**Rare Metal Materials and Engineering**
Volume 47, Issue 3, March 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

ScienceDirect

**Cite this article as:** Rare Metal Materials and Engineering, 2018, 47(3): 0754-0758.

ARTICLE

# Effect of Catalysts on Hydrolysis Hydrogen Release of Sodium Borohydride

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**Abstract:** The hydrolysis process of $NaBH_4$ using mixed catalyst $Co_2B/Pr_6O_{11}$ was studied by a drainage method. The results show that the effects of the ratios of $Co_2B$ to $Pr_6O_{11}$ and the amount of mixed catalyst $Co_2B/Pr_6O_{11}$ on the amount of hydrogen release of $NaBH_4$ are very obvious. When the doping amount is varied between 1% and 6%, the hydrogen release rate of doped samples increases firstly and then decreases as the doping amount increases. Conversely, the effect of the amount and the ratio of mixed catalyst $Co_2B/Pr_6O_{11}$ on the hydrogen desorption amount of $NaBH_4$ is not obvious. However, after $NaBH_4$ is catalyzed by the mixed catalyst $Co_2B/Pr_6O_{11}$, the hydrogen desorption amount of the sample is obviously changed and the hydrogen desorption amounts of most samples are between 410 and 525 mL. In all samples, the one doped with 4% (70%$Co_2B$/30%$Pr_6O_{11}$) has the maximum hydrogen release rate of 540 mL/min and the maximum hydrogen desorption amount of 540 mL (12.1 wt%).

**Key words:** $NaBH_4$; mixed catalyst; amount of hydrogen desorption; hydrogen release rate

Nowadays, the demand for energy is growing, but the extensive use of traditional fossil fuels has led to energy shortages and environmental pollution. In order to meet the requirements of the international community and to achieve sustainable development of the national economy, finding the new environmentally friendly energy to replace the traditional fossil fuels has become a strategic issue [1]. Hydrogen is a clean secondary energy carrier, and it has many advantages, for example: efficient, non-pollution, renewable, high conversion rate and wide variety of sources, so hydrogen is one of the most promising clean energy to solve the demanding problem for the future. In the practical application of hydrogen energy, the preparation technology of hydrogen energy has become one of the key issues that need to be resolved. Among all the preparative techniques of hydrogen, because of its convenience, utility, and high efficiency, hydrolysis of $NaBH_4$ became one of the best method to produce hydrogen energy for the proton exchange membrane fuel cell (PEMFC).

$NaBH_4$ is a commonly used reducing agent in chemical industry, which was first compounded by Schlesinger and Brown[2]. In the 1950s and 1960s, Schlesinger and Brown realized that $NaBH_4$ has a potential use, so they researched a lot about hydrogen generation by hydrolysis reaction of $NaBH_4$[3]. The study from Schlesinger and Brown found that, $NaBH_4$ has a hydrolysis reaction in water but it is very stable in aqueous alkali. Under the effect of an appropriate catalyst, $NaBH_4$ solution has hydrolysis reaction and releases hydrogen, and the hydrolysis reaction is shown as follows:

$$NaBH_4 + 2H_2O \xrightarrow{cat} 4H_2 + NaBO_2 \quad (1)$$

Experiments show that when the ratio is (25%~30%) $NaBH_4$ + (75% ~ 80%) $H_2O$, then the hydrogen storage capacity of $NaBH_4$ can reach to 5.3 wt%~6.35 wt%.

In order to improve the dehydriding performance of $NaBH_4$, a large number of studies focused on how to find a better catalyst. For example, Japanese Kojima [4] team from Toyota R & D Center studied the effect of transition metal on the

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Received date: March 14, 2017
Foundation item: National Natural Science Foundation of China (50806007); Shanxi National Science Foundation (2014JM7262); Chang'an University School Fund (310831163501)

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catalytic activity of the preparation of hydrogen from $NaBH_4$, using a supercritical method to produce the transition metal (Pt, Rh, Ru, Pd, Ni, Fe) catalyst, which is loaded by $TiO_2$. The result shows that in the transition metal catalysts, the highest hydrogen production rate belongs to Pt-$TiO_2$ catalyst. Based on the one-component metal catalysts, Krishnan and others [5] further investigated PtRu bimetallic catalyst. Compared with single-component Pt or Ru catalyst, when using the 5 wt% and 10 wt% $NaBH_4$ solutions as raw materials, the activity has been nearly doubled. In addition, Schlesinger and others [3] first studied $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ catalysts and found that $CoCl_2$ has the best catalytic performance. In addition to the precious metal catalysts [6,7], the transition metal salt solution catalysts [8,9], have also been rapidly developed recently, such as Ni-B and Co-B[10-12] catalysts. In these catalysts, Co-B has been favored by researchers for its excellent catalytic performance. In this background, the present paper researched the mixed catalyst $Co_2B/Pr_6O_{11}$ and mainly analyzed the effect of different proportions and the amount of the mixed catalyst on the performance of hydrolysis hydrogen desorption of $NaBH_4$ at room temperature.

