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Recent progress of $NaBH_4$ for hydrogen production

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Abstract. Hydrogen energy is gaining more and more attention because of its high calorific value and environmental friendliness. Hydrogen production technology, which determines the cost of hydrogen, become a focus of attention in the 21st century. Among many hydrogen production technologies, hydrogen production by hydrolysis of $NaBH_4$ is one of the best sources of hydrogen as it can produce high purity hydrogen in a convenient, practical and safe way. This paper focuses on the catalysts used in $NaBH_4$ hydrolysis for hydrogen production, as well as new methods for the regeneration of $NaBH_4$ from hydrolysates. The latest development and achievements of $NaBH_4$ for hydrogen production was presented and future perspectives were discussed.

1.Introduction

As the world's oil reserves continue to dwindle and the ecological environment of earth deteriorates, energy and environmental issues are becoming important factors limiting the development of all countries [1]. Hydrogen energy with the advantages of high energy, abundant reserves and no pollution is an ideal energy. However, the application of hydrogen energy is limited by the technology used to produce hydrogen. Commonly used hydrogen production technologies include electrolysis of water [2], thermochemical hydrogen production [3], hydrolysis of metal hydrides [4], etc. Among them, hydrogen hydrolysis of metal hydrides has the advantages of easy handling, high hydrogen storage density and flexible applications [5]. The hydrolysis of $NaBH_4$ has the following advantages: the reaction rate can be controlled, the purity of the prepared hydrogen is high, and non-polluting by-product $NaBO_2$ can be recycled, etc [6].Nevertheless, the slow rate of $NaBH_4$ hydrolysis reaction limits its application for hydrogen production. In order to increase the rate of hydrolysis, measures such as using catalysts, adding acid and increasing the temperature have been studied. Compared with the various methods, the addition of catalysts is an easy to implement and most effective method.

This paper provides a detailed summary of the metallic and metal-free catalysts used for hydrogen production from $NaBH_4$ hydrolysis as well as regeneration process, and provides an outlook on the development of $NaBH_4$ hydrolysis technology.

2.Catalysts

2.1Metal catalysts

Metal catalysts are widely used because of their high catalytic activity and good stability. Metal catalyst materials are generally selected from noble metals, magnetic metals, and high entropy alloys.

Noble metals-based catalysts are widely used in the hydrogen production from $NaBH_4$ due to their superior performance to conventional metals. Common noble metals include, Ru, Pt, Pd, etc. Ruthenium-based catalysts are generally loaded in different materials such as graphite carriers (Ru/G) [7], carbon (Ru/C) [8], nanobox-structured CoP [9]. Zhang jiapeng et al. [10] prepared Ruthenium nanocatalysts containing 0.07 wt% Ru on chitinous nanofibers. The catalyst promoted hydrogen production from $NaBH_4$ hydrolysis was up to 55.29 L min^{-1} g_{Ru}^{-1} at 30 ºC with a reaction activation energy of 39.16 $kJ \cdot mol^{-1}$.

Although noble metals play an important role in hydrogen production from hydrolysis of $NaBH_4$, their high cost makes the experiments less economical. In this context, some magnetic metallic materials such as Fe, Co, Ni and other metals have attracted the attention of researchers. These metals are abundant and easily available. They can be applied as cheap catalysts for the hydrolysis of $NaBH_4$, replacing precious metals such as Ru and Pt or reducing the amount of precious metals.

Recently great progress has been made in the study of multifaceted nickel-based catalysts. Lai et al. [11] investigated in the literature the development of core@shell nanocomposites ($NaBH_4$@Ni) by loading metallic nickel catalysts to promote hydrolysis directly onto $NaBH_4$ nanoparticles, and optimized the effective weight hydrogen storage of $NaBH_4$@Ni nanoparticles by adjusting the amount of water required for hydrolysis, obtaining an effective hydrogen storage of 4.4 wt%. Experimental data show that the catalyst produces hydrogen from $NaBH_4$ hydrolysis at 60 ºC in the presence of excess water at a rate of up to 22.5 L min^{-1} g^{-1}. Composites of metallic Ni with other materials such as Ni-

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Al [12], Ni-La-B[13], Ni-Cu-B [14], Ni/Al_2O_3 [15], Ni_2P-CoP [16] have also shown good properties. For example, Yu-Jin Lee et al. [12] synthesized a new Ni-Al alloy catalyst by aluminizing nickel foam, post-annealing, and selective aluminum leaching. This nickel-based catalyst promoted hydrogen production from $NaBH_4$ hydrolysis at rates up to 400±27 $sccm \cdot g^{-1}_{catalyst}$ and had superior persistence.

