demonstrated catalytic activity with hydrogen generation rates of 4.0, 6.7 and 60 ml H_2 min^{-1} g^{-1}, respectively. Moreover, hydrogen generation rates were found as a function of catalyst weight, $NaBH_4$ concentration and temperature. When the catalyst amount increased from 0.25 to 5 g, the hydrogen generation rates of starch, cellulose and coffee increased from 1.25, 1.78, and 17 to 18.9, 30.8 and 283 ml H_2 min^{-1}, respectively. Additionally, as the $NaBH_4$ concentration increased from 0.01 M to 0.3 M, the hydrogen generation rates increased from 1.19, 1.75 and 20 to 21.12, 33.28 and 308 ml H_2 min^{-1}, respectively. Also, when temperature was raised from 20 to 45ºC, the hydrogen generation rates increased from 4.0, 6.7 and 60 to 9.6, 11.7 and 96 ml H_2 min^{-1} g^{-1}, respectively. Moreover, their activation energies of the reactions were calculated as 27.4, 17.1 and 14.5 kJ mol^{-1} for starch, cellulose and coffee respectively. The study showed that natural sources could be used directly as catalysts in the dehydrogenation of chemical hydrides. In future studies, other natural sources will be analyzed in the dehydrogenation of various chemical hydrides.

Authorship Contributions

All contributions to this work were made by the author.

Declaration of conflicting interests

The author declare no competing interests.

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Ethics

There are no ethical issues with the publication of this manuscript.

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