## 1 Experiment

### 1.1 Catalyst preparation

Preparation of the catalyst consisted of two steps, the first step was the preparation of $Co_2B$, and the second step the preparation of $Co_2B/Pr_6O_{11}$.

In the preparation of $Co_2B$, firstly, 2 g sodium borohydride ($NaBH_4$) and 7 mL aqueous alkali were added in the three-caliber flask, and then 0.2 g cobalt chloride ($CoCl_2$) fully was dissolved in the water. At the end, the $CoCl_2$ solution was added into the $NaBH_4$ solution. The reaction in the three-caliber flask is as follows:

$$CoCl_2 + 2NaBH_4 + 3H_2O \rightarrow 6.25H_2 + 0.5Co_2B + 2NaCl + 1.5HBO_2 \qquad (2)$$

When the reaction completely finished, the mixture was taken out from the flask; then the mixture was filtered and dried; finally the $Co_2B$ was obtained. Then a right amount of $Co_2B$ and $Pr_6O_{11}$ sample was weighed and put into a sample bottle, which had mill balls in it. The sample bottle was shaked by hands. The ratio of the mixture to the mill ball was 1:40, and the mass percentage of $Co_2B$ and $Pr_6O_{11}$ were 40%:60%, 50%:50%, 60%:40%, 70%:30% and 80%:20%.

### 1.2 Preparation of an alkaline solution of $NaBH_4$

At first, 0.2 g NaOH was added in a small beaker containing 4 mL water, and then 0.4 g $NaBH_4$ was added in the alkaline solution to prepare an alkaline solution of $NaBH_4$.

### 1.3 Hydrolysis hydrogen desorption of sodium borohydride ($NaBH_4$)

The weighed mixed catalyst $Co_2B/Pr_6O_{11}$ was firstly added in the three-caliber flask, and then injected into 2 mL alkaline solution (in process 2). The three-caliber flask was covered rapidly by the cork, and put in a 30 °C thermostat water bath. The amount of discharged hydrogen was measured, and the time of hydrogen desorption was obtained by the drainage method. Then the curve of hydrogen desorption capacity and hydrogen desorption time was drawn. Different ratios of the amount of mixed catalyst $Co_2B/Pr_6O_{11}$ on the influence of the hydrogen desorption capacity of sodium borohydride were analyzed.

## 2 Results and Discussion

In this work, the phases of the catalysts $Co_2B$ and $Pr_6O_{11}$ were analyzed by XRD (Fig. 1 and Fig. 2). The result from Fig. 1 is similar to that reported by A. Corrias [13]. According to Fig. 2, it is easy to find that there are not other phases except for $Pr_6O_{11}$.

Fig. 3 shows relations between hydrogen desorption amount and time of $NaBH_4$ doped with different amount of 40%$Co_2B$/60%$Pr_6O_{11}$. As seen in Fig. 3, hydrogen desorption amount of sodium borohydride and time has a linear relation. As the amount of mixed catalyst 40%$Co_2B$/60%$Pr_6O_{11}$ increases, the hydrogen release rate of $NaBH_4$ becomes significantly faster.