Cobalt-based catalysts can be classified loaded and unloaded based on the presence or absence of a carrier. The presence of loading increases the surface area of the catalyst, meanwhile the catalyst is easier to separate from solution and can be easily reused. Zhang et al [17] synthesized an efficient catalyst consisting of ultrafine bimetallic Pt and Co. The catalyst exhibited excellent performance in kinetic and thermodynamic tests. The experimental results showed that the rate of hydrogen production increased significantly with the increase of temperature. The time of complete hydrolysis of $NaBH_4$ was shortened from 3.5 min at 25 ºC to 0.8 min at 45 ºC. The hydrogen production rate (HGR) was as high as 8943 $mL\ min^{-1}\ g^{-1}$, the initial conversion rate (TOF) value was 280.1 $mol \cdot min^{-1} \cdot mol_{Pt}^{-1}$, and the activation energy (Ea) was reduced to 38.0 $kJ \cdot mol^{-1}$. The catalyst maintained a very high catalytic activity with 100% hydrogen conversion even after 5 hydrolysis of $NaBH_4$.

Iron-based catalysts have attracted the attention of researchers because of ease of recycling. Recently, Zhao et al. [18] investigated a method for hydrogen production from $NaBH_4$ hydrolysis using industrial wastewater as a raw material and Fe-Al-Si composite as a catalyst. Mechanism of Fe-Al-Si catalysis as follows figure 1. This method not only has a high rate of hydrogen production but also can remove elemental Cr from industrial wastewater. At 30 ºC, the hydrogen generation rate increased significantly from 32.04% to 80.70%. The total chromium removal rate also showed a significant increase from 46.72% to 98.96%.

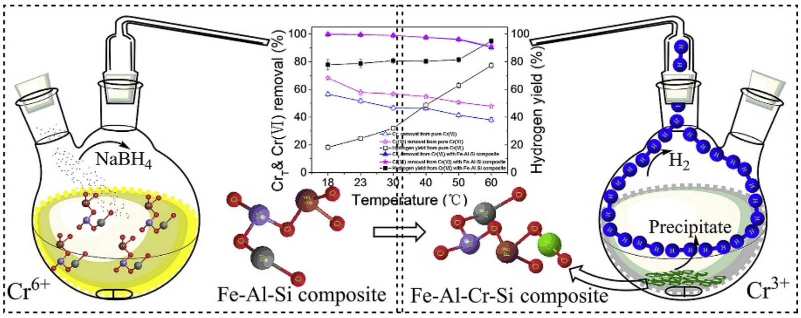

Figure 1 Mechanism of catalysis [18].

High entropy alloys have been of great interest to researchers because of their tunable electronic structure, optimizable d-band center, and outstanding structural stability [19]. Juan Mu et al. [20] designed a high entropy alloy $Fe_{10}Co_{10}Ni_{10}Cr_{10}Mn_{60}$ ribbon catalyst with a face-centered cubic structure by using Co, Ni as the main catalytic elements and Fe, Mn, Cr as auxiliary catalytic elements. The XRD and SEM images of this catalyst after synthesis are shown in figure 2. The catalyst underwent a large amount of element-selective corrosion during the corrosion by the acid solution, exposed a large number of Co and Ni atoms and increased the specific surface area, which in turn formed a large number of vacancies and dislocations, resulting in a positron effect, leading to electron enrichment of Co and Ni and favoring the catalytic $NaBH_4$ hydrolysis. rate close to 18.46 $L \cdot (m^2 \cdot min)^{-1}$. XRD and SEM images of this catalyst after acid etching are presented in figure 2.

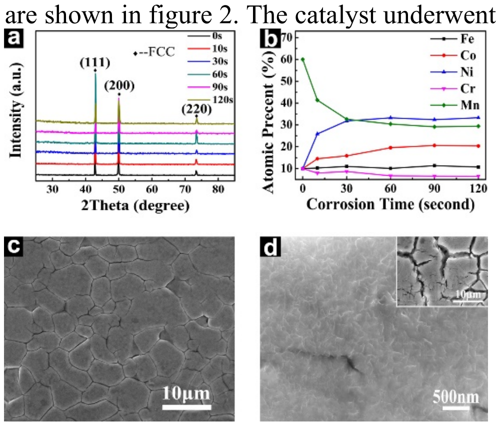

Figure 2 (a) $Fe_{10}Co_{10}Ni_{10}Cr_{10}Mn_{60}$ ribbons in as-cast and corroded XRD patterns. (b) The ingredients of the corroded ribbon. SEM images of (c) the ribbon as-cast and (d) the ribbon after corrosion for 120 seconds [20].

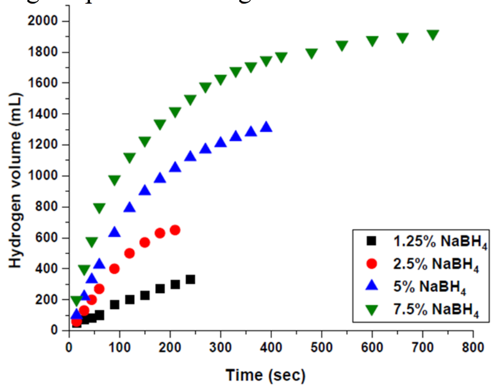

Figure 3 H_2 production from methanolysis of NaBH4 at 30 ºC with 10 mg S-KOH-S-P catalyst at 1%, 2.5% and 5% NaBH4 concentrations, respectively [21].

