

Generation of Hydrogen in the Hydrolysis of NaBH₄ Using Ir(0) Catalyst

MECIT AKSU^{1,2,*}

¹Department of Chemistry, King Abdulaziz University, 21589 Jeddah, Saudi Arabia

²Department of Chemistry, Duzce University, 81100 Duzce, Turkey

*Corresponding author: E-mail: mecitaksu@duzce.edu.tr

Received: 15 April 2014;

Accepted: 28 May 2014;

Published online: 15 November 2014;

AJC-16321

This study reports the results of kinetic of hydrogen generation from the catalytic hydrolysis of sodium borohydride. Iridium(0) particles catalyst was stabilized by diethylene glycol. Catalyst iridium was characterized by field emission scanning electron microscopy and energy dispersive X-ray spectroscopy. Hydrolysis of sodium borohydride was carried out both with and without stirring. Effect of stirring, sodium hydroxide concentration and sodium borohydride concentration on hydrogen volume and yield of hydrogen generation was investigated for optimization. It was found that rate of H₂ generation decreased with increasing NaOH concentration while increased with increasing concentration of NaBH₄. Stirring has positive effect on rate of hydrogen generation.

Keywords: Iridium catalyst, Sodium borohydride, Hydrogen generation, Hydrolysis.

INTRODUCTION

The synthesis of metal nanoparticles with controllable size and size distribution is of great importance because of their potential applications in many fields, including catalysis¹. Today, a challenging issue in the synthesis of metal nanoparticles is the achievement of the compositionally well-defined shape and size controllable nanoparticles as the catalytic activity of metal nanoparticles is drastically influenced by their size and shape, as they control the surface structure, electronic and oxidation states. Therefore, the use of well defined metal nanoparticle catalysts allows us to assess the nature of active sites in the catalytic reaction, which is vital for the rational design of catalysts. Recent progress in the fabrication techniques has enabled the synthesis of metal nanoparticles with precisely controlled size, shape and composition¹⁻⁶. Ruthenium(0) nanoparticles^{7,8}, hydrogen phosphate stabilized nickel(0) nanoparticles⁹, CoB nanoparticles¹⁰, PVP stabilized nickel(0)¹¹ and cobalt(0) nanoparticles¹², Co₂B nanoparticles¹³, bimetallic Pt_xNi_{1-x} nanoparticles¹⁴, Co-La-Zr-B quaternary amorphous nanoalloy², Fe-B nanoparticles³, surface-alloyed Ni foam⁴, Ru-RuO₂/C¹⁵, carbon nanosheets supported Zr/Co¹⁶, Ni-Ru nanocomposite¹⁷, Co-Cu-B¹⁸ catalysts were tested in the hydrolysis of sodium borohydride.

Hydrogen is a potential and economical clean energy carrier stored in molecular (pressurized vessels, liquified H₂ tanks), atomic (metal hydrides), or hydride forms (protide compounds). Although there has been enormous efforts to

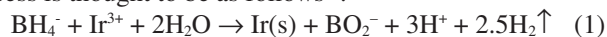
develop suitable hydrogen storage and releasing materials in the last few decades, the efficient storage and production of hydrogen are still two key problems in the "Hydrogen economy"^{19,20}. Hydrogen storage techniques that are related to liquid-phase chemical hydrogen storage materials, such as aqueous NaBH₄, H₃NBH₃, N₂H₄, N₂H₄BH₃ and HCO₂H, have attracted considerable attention^{4,21}.

The concentrations of NaBH₄ and NaOH exert important influences on the practical performance of on-demand hydrogen generation system. Higher NaBH₄ concentration is highly wanted for achieving high hydrogen capacity, but gets restricted by the solubility limitation of NaBH₄ itself and hydrolysis product NaBO₂ in water. Certain amount of NaOH is required for stabilizing the NaBH₄ fuel solution, but causes capacity loss and may pose a problem for rapid hydrogen generation and instant response for hydrogen generation requirement²². This study is aimed to illustrate the optimization of hydrogen generation reaction from NaBH₄ via Ir(0) stabilized by diethylene glycol as catalyst and effect of concentration of NaOH, NaBH₄, stirring and unstirring of reaction media on rate of hydrogen production yield will be illustrated.

EXPERIMENTAL

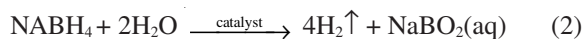
Catalyst preparation: All reagents were of analytic grade and double-distilled water was used throughout the experiments. Ir(0) was prepared by reducing its precursor with NaBH₄ solution. Borohydride reduction of metal ions has been studied extensively and it is well-known that Ir is obtained

upon reduction of iridium salt (IrCl_3). The aqueous reduction process is thought to be as follows²³.



