Effects of Composite Catalyst Co_2B/TiO_2 on Hydrolysis of $NaBH_4$

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Abstract: For the purpose of improving hydrogen release capacity of $NaBH_4$, hydrogen generation performance of $NaBH_4$ was catalyzed by Co_2B and TiO_2 compound with different mole ratio and percentage composition are investigated. The experiment mainly concentrated in the hydrogen generation rate and the hydrogen generation volume. The results indicate that the effects of hydrogen release of $NaBH_4$ when the proportions and amount of Co_2B/TiO_2 are not obvious. Changing the proportions and the amount, the amount of hydrogen release by hydrolysis of $NaBH_4$ are between 343-375*ml*. However, the study on the rate of hydrogen release finds that the effects of the proportion and amount of the compound catalyst on the rate of hydrogen release are very marked. The rate of hydrogen release of the catalyst samples presents an obvious increase when the amount of Co_2B/TiO_2 is between 1-4%. Among all the samples of compound catalyst, the rate of hydrogen release of the sample with 5% $Co_2B/2TiO_2$ is the largest.

Keywords: Amount of hydrogen release, compound catalyst, $NaBH_4$, rate of hydrogen release.

1. INTRODUCTION

As a common deoxidizer, $NaBH_4$ is used in chemical industry. It was compounded by Schlesinger and Brown [1], and $NaBH_4$ solution can undergo hydrolysis and release of hydrogen is as follows. The hydrolysis reaction of $NaBH_4$ is as given below, four moles H_2 is generated during efficient hydrolysis reaction per mole $NaBH_4$ [1-3].

$$NaBH_4+2H_2O \xrightarrow{cat} 4H_2+NaBO \quad (1.1)$$

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

Achieving the appropriate catalysts have been recognized as a key technology, which needs to improve the hydrogen storage performance of $NaBH_4$, and also benefits from the research of catalysis [4-8]. So far, the catalysts as Ru, Pt to Co, $CoCl_2$, Co-B, etc. [9] have been widely studied. Among them, Co-B is considered to be an excellent candidate for the H_2 production by catalytic hydrolysis of $NaBH_4$ owing to its relevant chemical stability and low cost. However, a lot of research is limited by the catalyst combination, that failed to exert the best efficiency of hydrogen release, and got higher hydrogen generation rate (HGR) and hydrogen generation volume (HGV), so the focus of current research is to find the catalyst combination with better catalytic ability. Few literatures of science and technology are reported about mixed catalysis in the present study [10-14].

In addition to the precious metal and transition metal catalyst [15], some non-noble metal catalysts have recently obtained the rapid development, such as Ni-B and Co-B [16, 17] catalyst, etc. In these catalysts, the Co-B has been favored by researchers because of its excellent catalytic performance. In the present little literature are reported about mixed catalysis of Co_2B/TiO_2 [18-21], so this paper tries to research the HGR and HGV of the composite catalysts. Accordingly, the experiment analyzes emphatically the influence law of different proportion composite catalyst, the amount of water added, and the liberation of hydrogen on the performance of $NaBH_4$. Hope this study on hydrogen release of $NaBH_4$ provides important reference significance for the other effect of catalysts.

2. MATERIALS AND METHOD

2.1. Preparation of Co_2B

The 2g sodium $NaBH_4$ and 7ml water are mixed into aqueous solution in the three flasks, and then weigh 0. 2g. Cobalt chloride ($COCl_2$) to be soluble completely in water, finally the $COCl_2$ sedimentary solution is added into $NaBH_4$ solution. The reaction process of solution:

$$CoCl_2+2NaBH_4+3H_2O \rightarrow 6.25H_2+0.5Co_2B+2NaCl+1.5HBO_2 \quad (1)$$

After the reaction, the mixture in the flask is filtered and dried, then Co_2B is obtained.

