

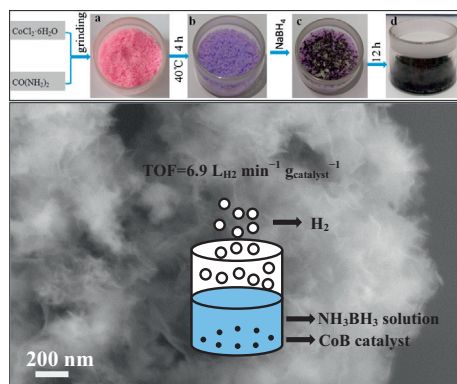


## Short Communication

## Solid-state-reaction synthesis of cotton-like CoB alloy at room temperature as a catalyst for hydrogen generation

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## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel room-temperature solid-state reaction is developed to synthesize cotton-like CoB alloy (CoB<sub>SSR</sub>) catalysts with a large specific surface area of 222.4 m<sup>2</sup> g<sup>-1</sup>. In the hydrolysis of ammonia borane catalyzed by the CoB<sub>SSR</sub>, the rate of hydrogen generation can reach 68.7 mL min<sup>-1</sup> with a turnover frequency (TOF) value of ca. 6.9 L<sub>hydrogen</sub> min<sup>-1</sup> g<sub>catalyst</sub><sup>-1</sup> at 25 °C. The TOF value is about 2 times as large as that of CoB alloy prepared by a regular solid-state reaction, which is also much higher than those of the CoB catalysts recently reported in the literature. The activation energy of the hydrolysis of ammonia borane catalyzed by the CoB<sub>SSR</sub> is as low as 22.78 kJ mol<sup>-1</sup>, hinting that the CoB<sub>SSR</sub> possesses high catalytic activity, which may be attributed to the large specific surface area and the abundant porous structure. The high catalytic performance, good recoverability and low cost of the CoB<sub>SSR</sub> enable it to be a promising catalyst candidate in the hydrolysis of ammonia borane for hydrogen production in commercial application.

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## 1. Introduction

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) is one of the promising sources to produce clean hydrogen for “mobile application” due to its high hydrogen capacity, non-toxicity, and high stability in aqueous

solution [1]. To enhance and control the rate of hydrogen generation through hydrolysis of NH<sub>3</sub>BH<sub>3</sub>, an efficient and robust catalyst is necessary. To achieve the large-scale commercial application, it is crucial to develop the proper catalysts made up of elements that are cheap and abundant in our earth [2]. Interest in cobalt boride (CoB) as a catalyst for NH<sub>3</sub>BH<sub>3</sub> hydrolysis arise from their special features, such as its outstanding catalytic activity, low cost, easy preparation, and good strength, which make it a suitable catalyst for hydrogen production [3]. Regular CoB alloys are frequently

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synthesized by chemical reduction of  $\text{Co}^{2+}$  by  $\text{BH}_4^-$  in aqueous solution, which have vigorous and exothermic nature. As a result, the obtained CoB alloys display some negative features of low surface area, broadly distributed particle size and poor thermal stability, which would lead to a low catalytic activity for the hydrolysis of  $\text{NH}_3\text{BH}_3$ . To improve the catalytic activity via avoiding the agglomeration, several routes have been adopted in the reported work by varying the synthetic conditions [4–7], using organic templates [8–11], doping with transition metals [12–15], or supporting the catalyst on those materials with high surface area [16,17], and forming the metal film [18]. Although all these ways can improve the performance of CoB alloy catalysts, it still requires elaborate selection of proper catalyst form in order to implement the industrial scale production of hydrogen.

Solid-state reaction is an old technique to produce inorganic materials. Solid-state reaction at low temperature or even room temperature has been developed as an effective approach to synthesize metal alloys, inorganic oxides or coordination compounds [19]. Compared to the solid-state reaction at high temperature and the solution reaction, this approach has several distinguishing features: (i) it is simple and convenient, (ii) it involves less solvent and reduces contamination, and (iii) it gives a high yield product [20–23]. Generally, in a solid state reaction process, metal alloys are prepared with the assistance of ball milling. The obtained metal alloys often have micro-scaled sizes, leading to a low surface area of the final products. It is still a big challenge to prepare metal alloys with large surface area by solid-state reaction at room temperature.

In this work, we synthesized cotton-like CoB alloy via a solid-state reaction at room temperature, which has a large surface area of  $222.4\text{ m}^2\text{ g}^{-1}$ . Furthermore, the as-prepared CoB alloy has a “clean” surface due to the fact that no templates or surfactants are used in the reaction system. It is found that the as-prepared CoB alloy exhibits high catalytic activity towards  $\text{NH}_3\text{BH}_3$  hydrolysis for hydrogen generation.

