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# Preparation and characterization of nanostructured Co–Mo–B thin film catalysts for the hydrolysis of ammonia borane

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## ARTICLE INFO

### Article history:

Received 15 March 2018

Received in revised form

19 July 2018

Accepted 27 July 2018

Available online xxx

### Keywords:

Co–Mo–B thin film

Electroless plating

Ammonia borane

Hydrogen generation

Hydrolysis

## ABSTRACT

Nanostructured Co–Mo–B thin film catalysts were prepared via electroless plating method on the foam sponge. The effect of depositional pH value on the hydrogen generation rate from the hydrolysis of ammonia borane was investigated. The results show that the hydrogen generation rate increases from 3890.9 to 5100.0 mL min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, when the pH value increases from 10.5 to 11.0. However, the hydrogen generation rate reduces to 3945.5 and 3242.3 mL min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, when the pH value further increases to 11.5 and 12.0, respectively. Hence, it can be seen that the as-prepared Co–Mo–B thin film catalyst (pH = 11.0) exhibits the highest hydrogen generation rate, which could be attributed to the smaller size and the synergistic effect of Co, Mo and B on the catalyst surface. Moreover, the activation energy of the catalytic hydrolysis reaction at 298 K was 41.7 kJ mol<sup>-1</sup>. The value is lower than that of the most of Ni–based and Co–based catalysts, even some noble metal catalysts. After 5 cycles, the catalytic activity of the Co–Mo–B thin film catalyst remains about 61.9% of its initial value. Based on the SEM analysis, the reduction of the catalytic activity could be ascribed to the agglomeration of the active substance and some impurity phase on the catalyst surface.

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## Introduction

On-board hydrogen storage is a critical technical issue for the large-scale utilization of hydrogen fuel cells for transportation. With high gravimetric and volumetric hydrogen storage capacities, chemical hydrides such as Mg<sub>2</sub>FeH<sub>6</sub>, Mg<sub>2</sub>NiH<sub>4</sub>, LiAlH<sub>4</sub>,

NaBH<sub>4</sub>, NH<sub>3</sub>BH<sub>3</sub>, and MgH<sub>2</sub> are considered attractive candidate hydrogen storage materials [1–5]. Among them, ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) has been extensively investigated due to high gravimetric hydrogen density (19.6 wt %) and good stability in aqueous solution [6,7]. As shown in Eq. (1), the stored hydrogen can be generated from the hydrolysis of NH<sub>3</sub>BH<sub>3</sub> at ambient conditions in the presence of appropriate catalysts [8–10].

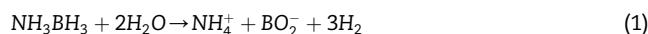
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<https://doi.org/10.1016/j.ijhydene.2018.07.180>

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To date, a range of research has been focused on the catalysts in the hydrolysis of  $\text{NH}_3\text{BH}_3$ . Significant developments have been achieved for the heterogeneous catalytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  with metal catalysts. Some noble metal-based catalysts, such as Rh, Ir, Ru, Ni/Pt and Pt, have showed remarkable catalytic activities [11–20]. However, considering the high costs and poor abundance of the noble metals, it is more attractive to develop an economical and earth-abundant metal catalyst for the improvement of the hydrogen generation kinetics properties for  $\text{NH}_3\text{BH}_3$  hydrolysis. Recent studies indicate that a series of non-noble metal catalysts have been widely studied in catalytic dehydrogenation of the hydrolysis of  $\text{NH}_3\text{BH}_3$ , including Co [21–23], Ni [24], Fe [25], CoCu [26,27], Co/ $\gamma$ - $\text{Al}_2\text{O}_3$ /SiO<sub>2</sub>/C [28], Co–B [29], Ni–P [30] and Co–Ni–P/TiO<sub>2</sub> [31]. Among them, Co–B is mostly considered as a good candidate for catalyzed hydrolysis of  $\text{NH}_3\text{BH}_3$  because of its low-cost, but its catalytic activity need to be further improved. For instance, Ke et al. [32] have revealed that the catalytic activity of Co–B catalysts can be enhanced by the modification of Mo element. In addition, there are a few reports available in literature on the catalytic performance of Co–Mo–B catalysts in  $\text{NH}_3\text{BH}_3$  hydrolysis system [33].

