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Salicylaldimine-Ni complex supported on Al_2O_3: Highly efficient catalyst for hydrogen production from hydrolysis of sodium borohydride

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ABSTRACT

In this study, the Ni-based complex catalyst containing nickel of 1% supported on Al_2O_3 is used as for the hydrogen production from $NaBH_4$ hydrolysis. The maximum hydrogen production rate from hydrolysis of $NaBH_4$ with Ni-based complex catalyst supported on Al_2O_3 containing nickel of 1% is 62535 ml min^{-1} g^{-1} (complex catalyst containing 1 wt% Ni). The resulting complex catalyst is characterised by XRD, XPS, SEM, FT-IR, UV, and BET surface area analyses. The Arrhenius activation energy is found to be 27.29 kJ mol^{-1} for the nickel-based complex catalyst supported on Al_2O_3. The reusability of the catalyst used in this study has also been investigated. The Ni-based complex catalyst supported on Al_2O_3 containing nickel of 1% is maintained the activity of 100% after the fifth use, compared to the first catalytic use. The *n* value for the reaction rate order of $NaBH_4$ is found to be about 0.33.

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Introduction

As an energy carrier, hydrogen has a high potential energy as well as its environmental properties [1,2]. Various methods for hydrogen storage have been investigated. One of these methods is the hydrolysis reactions of metal hydrides such as LiH [3], MgH_2 [4,5], CaH_2 [6], $NaBH_4$ [7–10] and $LiBH_4$ [11]. Among these chemicals, $NaBH_4$ has been extensively studied for the hydrogen production.

$NaBH_4$ has a theoretical gravimetric hydrogen storage capacity of 10.8%. In addition to these properties, $NaBH_4$ has very good hydrolysis controllability and good hydrogen purity [12–14]. For the first time in 1953, hydrogen production was generated from hydrolysis of $NaBH_4$ solution [7]. Hydrogen production from catalytic hydrolysis of sodium borohydride can be produced by the following Eq. (1).

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + heat\uparrow \quad (1)$$

The hydrolysis of $NaBH_4$ as an industrial and environmentally is important boron compound. Hence, there are many reports on the use of metal catalysts for the hydrogen production from hydrolysis of $NaBH_4$ solution, such as electrodeposited Co-Ni-P [15], Ni-B [16,17], raney Ni [18], Ni-Co-B [19], Co-Ni-B powder [20], electrolessly plated Ni-Ru [21], salicylaldimine-Ni complex catalyst [22], Ni/Ag/silica

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nanocomposite [23], Ni-B–silica [24], Ru NPs [25], Ru [17], Pt-C [26], Co-B [27], Co-B NPs supported on Al_2O_3 [28], Ni-Co-P supported on Al_2O_3 [29] etc …

The schiff bases have an important place in coordination chemistry because they can be easily synthesized and easily modified both electronically and sterically. Schiff bases produced from salicyl aldehydes are known as polydentate ligands coordinating in the neutral form. The multidenticity of such ligands plays an important role in permitting the formation of transition metal complexes, the stability of these complexes and the alteration of the steric and electronic properties affecting the reactivity of metal ions [30–32]. Salicyl aldimines are o-hydroxy derivatives of schiff bases. Salicyl aldimines have a special interest in coordination chemistry due to the asymmetric intermolecular hydrogen bond formed by oxygen and nitrogen atoms. They are widely used in different application areas such as antibacterial, antiviral, antifungal, homogeneous and heterogeneous catalysts [33].

However, the studies on the production of effective catalysts based on the interaction between metals and ligands in such large-scale application areas, which are based on such bases, continue [34,35]. The costs of catalysts used in hydrolysis reactions affect their effective use in application areas. Catalysts such as Ru, Pt used to obtain hydrogen from hydrolysis of $NaBH_4$ show significant catalytic activity whereas the costs of such catalysts significantly affect their use. Metals such as Co and Ni are widely used as catalysts in order to increase both the activity and the cost of the catalysts used in such hydrolysis reactions.