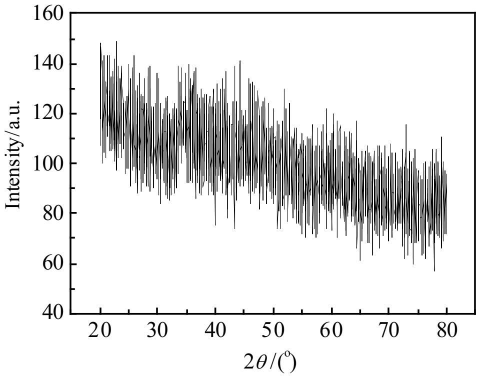

Fig. 1 XRD pattern of catalyst $Co_2B$

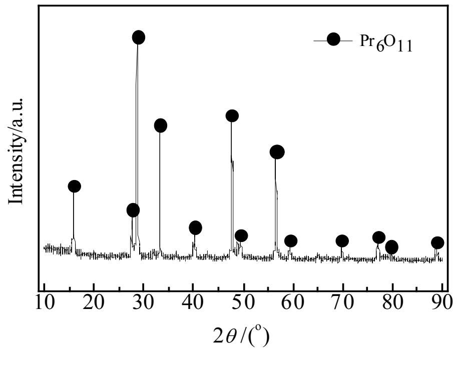

Fig. 2 XRD pattern of catalyst $Pr_6O_{11}$

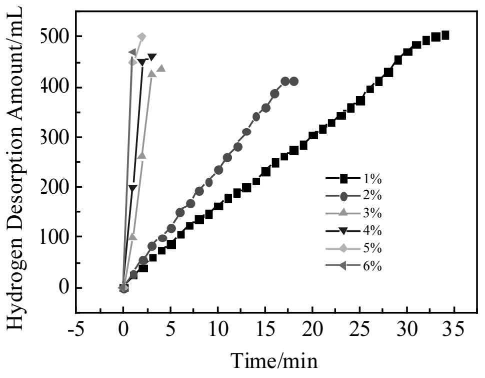

Fig.3 Relations between hydrogen desorption amount and time of $NaBH_4$ doped with different amount of $40\%Co_2B/60\%Pr_6O_{11}$

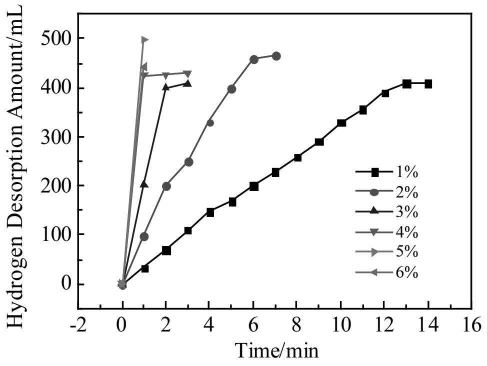

Fig.4 Relations between hydrogen desorption amount and time for $NaBH_4$ doped with different amount of $50\%Co_2B/50\%Pr_6O_{11}$

When the amount of $40\%Co_2B/60\%Pr_6O_{11}$ reaches to 5% and 6%, the hydrogen release rate of $NaBH_4$ is maximum and the two doped samples have the same hydrogen release rate; the whole desorption process requires only 1 min. Among all the doped samples, the sample doped with 1% and 5% mixed catalyst $40\%Co_2B/60\%Pr_6O_{11}$ has the largest desorption amount, 505 mL (11.3 wt%). In contrast, the hydrogen desorption amount of other samples are much lower than them.

Fig.4 shows the relationship between the hydrogen desorption amount and time of $NaBH_4$ doped with 1%~6% mixed catalyst $50\%Co_2B/50\%Pr_6O_{11}$. In all the doped samples, the sample doped with 5% mixed catalyst $50\%Co_2B/50\%Pr_6O_{11}$ has the maximum hydrogen desorption amount, 500 mL (11.2 wt%). The sample doped with 3% mixed catalyst $50\%Co_2B/50\%Pr_6O_{11}$ has the minimum hydrogen desorption amount, only 410 mL (9.2 wt%). Comparing the hydrogen release rate of all the samples, it is easy to find that all the hydrogen release rate of the doped samples and the sample doped with mixed catalyst $40\%Co_2B/60\%Pr_6O_{11}$ have the similar regular pattern, i.e, with the increase of the doping amount, all the hydrogen release rate of the samples presents an obvious increasing trend, and the samples doped with 5% and 6% catalyst have the maximum hydrogen release rate. The entire desorption process only takes a very short time, less than 1 min. The sample doped with 1% catalyst has the minimum hydrogen release rate, and the desorption time reaches 14 min.

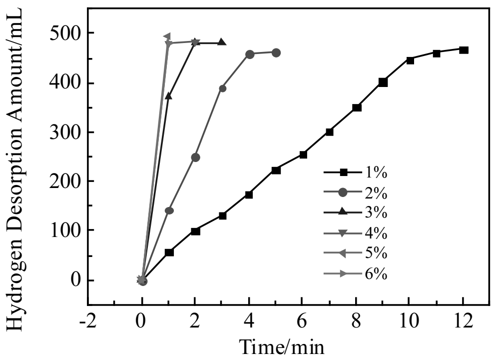

Fig.5 Relations between hydrogen desorption amount and time of $NaBH_4$ doped with different amount of $60\%Co_2B/40\%Pr_6O_{11}$

