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Hydrogen generation from hydrolysis of sodium borohydride with a novel palladium metal complex catalyst

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ABSTRACT

Generally, the complex catalyst is considered homogeneous catalyst, which is coordinated some ligands. In this study, we have treated a solid–state complex catalyst for $NaBH_4$ hydrolysis. We report the synthesis of salicylaldimine ligand and its Pd metal complex. The obtained Pd catalyst is tested for hydrogen generation from the hydrolysis of $NaBH_4$. The effects of temperature, $NaBH_4$ concentration, NaOH concentration and catalyst amount on the catalytic activity toward hydrogen production from hydrolysis of $NaBH_4$ are comparatively investigated. The Pd-containing catalyst is characterized by various techniques, including X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier transform infrared spectroscopy (FTIR).

1. Introduction

As a clean fuel, hydrogen is considered to be one of the candidates for an alternative energy carrier to replace fossil fuels. However, the storage and on-board production of hydrogen restrict the application and development of hydrogen energy. Hydrogen can be stored in tanks of compressed or liquefied hydrogen, carbon nanotubes, metal hydrides and chemical compounds. Among the methods of hydrogen storage, chemical hydrides ($NaBH_4$, KBH_4, $LiBH_4$, etc.) have been studied intensively [1–5] as hydrogen sources for portable PEM fuel cells.

$NaBH_4$ is very stable, non-flammable, non-toxic in nature, and able to store hydrogen with theoretical gravimetric hydrogen generation value of 10.8%. Therefore, there is a growing interest in hydrogen generation using $NaBH_4$. Despite this, the hydrolysis of NaBH4 is severely restricted in alkaline solution due to acts as a stabilizer to prevent the self-hydrolysis of $NaBH_4$ in aqueous solution [6–8].

The efficiency of hydrogen release by using suitable catalysts can be significantly enhanced. Schlesinger et al. [9] show that the hydrogen generation from alkaline $NaBH_4$ could accelerate via the following reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + \text{heat}(217\ \text{kJ/mol}) \quad (1)$$

The rate of hydrogen generation from self-hydrolysis of $NaBH_4$ is not satisfactory at room temperature. Researchers are done to find these suitable catalysts. Different catalysts such as ruthenium (Ru) [10–12], cobalt (Co) supported catalyst [13–17], nickel (Ni) based catalyst [18], Co–Ni catalyst [19], Ni–B catalyst [20], Ni–CoB catalyst [21], copper (Cu)–Co catalyst [22],rhodium (Rh) [23], platinum (Pt) [24],

PtRu [25], Co–B/Pd Pd, Pt–Ru, Pt–Pd alloys [26–28] etc have been extensively studied. However, due to the high price of noble metal catalysts, there is the need to develop alternative catalysts based on cheaper transition metals. In addition, only a few studies on the application of complex catalysts to the hydrogen production have been reported [29–37]. The catalytic activities of the metal-ophthalocyanine derivatives complexes have been investigated in only one study for hydrogen production from hydrolysis of $NaBH_4$ [37].

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The cost and availability of catalyst in the process hydrogen generation from hydrolysis of $NaBH_4$ with various catalysts are predominantly parameters. Unfortunately, there are many engineering problems, such as high cost, low catalyst durability caused by the solubility limitations of sodium by-products, borohydride and sodium metaborate ($NaBO_2$) in an aqueous solution [38]. The abundance of Pd on the Earth's crust is 200 times higher than Pt (0.6 ppb vs. 0.003 ppb), the comparatively low price of Pd (only 30%–40% compared to Pt) makes it attractive for large-scale fuel cell applications [39].

Generally, the complex catalyst is considered homogeneous catalyst which is coordinated some ligands. In this study, we have treated a solid state complex catalyst for NaBH4 hydrolysis. In our present study, metallic Pd complex catalyst is synthesized by 4-4′-methylene bis(2,6-diethyl) aniline-3,5-di-tert-butylsalisilaldimin ligand (MA:742) with the reaction of -4′-methylene bis(2,6-diethyl) aniline. The basic aim of this study is to develop a feasible new catalyst system for hydrogen generation by catalytic hydrolysis of $NaBH_4$. The method is an alternative approach for the hydrogen production with metal catalysts. The effects of complex catalyst, $NaBH_4$ concentration, NaOH concentration, catalyst amount and temperature on the rate of hydrolysis were investigated. The prepared complex catalyst is characterized using SEM, FT-IR and XRD.