2.2Metal-free catalysts

Metal catalysts have played an important role in tuning the hydrolysis of $NaBH_4$ in numerous studies. However, they lack environmental friendliness and are relatively costly. Therefore, metal-free catalysts have been explored as an alternative to metal-based catalysts mainly including treated microalgae, polymeric catalysts.

2.2.1Microalgae. Microalgae are characterized by fast growth, high conversion rate, good adaptability and good carbon sequestration. Cafer Saka [21] prepared Sulfur (S) and phosphorus (P) doped metal-free carbon catalysts (S-KOH-S-P, S-KOH-S) based on KOH activated microalgae. The H_2 production from the methanolysis of $NaBH_4$ promoted with 10 mg of this catalyst at 30 ºC and $NaBH_4$ concentrations of 1%, 2.5%, 5% and 7.5% is shown in figure 3. The maximum hydrogen generation rate (HGR) was calculated to be 18571 $ml\cdot min^{-1}\cdot g^{-1}$. The activation energy (Ea) value for S-KOH-S-P was calculated to be 12.54 $kJ\cdot mol^{-1}$.

2.2.2 Polymer catalysts. The polymer catalysts showed good performance in catalytic hydrogen production, but the catalytic activity of the metal-free polymer catalysts for methanol cracking of $NaBH_4$ decreased after a few cycles [22]. Cafer Saka et al [23] prepared the first metal-free catalysts from apricot shells by a two-step activation. The mechanism of this catalyst is as shown in figure 4. The HGR and Ea of this catalyst (10 mg) were 14,444 $ml\cdot min^{-1}\cdot g^{-1}$ and 7.86 $kJ\cdot mol^{-1}$, respectively. In addition, the metal-free catalyst has the advantage of being reusable.

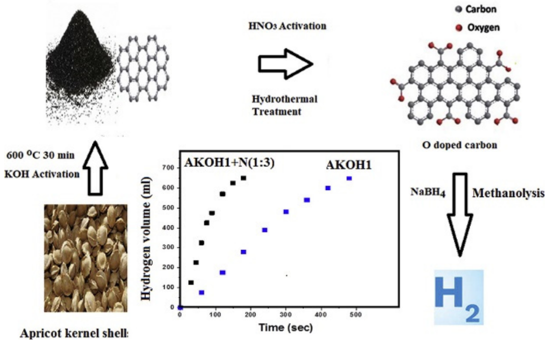

Figure 4 Mechanism of catalysis [23].

3.Regeneration

The preparation of $NaBH_4$ requires a large amount of valuable sodium metal, which is costly and also limits the application of this product. Chen et al [24] investigated that 90% of $NaBH_4$ could be obtained by grinding the hydrolysis by-product $NaBO_2\cdot H_2O$ with MgH_2.

Ouyang et al.[25, 26] have developed a convenient method for regenerating $NaBH_4$/$LiBH_4$ from hydrolysis products, where the hydrolysis product $NaBO_2$ reacted with carbon dioxide in aqueous solution to form $Na_2B_4O_7\cdot 10H_2O$ and Na_2CO_3, both of which were ball-milled with magnesium under ambient conditions to form $NaBH_4$ in yields of up to nearly 80%. The cost of this new method is significantly lower than previous studies because it does not require high-pressure H_2 gas, expensive reducing agents (e.g., MgH_2) and reduced energy consumption for water removal from $Na_2B_4O_7\cdot 10H_2O$. The hydrogen precipitation properties of regenerated $NaBH_4$ are important for the practical application of this method. The experimental data showed that the regenerated $NaBH_4$ hydrolysis at a rapid rate, producing 2317 $ml\cdot g^{-1}$ H_2 in 1.8 min.

4.Conclusions

This paper summarizes the optimization method of $NaBH_4$ hydrolysis to hydrogen production technology, on the one hand summarizing the development status of the catalysts used in $NaBH_4$ hydrolysis technology, and on the other hand detailing the significance of $NaBH_4$ regeneration technology and the cutting-edge achievements. Catalysts are mainly divided into metallic catalysts and non-metallic catalysts. The hydrolysis and regeneration of $NaBH_4$ has closed the loop of $NaBH_4$ hydrolysis and regeneration, which has a significant role in the application of $NaBH_4$ in practice. Future $NaBH_4$ hydrolysis technology should focus on the following areas.

(1) Although the addition of catalysts to the $NaBH_4$ hydrolysis process can effectively improve the hydrolysis performance of $NaBH_4$, a significant gap still exists before it can be put into large-scale practical application. Therefore, we should invest more time and effort to seek catalysts with better catalytic effect for practical applications.

(2) The regeneration technology of $NaBH_4$ has been fully developed, but still faces problems such as high cost and low yield. The pursuit of a regeneration technology with low cost, high yield and safe and simple operation should be the goal of future research.

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