In the following experiments, the effect of amount of the mixed catalyst $60\%Co_2B/40\%Pr_6O_{11}$ on the hydrogen desorption amount and release rate has been studied. The result is shown in Fig.5. With the increase of the doping amount, the hydrogen release rate of $NaBH_4$ presents a remarkable decreasing process after a very fast increase. And the samples doped with 3%, 4% and 5% mixed catalyst have the same hydrogen release rate in the first 30 s, the amounts of hydrogen release are also very close, but the hydrogen release rates of other samples are significantly lower than these three doped samples. In particular, the desorption time of the sample doped with 1% catalyst reaches 12 min, much longer than the time of the samples doped with 3%, 4% and 5% catalyst.

Fig.6 shows the curve of the hydrogen desorption amount and time of $NaBH_4$ doped with mixed catalyst $70\%Co_2B/30\%Pr_6O_{11}$. Obviously, with the increase of the mixed catalyst doping amount, the hydrogen desorption amount of the sample first increases and then decreases. When the amount of the catalyst is 4%, the hydrogen desorption amount and release rate of the samples reach maximum, 540.00 mL (12.1 wt%) and 540.00 mL/min, respectively. When the doping amount of the catalyst is 5%, the hydrogen desorption amount and release rate all have an obvious decrease. In all the samples, when the doping amount of the catalyst is 1% the hydrogen desorption amount and release rate is minimum, 345 mL (7.7 wt%) and 23.00 mL/min, respectively.

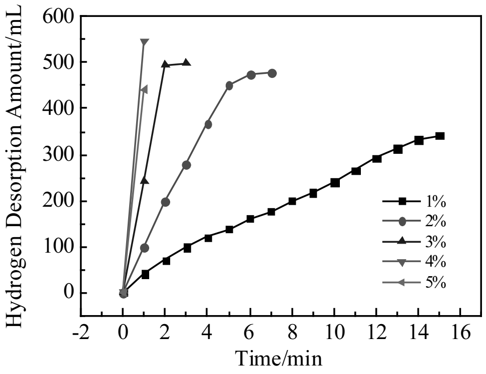

Fig.6 Relations between hydrogen desorption amount and time of $NaBH_4$ doped with different amount of $70\%Co_2B/30\%Pr_6O_{11}$

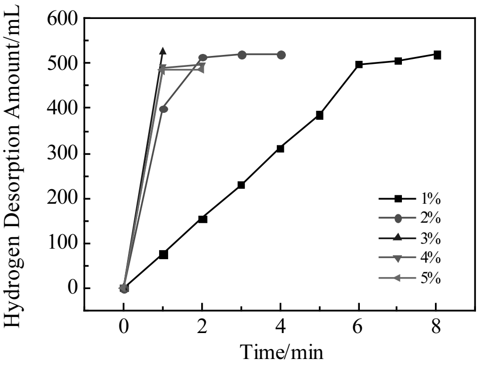

Fig.7 Relations between hydrogen desorption amount and time of $NaBH_4$ doped with different amount of $80\%Co_2B/20\%Pr_6$

**Table 1 Hydrogen desorption amount and release rate of $NaBH_4$ doped with different catalysts**

| Hydrogen desorption amount and release rate | Amount of mixed catalyst $Co_2B/Pr_6O_{11}$/% | $40\%Co_2B/60\%Pr_6O_{11}$ | $50\%Co_2B/50\%Pr_6O_{11}$ | $60\%Co_2B/40\%Pr_6O_{11}$ | $70\%Co_2B/30\%Pr_6O_{11}$ | $80\%Co_2B/20\%Pr_6O_{11}$ |
|---|---|---|---|---|---|---|
| Hydrogen desorption amount/mL | 1 | 505 | 417 | 475 | 345 | 520 |
| | 2 | 420 | 475 | 465 | 474 | 525 |
| | 3 | 435 | 410 | 482 | 495 | 525 |
| | 4 | 460 | 437 | 482 | 540 | 495 |
| | 5 | 505 | 500 | 495 | 440 | 485 |
| | 6 | 470 | 454 | 480 | - | - |
| Hydrogen release rate/$mL\cdot min^{-1}$ | 1 | 15.15 | 29.79 | 39.58 | 23.00 | 65.00 |
| | 2 | 23.33 | 67.86 | 93.00 | 67.71 | 131.75 |
| | 3 | 108.75 | 136.67 | 160.67 | 165.00 | 525.00 |
| | 4 | 153.33 | 145.67 | 241.00 | 540.00 | 247.50 |
| | 5 | 252.50 | 500.00 | 495.00 | .440.00 | 242.50 |
| | 6 | 470.00 | 454.00 | 480.00 | - | - |
| Maximum of hydrogen desorption/mL | 2 | - | - | - | - | 527 |
| | 5 | 505 | 500 | 495 | 540 | - |
| Maximum of hydrogen release rate/$mL\cdot min^{-1}$ | 5 | 252.50 | 500.00 | 495.00 | 540.00 | 525.00 |