Traditionally, Co-based catalysts have been mainly prepared by the chemical reduction method to obtain powder samples. Nevertheless, powder catalysts have some disadvantages such as difficult to separate from the reaction system, and easily aggregate during the preparation and storage process. Nowadays, several deposition technologies have been used to obtain the thin film catalysts and solve above-mentioned problems [2,31,34]. Owing to the advantages of easier control and lower processing temperature, electroless plating technology is applied as an efficient method to prepare thin film catalysts [35–37]. During the process of electroless plating, Cu sheet [38], Ni/Cu foam [3,37,39] and carbon cloth [40] have been usually chosen as substrate materials. But so far, it has rarely been reported that foam sponge is used as the substrate of the catalyst for  $\text{NH}_3\text{BH}_3$  hydrolysis.

In this work, a nanostructured Co–Mo–B thin film catalyst was prepared on the foam sponge by electroless plating at ambient temperature. The effect of depositional pH value on the particle size and the catalytic activity for the hydrolysis of  $\text{NH}_3\text{BH}_3$  was systematically investigated. The Co–Mo–B thin film catalysts with smaller particle size make them possess a defect-rich structure, which contributes to improve catalytic activity towards the hydrolysis of  $\text{NH}_3\text{BH}_3$ . Compared with those conventional non-noble metal powder catalysts and even noble metal catalysts, the as-prepared Co–Mo–B thin film catalyst shows a significant enhancement of the catalytic activity for the hydrolysis of  $\text{NH}_3\text{BH}_3$ .

## Experimental

### Preparation of Co–Mo–B thin film catalysts

The commercial foam sponge with a projected surface area of  $4 \times 4 \text{ cm}^2$  was used as the supporting substrate. The electroless plating method was employed to fabricate the Co–Mo–B

thin films. All of the reagents were purchased from Sino-pharm Chemical Reagent Co., Ltd., except for  $\text{NH}_3\text{BH}_3$  (97% purity, Sigma Aldrich). Before plating, the tailored foam sponge was first immersed into acidic eroded solution and hot alkaline solution to remove the greasy dirt and other impurities according to our previously described process [41]. Then, it was sensitized in the solution ( $1 \text{ g L}^{-1} \text{ SnCl}_2 + 1 \text{ mL L}^{-1} \text{ HCl}$ ) for 3 min, activated in the solution for 2 min, washed with distilled water and absolute ethyl and dried in vacuum atmosphere at 298 K for 24 h. Finally, weigh above-pretreated foam sponge to determine the weight of the bare foam sponge (denoted as  $m_{\text{foam sponge}}$ ). The electroless plating of the Co–Mo–B thin film catalysts was conducted in a typical solution and the composition of the bath solution is presented in Table 1. The depositional pH value was adjusted to a series of values, including 10.5, 11.0, 11.5 and 12.0. When the procedure of electroless plating was over under the designed pH value, the Co–Mo–B/foam sponge was taken out from plating bath, washed, dried and weighed (denoted as  $m_{\text{Co–Mo–B/foam sponge}}$ ). So the weight of the deposited Co–Mo–B thin film catalyst (denoted as  $m_{\text{Co–Mo–B thin film catalyst}}$ ) was calculated with Eq. (2)

$$m_{\text{thin film Co–Mo–B catalyst}} = m_{\text{Co–Mo–B/foam sponge}} - m_{\text{foam sponge}} \quad (2)$$

### Catalyst characterization

The inductively coupled plasma-optical emission spectroscopy (ICP-OES, ICP-9000, Thermo Jarrell-ASH Corp) has been carried out to determine the chemical atomic composition of the as-prepared Co–Mo–B thin film catalysts. The as-prepared Co–Mo–B thin film catalysts were characterized by powder X-ray diffraction (XRD, Rigaku-Dmax 2500, Cu Ka radiation,  $\lambda = 1.54178 \text{ \AA}$ ), scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, HITACHI HT7700) and atomic force microscopy (AFM, Bruker Dimension icon). X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos Axis Ultra DLD multi-technique electron spectrometer.

### Hydrogen generation testing

In a typical hydrogen generation experiment, 8 mL  $\text{NH}_3\text{BH}_3$  aqueous solution (containing 40 mg  $\text{NH}_3\text{BH}_3$ ) was placed into a three-necked round-bottom flask with a temperature control device. Then, a certain amount of the Co–Mo–B thin film catalyst loaded on the foam sponge was completely dipped into the solution without stirring. The volume of the released

**Table 1 – Bath composition and electroless plating conditions for the deposited Co–Mo–B thin film catalysts.**

Bath composition	Electroless plating conditions
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	$0.05 \text{ mol L}^{-1}$
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	$0.05 \text{ mol L}^{-1}$
$\text{NH}_2\text{CH}_2\text{COOH}$	$0.6 \text{ mol L}^{-1}$
$\text{NaBH}_4$	$0.6 \text{ mol L}^{-1}$
Depositing temperature	298 K
pH	10.5, 11.0, 11.5, 12.0
Depositing time	5 min

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