

Accelerated Hydrolysis of Solid-state NaBH₄/Al System by Co₂B Milled with Li for Hydrogen Generation

Jiasong Chang¹, Wenlong Song^{1,2}, Ting Li¹, Jindan Chen¹, Hanmei Wu¹, Chengming Li¹ and Meiqiang Fan^{*,1,2}

¹Department of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China

²Zhejiang Tianneng Energy Technology Co., Ltd., Changxing County, Zhejiang Province 313100, China

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Abstract: Co₂B catalyst was milled with Al and Li to form Al-Li-Co₂B composite, and the hydrogen generation performance of Al-Li-Co₂B/NaBH₄ system was investigated in this study. 100% hydrogen yield was reached, and high hydrogen generation rate was regulated by optimizing the composition design and preparation technology. The improvement was attributed to the synergetic effect of Co₂B and Li in the preparation process, whereas a large specific surface area was obtained with the increase in Li content, Co₂B, and milling time. In addition, the catalytic activity of Co₂B and LiOH from Li hydrolysis was heightened for the hydrolysis of the Al/NaBH₄ system because of the addition of Al(OH)₃, LiAl₂(OH)₇·xH₂O, and NaBO₂ in the hydrolysis process.

Keywords: Al-Li-Co₂B/NaBH₄ system, hydrolysis kinetic, hydrogen generation.

1. INTRODUCTION

Sodium boron hydride (NaBH₄) is a good hydrogen source for portable fuel cells, as it has 10.8% of theoretic hydrogen storage value and mild hydrolysis temperature [1]. NaBH₄ is stable in alkali solutions, and its hydrolysis can be controlled by the addition of catalysts. Catalysts are an important center for NaBH₄ hydrolysis. Notable metals, alloys, and salts have high catalytic activity and are accessibly used for NaBH₄ hydrolysis [2, 3]. However, high costs limit their commercial application. Cheap catalysts with high catalytic activity must be developed in the future.

Co₂B-based catalysts have been studied in the past 10 years, as Co₂B has lower cost than notable metals but higher catalytic activity than other non-notable metals. Many composition designs and preparation technologies have been developed to improve the catalytic activity of Co₂B [4, 5]. The nanostructure formation of Co₂B deposited on the carriers, such as SiO₂, TiO₂, CeO₂, Al₂O₃, and carbon, has improved catalytic activity for NaBH₄ hydrolysis [6-9]. Yu reported that the Co₂B formed on zeolitic imidazolate frameworks had 3641.69 ml min g⁻¹(Co) at 313 K and showed good stability at different temperatures [8]. The addition of other metals into Co₂B catalyst is another effective method for improving the hydrolysis of NaBH₄. Metals such as Ni, Cu, and La have been

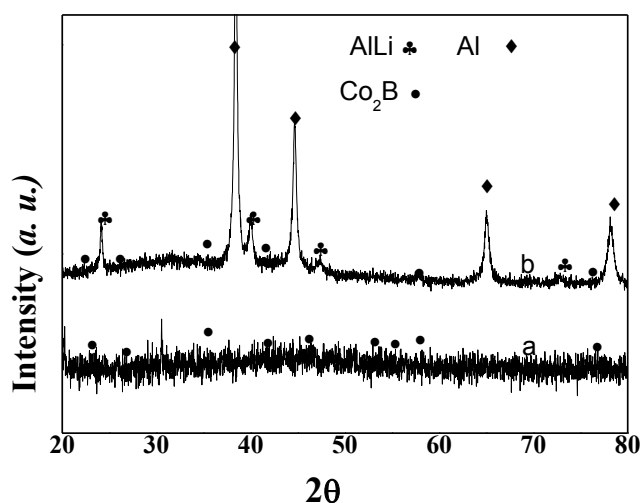


Figure 1. XRD patterns of Co₂B, Al-Li-Co₂B composite

reported to heighten the catalytic activity and stability of the catalyst [10-12]. However, the catalysts have to be used in NaBH₄ solution, as the hydrolysis byproduct NaBO₂ has low solubility,