Fig.7 shows the curve of the hydrogen desorption amount and time of the samples doped with 1%~5% mixed catalyst $80\%Co_2B/20\%Pr_6O_{11}$. Compared with other samples doped with mixed catalyst, the hydrogen release rate of the sample doped with 1% mixed catalyst $80\%Co_2B/20\%Pr_6O_{11}$ is much faster and the hydrogen desorption amount is also higher. Moreover, according to Fig.5, the samples doped with 3%, 4% and 5% mixed catalyst have the similar hydrogen release rate in the first 1 min. Comparing the hydrogen release rates of all the samples, it is easy to find that with the increase of the mixed catalyst amount, the hydrogen desorption amount first increases and then decreases. When the mixed catalyst amount reaches 2% and 3%, the hydrogen desorption amount reaches the maximum, 525.00 mL/min.

As can be seen from Table 1, when the mixed catalyst is 70% $Co_2B$ + $30\%Pr_6O_{11}$ and the amount is 4%, $NaBH_4$ has the maximum hydrogen desorption amount, 540 mL (12.1 wt%); when the catalyst is $60\%Co_2B+40\%Pr_6O_{11}$ and the amount is 5%, $NaBH_4$ has the maximum hydrogen release rate, 495 mL/min.

## 3 Conclusions

1) The hydrogen release rate of $NaBH_4$ is affected by the amount and the ratio of mixed catalyst $Co_2B/Pr_6O_{11}$. When the doping amount is varied between 1% and 6%, the hydrogen release rate of doped mixed catalyst samples increases firstly and then decreases as the doping amount increases. Conversely, the effect of the amount and the ratio of mixed catalyst $Co_2B/Pr_6O_{11}$ on the hydrogen desorption amount of $NaBH_4$ is not obvious. However, after $NaBH_4$ is catalyzed by the mixed catalyst $Co_2B/Pr_6O_{11}$, the hydrogen desorption amount of the sample is obviously changed. Changing the amount and ratio of mixed catalyst, the hydrogen desorption amounts of doped $NaBH_4$ samples are between 345 and 540 mL, and the hydrogen desorption amounts of most samples are between 410 and 525 mL.

2) In all samples doped with mixed catalyst $Co_2B/Pr_6O_{11}$, the hydrogen desorption performance of the sample doped with 4% (70%$Co_2B$/30%$Pr_6O_{11}$) is significantly better than that of other samples. It has the maximum hydrogen release rate 540 mL/min and the maximum hydrogen desorption amount 540 mL (12.1 wt%). In contrast, the sample doped with 1% (70%$Co_2B$/30%$Pr_6O_{11}$) has the worst hydrogen desorption amount 345 mL (7.7 wt%), and the hydrogen release rate of the sample doped with 1% (40%$Co_2B$/60%$Pr_6O_{11}$) is the lowest only 15.15 mL/min.

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# 催化剂对 $NaBH_4$ 水解放氢的影响

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**摘 要**：通过排水法研究了采用混合催化剂$Co_2B/Pr_6O_{11}$的硼氢化钠的水解过程。$Co_2B$与 $Pr_6O_{11}$的比例和混合催化剂$Co_2B/Pr_6O_{11}$的加入量对硼氢化钠放氢量的影响非常明显。当掺杂量在1%~6%之间变化时，试样的放氢速率随着掺杂量先增加后减少。相比之下，混合催化剂$Co_2B/Pr_6O_{11}$的加入量以及混合比例对$NaBH_4$的放氢量的影响并不明显。然而，$NaBH_4$被$Co_2B/Pr_6O_{11}$催化后，硼氢化钠的放氢量明显被改变了，所有的掺杂试样的放氢量在410~525 mL之间。在所有试样中，掺杂量4% 的(70%$Co_2B$/30%$Pr_6O_{11}$)试样具有最大的放氢速率540 mL/min和最大的放氢量540 mL。

**关键词**：$NaBH_4$；混合催化剂；放氢量；放氢速率

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