2. Materials and methods

All chemicals were of analytical reagent grade and purchased from Sigma or Merck. A FT-IR spectrum was recorded as KBr pellets on a Perkin–Elmer FT-IR spectrometer in the range 4000–450 cm^{-1}. Catalyst structure was characterized over the two-theta range from 20 ɵ to 70 ɵ by X-ray diffraction (XRD, STOE IPDSII) using Mo K α radiation ($\lambda = 0.154184$ nm) from a suitable single crystal mounted on a glass fiber. Catalyst morphology was examined by SEM (JSM-7401F, JEOL, Japan).

2.1. Synthesis of the salicylaldimine ligand

4-4′-methylene bis (2, 6-diethyl) aniline-3,5-di-tert-butylsalisilaldimin ligand was synthesized by the reaction of 2.0 mmol 4-4′-methylene bis(2,6-diethyl) aniline in 30 mL absolute ethanol with 1.0 mmol 3,5-di-tert-butylsalisilaldimin, according to the similar method reported in the literatures [37,40,41]. Fig. 1 shows the 4-4′-methylene bis (2, 6-diethyl) aniline-3,5-di-tert-butylsalisilaldimin ligand. In addition, 3–4 drops of formic acid were added as a catalyst. The mixtures were refluxed for 5–6 h, followed by cooling to room temperature. The resulting crystals were filtered under vacuum. Then, the products were recrystallized from absolute methanol [37].

2.2. Synthesis of the complex

A Solution of Pd (II) acetate in absolute ethanol was added to a solution of 4-4′-methylene bis (2, 6-diethyl) aniline-3, 5-di-tert-butylsalisilaldimin ligand with equal molar amounts, according to the similar method reported in the literatures [37,40,41]. The stirred mixture was refluxed for 60 min. The volume was reduced to 15–20 mL and left to cool to room temperature. The compound was precipitated, filtered and washed with a small amount of methanol. The product was recrystallized in methanol and chloroform. Fig. 2 shows the Pd complex.

2.3. Hydrogen generation

The hydrogen generation experiment was performed in a 200 mL three-neck flask immersed in a water bath, which was described in details along with its experimental setup in our previous work [42]. The catalytic activity of the Pd complex catalyst was determined by recording the volume of hydrogen that was generated by the hydrolysis of 10 mL $NaBH_4$ including 5 wt% $NaBH_4$. A freshly prepared aqueous solution of $NaBH_4$ was placed into the reactor. The known amount of catalyst was then added, and the volume of produced hydrogen gas was measured with a gas burette. The temperature of the water bath was maintained constant. A measured volume of released gas was subsequently converted into yield of produced hydrogen after the total amount of gas had been collected.

3. Results and discussion

3.1. Crystalline structures of complex catalysts

Fig. 3a and b compare the XRD patterns taken before and after of $NaBH_4$ hydrolysis. The three peaks at around 10°, 35°, and 62° are ascribed to the typical planes of Pd. This finding further demonstrates that Pd is mainly deposited on the surface of the complex. It is also observed that the three diffraction peaks of Pd at around 10°, 35°, and 62° disappeared after $NaBH_4$ hydrolysis. However, the peaks for Pd

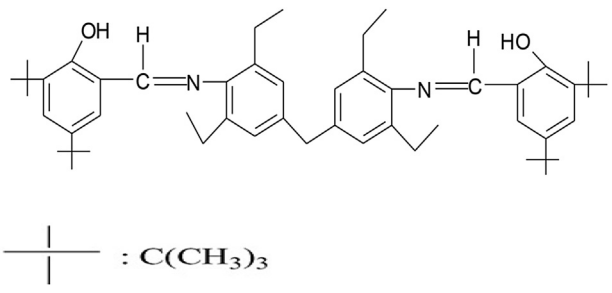

Fig. 1. Structures of 4-4′-Methylene bis (2,6-diethyl)aniline- 3,5-di-tert-butilsalisilaldimin ligand (MA:742).