In recent years, there has been considerable research in the use of Al_2O_3 as a carrier for immobilizing the metal catalyst [28,36]. Interactions between support material and metal nanoparticles greatly influence the activity of heterogeneous catalysts. Support materials such as carbon [37,38], zeolite [39], metal oxides [37] and Al_2O_3 [28,36] have been proposed for the hydrolysis of $NaBH_4$. Al_2O_3 possesses unique surface properties such as bifunctional Brønsted and Lewis acid and base sites [40,41]. Al_2O_3 is responsible for the deactivation of Ni/Al_2O_3 catalysts due to nickel sintering and carbon deposits, although Al_2O_3 is a suitable support material for Ni catalysts due to their chemical and physical stability and mechanical properties. Therefore, many researchers have tried to improve the properties of Ni/Al_2O_3 using different preparation methods [42,43]. Catalyst modification can be used to block active species on the metal surface or to alter the electronic properties or geometric structure of the catalyst surface [44]. In our previous studies, we have investigated the formation of hydrogen from $NaBH_4$ hydrolysis with complex catalysts resulting from the interaction of ligands with metals [8,9,44,45]. We have recently reported a Ni–salicylaldimine complex for the hydrogen production from $NaBH_4$ hydrolysis [22]. Notably, Ni–salicylaldimine complex exhibited remarkable catalytical efficiency. Herein, we continue our investigations on the catalytical reaction and structural characterization of Ni–salicylaldimine complex supported on Al_2O_3 to produce hydrogen from hydrolysis of $NaBH_4$. The resulting complex catalyst was characterised by XRD, XPS, SEM, FT-IR, UV and BET surface area analyses.

Materials and methods

Synthesis of catalyst

All the chemicals in the experiment were analytical grade and used without further treatments. Nickel (II) chloride hexahydrate and salicylaldehyde were obtained from Merck and were used without further purification. Ethanol (99.5%, Sigma-Aldrich) was used in washing processes. $NaBH_4$ (98%, Merck) was used for preparation of hydrolysis reactions as strong reducing agent, and as H_2 source. Sodium hydroxide (NaOH) (97%, Sigma-Aldrich) was used in H_2 generation reactions from hydrolysis of $NaBH_4$. Methanol ($\geq$%99.5) was supplied from Merck. Chloroform (99% v/v) and formic acid ($\geq$95% v/v) were purchased from Sigma-Aldrich. Salicylaldehyde was provided by Tianjin Guangfu Fine Chemical Industry Research Institute. Alumina (Al_2O_3) was purchased from Sigma–Aldrich.

The ligand was obtained by adding a few drops of formic acid catalyst to 1 mmol of 3, 5-ditertbutylsalisylaldimine in 30 ml of ethanol, followed by refluxing at 100° C for 5–6 h at 100 °C. The yellow-orange coloured ligand was observed. The ligand was then washed with methanol and chloroform, recrystallized and dried. The complex synthesis of the Ni metal with the 5-amino-2, 4-dichlorophenol-3, 5-ditertbutylsalisylaldimine was performed in ethanol, taking the metal to ligand ratio of 1:2. The resulting complex, recrystallized by washing with methanol and chloroform, then the product was dried. The 5-amino-2,4-dichlorophenol-3,5-ditertbutylsalisylaldimine Ni complex obtained in our previous work was dissolved in 20 ml of ethyl alcohol in 0.5, 1, 5, 10, 15 and 20 wt% Ni. 0.1 g of Al_2O_3 was slowly added to this solution and stirred at room temperature for 3 h. Subsequently, this solvent was heated to 5 ml solution. The solid obtained by filtration was dried. The synthesis reaction of the ligand and the nickel metal is given in Fig. 1.

Hydrogen production measurement

The amount of hydrogen production was performed with a two-necked round bottom flask and a thermometer inserted

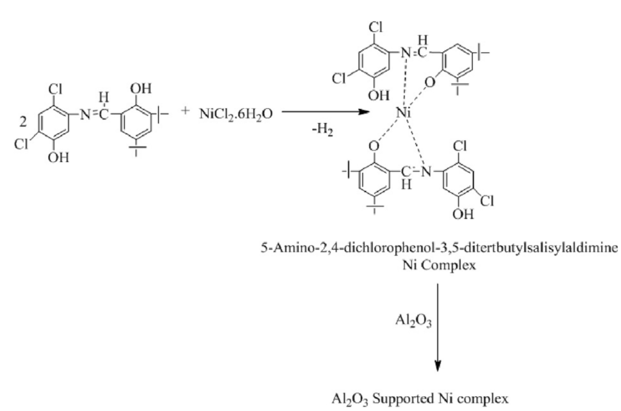

Fig. 1 – The synthesis reaction of the salicylaldimine-Ni complex supported on Al_2O_3.

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