0.299 g (1 mmol) IrCl_3 suspended in 50 mL diethylene glycol (Digol) with vigorous stirring at 80 °C adding 5 mL of water. 0.076 g (2 mmol) NaBH_4 was dissolved in 5 mL of distilled water. Two solutions were mixed and heated to 230 °C rapidly. A strong dark colour was observed immediately after mixing. The system was maintained under magnetic stirring condition at 230 °C for 2 h and subsequently the heating was turned off. A very stable colloidal dispersion was formed with this procedure. In order to isolate the resulting Ir(0) particles, 50 mL of acetone was added to the dispersion. A black solid was formed by precipitation, which was separated by centrifugation, washed several times with acetone and ethanol and dried at room atmosphere.

Generation of hydrogen: The hydrolysis reaction (reaction 1) was conducted in a 50 mL capacity batch reactor with an internal volume of 25 mL. In a typical experiment, 10 mL 0.5-4.0 wt. % NaBH_4 solution containing 0-6 wt. % NaOH was placed in the reactor fitted with an outlet tube (connecting to a mass flow meter) for collecting evolved H_2 gas. The outlet tube exhaust was placed under an inverted, water-filled gas burette which was situated in a water-filled vessel. 50 ± 5 mg Ir(0) catalysts was added into the solution under mild stirring. The reactions were carried at 293 K and the reaction temperature was maintained within ± 1 K of its set point using an external water jacket. The hydrogen generation rate ($\text{mL min}^{-1} \text{g}^{-1}$, based on the weight of Ir catalyst used) was recorded by the mass flow meter and the volume of generated H_2 was measured by the water displacement method²³.



The yield of hydrogen is defined as follows based on reaction. 2.

$$\chi = \frac{n_{\text{generated H}_2}}{4 \times n_{\text{NaBH}_4}} \times 100 \%$$

RESULTS AND DISCUSSION

Field emission scanning electron microscopy (FE-SEM) images obtained with JEOL JSM-7600F device and EDS patterns were determined *via* Xmax large area SSD connected to it.

FE-SEM images are given in Fig. 1. It is seen from micrographs that Ir(0) catalyst contains flaky particles that resulting products agglomerate with varying sizes. It shows heterogeneous morphology. EDX patterns given in Fig. 2 indicate that that pure Ir(0) particles are obtained.

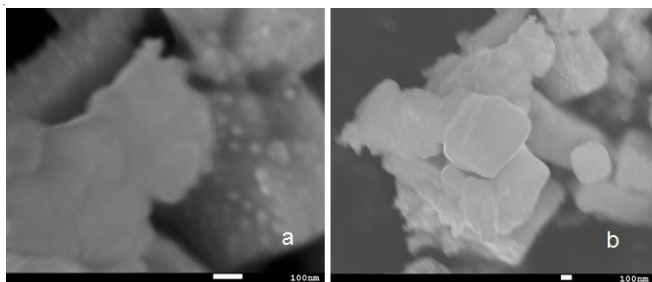


Fig. 1. SEM images of Ir(0) catalyst

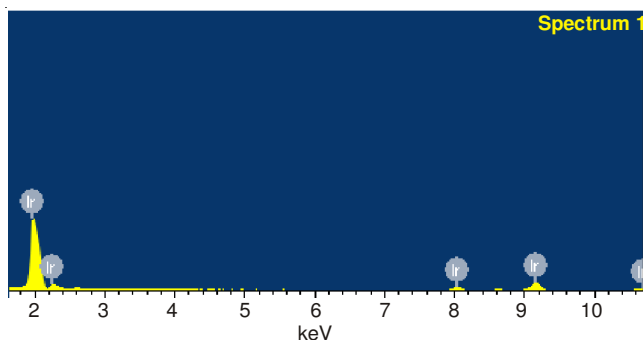


Fig. 2. EDS patterns of Ir(0) catalyst

The hydrogen generation from the hydrolysis of NaBH_4 with Ir(0) catalyst in the presence of NaOH and effects of stirring on hydrogen generation were investigated.

Figs. 3 and 4 show the hydrogen generation volume from NaBH_4 with Ir(0) catalyst produced for both with stirred and unstirred solutions. Fig. 5 shows the effect of NaOH concentration on hydrogen generation from NaBH_4 . It can be seen that hydrogen production from hydrolysis reaction of NaBH_4 with Ir(0) catalyst reduced in the presence of NaOH in 20 min.