2.2. Preparation of Composite Catalyst Co_2B/TiO_2

To weigh the amount of Co_2B and TiO_2, put it into the sample bottle with grinding ball and shake it well. The mass ratio of mixture and the grinding ball is 1:40, the molar ratio of Co_2B and TiO_2 is 2:1, 1:1, 1:2, 1:3 and 1:4 respectively.

2.3. The Preparation of $NaBH_4$ Alkali Solution

Add 0.2 g sodium hydroxide into the small beaker filled with 4ml water to prepare alkali solution, and then weigh 0.4g $NaBH_4$ to add into sodium hydroxide solution.

2.4. Hydrolysis of $NaBH_4$

To weigh the amount of the composite catalyst Co_2B/TiO_2, to add into the three neck flask, and inject 2ml alkaline solution (2.2). Subsequently, place the three necked flask into the constant temperature water box of 30degrees. Wait a mount to measure the hydrogen generation volume (HGV) and the hydrogen generation rate (HGR) using drainage method. Then draw the curve of HGV-HGR, and study the law of HGV through comparing of different proportion and the amount of composite catalysts of Co_2B/TiO_2, The purpose is to acquire the suitable ratio and addition amount.

3. RESULTS AND DISCUSSIONS

In the work, mixed catalysts are studied. The relation curve of the HGV and HGR is shown in Fig. (**1**), when the composite catalyst is $2Co_2B/TiO_2$, and the HGV shows a gradually increasing trend which may be seen in the chart with the increase of $2Co_2B/TiO_2$ addition, and the HGV is the biggest with the samples with 5% compound catalyst. In the meantime, the hydrogen *via* time is only about 1min. In contrast, when the quantity of composite catalyst is 2%, the HGV is somewhat lower than in other specimens. In addition, among the other specimen hydrogen capacity is very close.

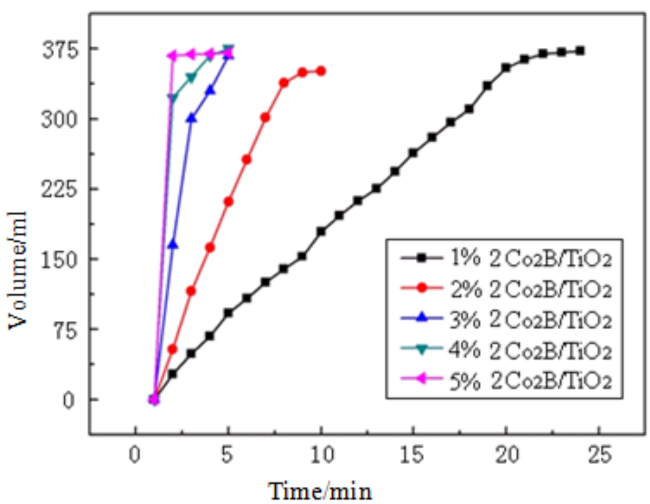

Fig. (1). Relations on amount and time of hydrogen release of $NaBH_4$ with $2Co_2B/TiO_2$.

The Fig. (**2**) shows the curve of the HGV and HGR when the composite catalyst is Co_2B/TiO_2, the experiment results show the HGR of samples doped 4% combined catalyst is faster than others, but the release time of hydrogen is merely 0. 5min or so, it has the minimum amount of hydrogen, only 356ml, moreover, the hydrogen capacity is 369ml with samples doped with 2% Co_2B/TiO_2. The second largest corresponding to the specimen doped 1% Co_2B/TiO_2. However, the hydrogen over time is 15 min with the sample doped with 1% Co_2B/TiO_2 and far more than the other specimen.