## 2. Experimental section

### 2.1. Synthesis

All reagents were of analytic grade, and double-distilled water was used throughout the experiments.  $\text{NaBH}_4$  (96.0%) was purchased from the company of Chinese Medicine Group Chemical Reagent Co. Ltd. The synthetic procedure of the cotton-like CoB alloy via solid-state reaction was illustrated in Fig. 1 and can be described as following: 100 mg  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (99.0%, Shanghai Zhongqin Chemical Reagent Co. Ltd) and 5 g  $\text{CO}(\text{NH}_2)_2$  (99.0%, Hedong District of Tianjin City Hongyan Reagent Factory) was mixed and grinded in an agate mortar. The pink mixture was put into a glass bottle, as displayed in Fig. 1a. The bottle was dried in an oven for 4 h at  $40^\circ\text{C}$ , and the color of the mixture became purple, as shown in Fig. 1b. Then, the grinded  $\text{NaBH}_4$  powder was evenly spread over the mixture. The solid-state reaction then started at room temperature. Fig. 1c and d presented the state of

the reaction system at different reaction stages. After 12 h, the resultant was rinsed with double-distilled water, and finally dried in a vacuum oven at  $60^\circ\text{C}$  for 6 h. Then, the product denoted as  $\text{CoB}_{\text{SSR}}$  was obtained. For comparison, another CoB alloy was prepared by grinding  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{NaBH}_4$  in an agate mortar, which was denoted as  $\text{CoB}_{\text{C}}$ .

### 2.2. Characterization

XRD patterns were recorded on a Shimadzu XD-3A (Japan) using filtered  $\text{Cu-K}\alpha$  radiation generated at 40 kV and 30 mA. Scanning electron microscopy (SEM) images were obtained using a Carl Zeiss Ultra Plus scanning electron microscope. Specific surface area was determined by Brunauer-Emmett-Teller (BET) method based on the sorption isotherms obtained on a Quantachrome Autosorb-1 volumetric analyzer. The molar ratios of Co to B in both CoB samples were determined by a Varian 720 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

### 2.3. Catalytic performance testing

Catalytic testing of CoB for the hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  (97%, Shanghai Viwit Medicine Technology Co., Ltd.) was carried out at  $25^\circ\text{C}$  under atmospheric pressure. Firstly, 10 mL of mixed solution containing  $\text{NH}_3\text{BH}_3$  (61.6 mg, 2 mmol) and NaOH (240 mg, 0.6 mmol) was prepared. A weighed catalyst of ca. 10 mg was placed in a three-necked-glass bottle, which was placed into a water bath for controlling the reaction temperature. Then the mixed solution of  $\text{NaBH}_4$  and NaOH was added into the three-necked-glass bottle. The volume of generated hydrogen was measured by a water-filled gas burette. To investigate the influence of reaction temperature, hydrolysis of  $\text{NH}_3\text{BH}_3$  was also carried out at  $30^\circ\text{C}$ ,  $35^\circ\text{C}$  and  $40^\circ\text{C}$ , respectively.

## 3. Results and discussion

To understand the process of the solid-state reaction, the intermediate samples obtained at different reaction stages (shown in Fig. 1) are characterized by XRD and the results are displayed in Fig. 2a. As shown in Fig. 2a, the XRD pattern indicates that the pink intermediate has a mixed crystalline phase of both  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2$  (JCPDS No. 14-0527) and  $\text{CO}(\text{NH}_2)_2$  (JCPDS No. 37-1464). The  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2$  intermediate was produced by the following reaction:  $\text{CoCl}_2\cdot 6\text{H}_2\text{O} + 2\text{CO}(\text{NH}_2)_2 = \text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2 + 2\text{CO}_2\uparrow + 2\text{H}_2\text{O}$ . The XRD pattern of the purple intermediate is similar to that of the pink intermediate, indicating the structure did not significantly change after dryness. The change of the color results from the loss of part of crystal water in  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2$ . In the XRD pattern of  $\text{CoB}_{\text{SSR}}$ , the peaks at ca.  $35^\circ$  and  $60^\circ$  can be ascribed to the crystal CoB alloy [24], and the weakly broad peak at  $2\theta \approx 45^\circ$  is related to the amorphous CoB alloy [24], respectively, implying there is a mixed phase of crystal and amorphous phase in the  $\text{CoB}_{\text{SSR}}$  sample. The  $\text{CoB}_{\text{C}}$  sample is amorphous evidencing by the broad peak at  $2\theta \approx 45^\circ$ . In addition, as shown in the inset in

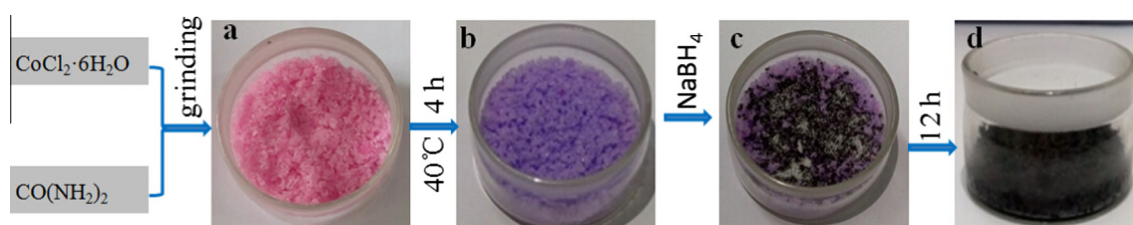


Fig. 1. Illustrations of the synthetic procedure of the cotton-like  $\text{CoB}_{\text{SSR}}$  alloy.

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