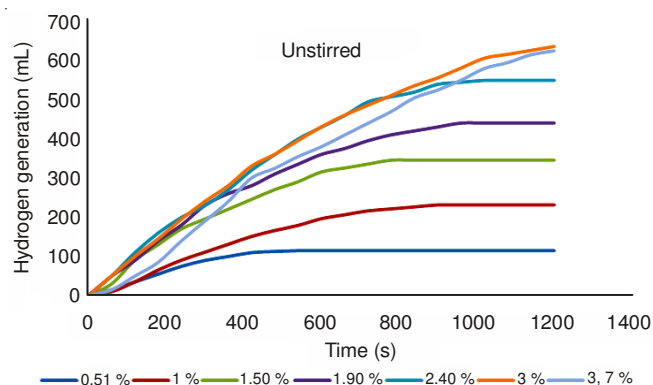


Fig. 3. Effect of unstirring on the hydrogen generation measured using 0.5 to 3.7 % NaBH_4 at 20 °C, using 50 ± 5 mg of Ir(0) catalyst

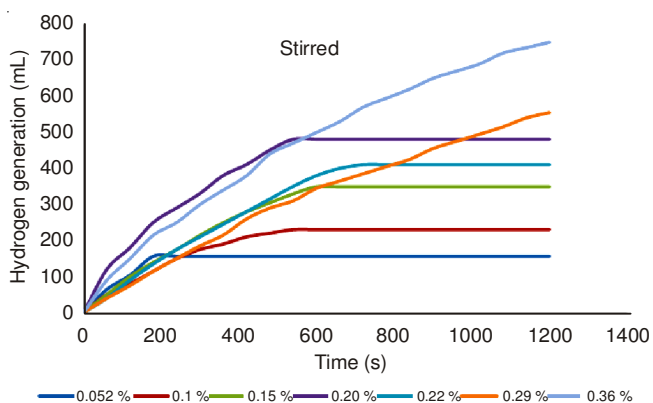


Fig. 4. Effect of stirring on the hydrogen generation measured using 0.5 to 3.6 % NaBH_4 at 20 °C, using 50 ± 5 mg of Ir(0) catalyst

Effect of NaOH concentration: Sodium hydroxide is usually added as a stabilizer into the NaBH_4 solution to prevent its self-hydrolysis. Fig. 5 illustrates the hydrogen generation volumes with different NaOH concentration, *i.e.* 0, 2, 4 and 6 wt. %, in 2,7 wt. % NaBH_4 solution with 50 ± 5 mg of Ir(0) catalyst at 20 °C. As seen in Fig. 5, the hydrogen generation

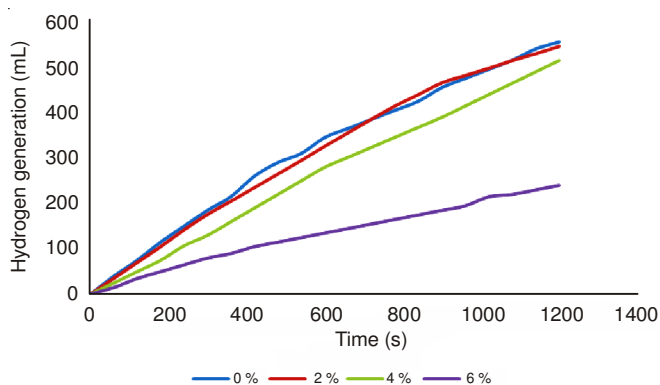


Fig. 5. Effect of NaOH concentration on the hydrogen generation measured using 0 to 6 % NaOH and 0.27 g NaBH₄ at 20 °C, using 50 ± 5 mg of Ir(0) catalyst

rate is decreased with increasing NaOH concentration in NaBH₄ solution with Ir(0) catalyst. Fig. 6 shows yield of hydrogen generation volume *versus* NaOH concentration, in which hydrogen generation yield decreased with increasing NaOH concentration. Depending upon the results, it is decided to perform all hydrogen generation tests with addition of 1 wt. % NaOH to solutions. Therefore, experiments are performed by placing the same amounts of the catalyst (0.050 g), NaOH and NaBH₄ dissolved in to the reactor to initiate the reaction. The effect of NaOH concentration on the NaBH₄ hydrolysis rate is similar to Ru-RuO₂/C catalysis but completely different from Ni(0) catalyzed reaction^{5,15}. As known, the presence of NaOH concentration in NaBH₄ solution is reduced activity of water and viscosity of solution, thus decreasing the available free water to react with NaBH₄.