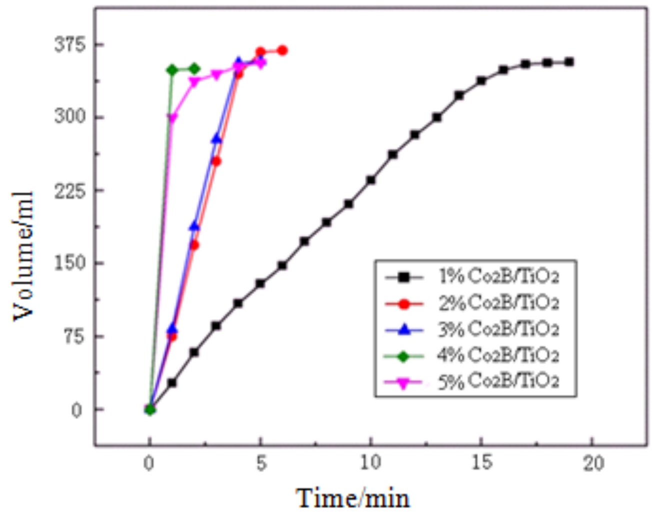

Fig. (2). Relations on amount and time of hydrogen release of $NaBH_4$ doped with Co_2B/TiO_2.

Obviously, the HGV shows a gradual increased trend which may be seen from the chart with the increase of $Co_2B/2TiO_2$ addition. We may get the biggest HGR when the additive amount of composite catalyst adds up to 5% or 6%. In all samples, except the sample doped with 5% compound catalyst $Co_2B/2TiO_2$, the hydrogen capacity of other specimens is very similar in 340ml to 350ml. If we add the sample doped with 5%, itcould generate the maximum HGV, 375ml.

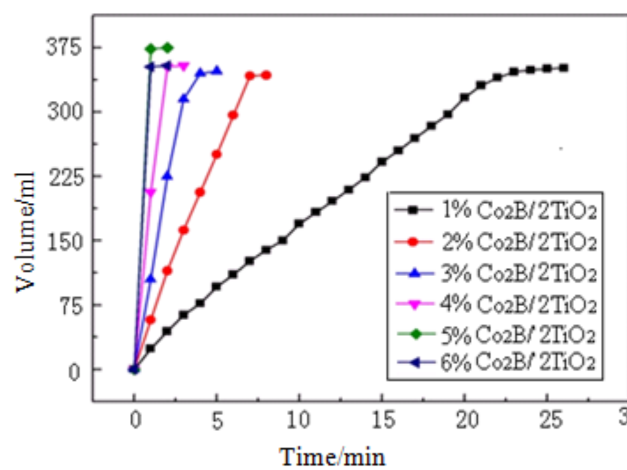

Fig. (3). Relations on amount and time of hydrogen release of $NaBH_4$ doped $Co_2B/2TiO_2$.

The result is unlike Figs. (**1-3**) with the catalyst $Co_2B/3TiO_2$, can be seen from the chart that the HGR shows the change trend of first increase and then decreases gradually. In the hydrogen discharge specimens of all specimens, the longest time hydrogen doped 1%$Co_2B/3TiO_2$ reaches 35min, more 34min than the 4% sample (although the HGR is higher than others). It is thus clear that the change regulations of HGV are very similar with the results changed with doping other ratio composite catalyst samples. In other words, the variation of HGV is not very obvious

Table 1. Amount and rate of $NaBH_4$ doped catalysts.

Co_2B/TiO_2 Mole Ratio	2:1	1:1	1:2	1:3	1:4	The Catalyst Percentage /%
HGV /ml	373	357	351	364	357	1
	351	369	343	350	358	2
	368	358	347	356	362	3
	375	356	354	359	356	4
	371	353	375	353	355	5
HGR ml/min	16.2	18.8	13.5	9.8	9.9	1
	39.0	61.5	42.8	21.9	17.0	2
	91.9	71.6	69.5	59.4	40.3	3
	93.8	71.2	118.0	119.5	59.4	4
	110.0	88.1	187.5	176.3	118.3	5

with the other sample, except for sample doped 4% $Co_2B/3TiO_2$.