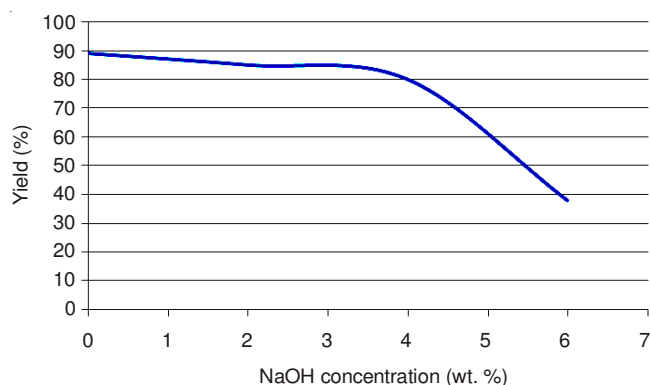


Fig. 6. Effect of NaOH concentration on yield in 20 min reaction at 20 °C

Effect of NaBH₄ concentration: Figs. 3 and 4 shows the influence of NaBH₄ concentration on the hydrogen generation rate for both stirred and unstirred conditions. Amount of 0.050 g of Ir(0) catalyst at 20 °C and 1 % wt NaOH was added to the solution. The hydrogen generation volumes with different NaBH₄ concentration, *i.e.* 0.5, 1.0, 1.5, 2, 2.5, 3 and 3.5 wt. %, in 1 wt. % NaOH solution with 50 ± 5 mg of Ir (0) catalyst at 20 °C are illustrated. It is found that the hydrogen generation rate increases with increasing NaBH₄ after reaching optimal concentration, decreases with increasing concentration of NaBH₄. Optimal concentration of NaBH₄ is found near 2.5 wt. % As reaction 1. proceeds, NaBO₂ eventually exceeds its solubility limit and precipitates out of solution²⁴. Increasing

concentration of NaBO₂ might be the reason for slow hydrogen generation for higher NaBH₄ concentrations. Interestingly, a more concentrated NaBH₄ solution does not necessarily produce hydrogen faster¹⁶. As can be seen from Figs. 3 and 4 upon reaching a critical point, hydrogen generation decreases gradually. Fig. 7 shows the influence of NaBH₄ on yield of hydrogen generation reaction. As seen, while yield is higher at low NaBH₄ concentrations, it decreases gradually after 2.5 wt. %.

Approximately 90-99 % of NaBH₄ conversion efficiency could be achieved concentrations less than optimal concentration, however it decreases down to 67 % at higher concentrations of NaBH₄ investigated in this work. However, the alkalinity and viscosity of the hydrolysis system also increase with the NaBH₄ concentration, which prevents hydrogen generation and leads to a decrease of the hydrogen generation rate. Similar case is also observed by Niu *et al.*²⁵ in optimizing preparation of carbon supported cobalt catalyst for hydrogen generation from NaBH₄.

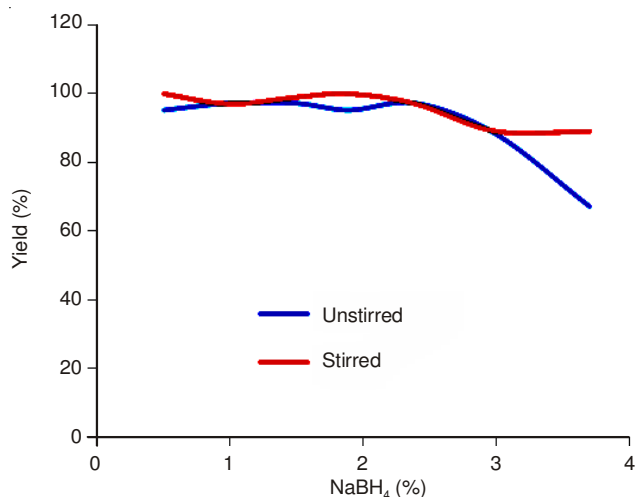


Fig. 7. Effect of stirring and unstirring on yield in 20 min reaction at 20 °C

Effect of stirring: The volumes of the generated hydrogen gas under unstirred and stirred conditions in the presence of Ir(0) catalysts are shown in Figs. 3 and 4 as a comparison. Yields of hydrogen generation both in stirred and unstirred conditions are given in Fig. 7. It is apparent from figures that stirring has a significant effect on the overall reaction rate and yield and thus supports the evidence of an external mass transfer resistance for the catalytic hydrolysis of sodium borohydride. Thus, the observed rate difference between unstirred and stirred conditions could be attributed to the effect of external mass transfer resistance only. Similar values were obtained by Rakap *et al.*²⁶ on study of hydrogen generation from hydrolysis of ammonia-borane using Pd-PVB-TiO₂ and Co-Ni-P/Pd-TiO₂ under stirred conditions.

Conclusion

In summary, Ir(0) catalyst stabilized by polyol method was employed for hydrogen generation tests both in stirred and unstirred conditions for the first time. Influence of NaOH concentration was illustrated. Stirring has positive effect on hydrogen generation and yield. Optimal concentration of NaOH is 1 wt. % and optimal concentration of NaBH₄ concentration was found to be 1 to 2.5 wt. %.

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