Continue to increase the proportion of TiO_2 to $Co_2B/4TiO_2$ (Fig. **5**), It is not difficult to see that the change regulations are very similar with the Fig. (**4**), that is to say, that the HGR Shows a trend of first increasing too, and compare 1% $Co_2B/4TiO_2$ with 4% $Co_2B/4TiO_2$, the release time of hydrogen is more than nearly 30min. In addition, we find the increase of HGV is not obvious although the proportion of different doped catalyst. This shows that the change of the doping amount exerts an influence not on HGV but HGR.

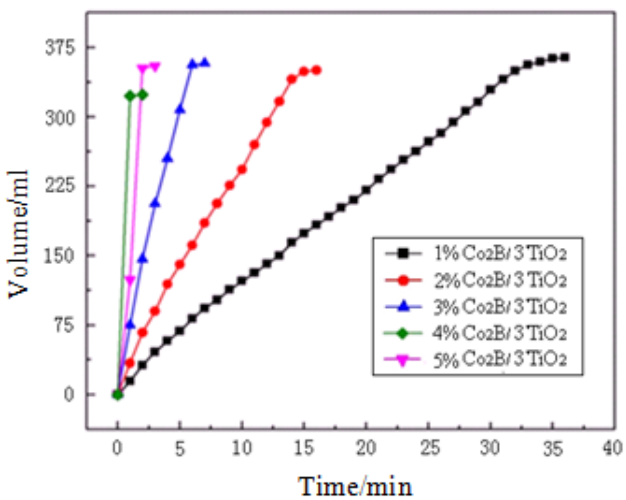

Fig. (4). Relations on amount and time of hydrogen release of $NaBH_4$ doped with $Co_2B/3TiO_2$.

For the purpose observing definitely the increasing trend of HGR and HGV, Table **1** is given according to all doped samples, through the table can be very intuitive to analysis the influence on the chemical reaction in the case of two kinds of distinct catalysts with different ratio combinations. As for the HGV, the sample with 4% or 5%$Co_2B/2TiO_2$ is highly efficient, yet the sample with 5%$Co_2B/2TiO_2$ is best with the consideration of HGR.

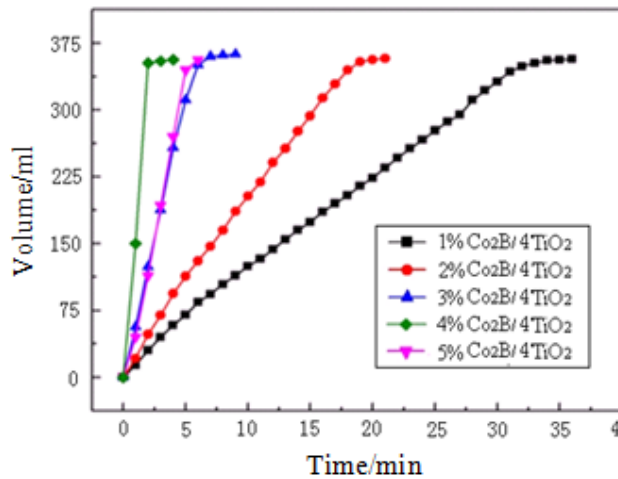

Fig. (5). Relations on amount and time of hydrogen release of $NaBH_4$ doped $Co_2B/4TiO_2$.

CONCLUSION

In this work, hydrogen generation performances are investigated with the samples of Co_2B/TiO_2 of different mole ratio and percentage composition. It is thus clear that the change regulations of HGV are very similar with the alterable results with catalyst samples of other ratio composites, and the experiment proofs the samples with 4%$Co_2B/2TiO_2$ or 5%$Co_2B/2TiO_2$ are high efficiency. The sample with 5%$Co_2B/2TiO_2$ is best with the consideration of HGR. All in all, this study on hydrogen release of $NaBH_4$ provides an important reference significance for the other effect of catalysts.

LIST OF ABBREVIATIONS

HGR = Hydrogen generation rate

HGV = Hydrogen generation volume

CONFLICT OF INTEREST

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled. "The authors declare that there is no conflict of interests regarding the publication of this paper."

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