*To whom correspondence should be addressed: Email: fanmeiqiang@126.com

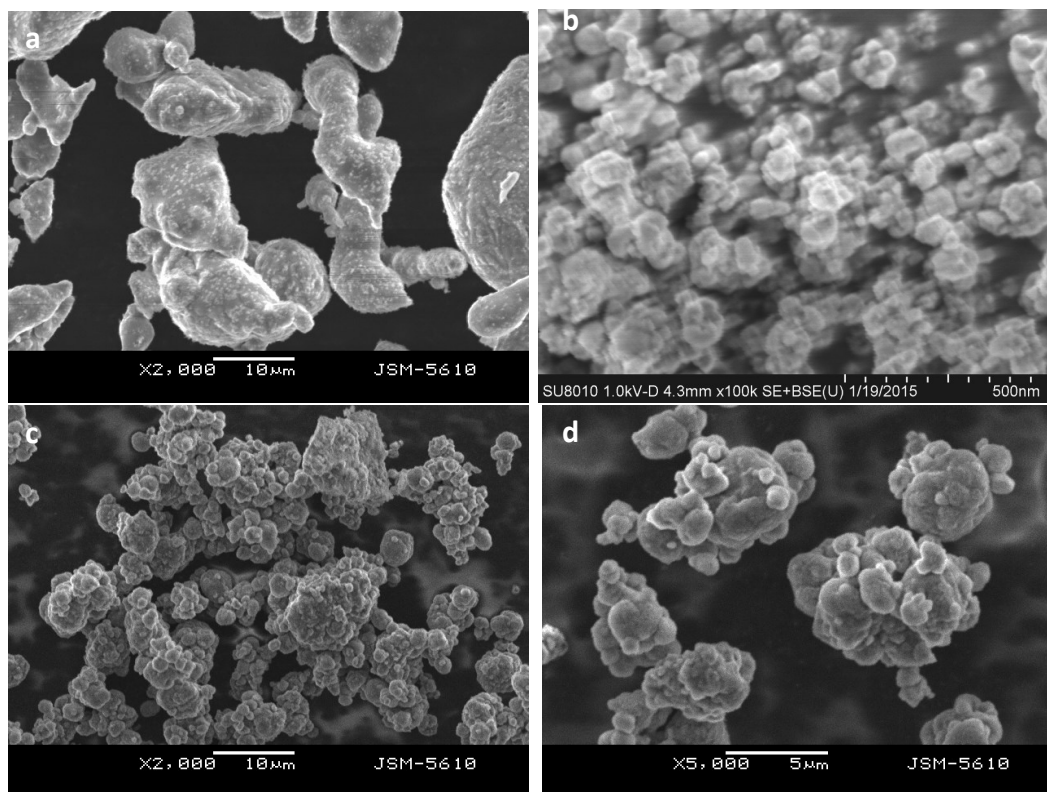


Figure 2. Morphologies of Al, Co_2B and Al-Li- Co_2B composite

and a large amount of solid-state NaBO_2 deposited on the catalyst surface deactivates the catalytic activity. Hydrogen generation from the traditional NaBH_4 solution presents 1–3 wt.% hydrogen storage density and cannot meet the requirement of portable fuel cells.

Recently, the hydrolysis of solid-state sodium boron hydride in limited water has been used to improve hydrogen density. Liu reported that the milled NaBH_4 and Ru-based catalyst presented above 6.7 wt.% hydrogen densities in limited water [13]. Combined with aluminum metal or alloy, solid-state NaBH_4 catalyzed by Co-based catalyst had high hydrogen performance in water. The Al-Co/ NaBH_4 [14] and Al/ NaBH_4 / CoCl_2 systems [15] presented approximately 5 wt.% hydrogen densities in alkali solution at 298 K. The alkali solution is not easily handled and may bring about damages for common users, and this effect is undesirable.

The Al/ NaBH_4 system has low cost in large scale application because the hydrolysis byproducts $\text{Al}(\text{OH})_3$ and NaBO_2 can be recycled. The cost of recycled aluminum is approximately 1.8 dollar/Kg via the Bayer-Heroult-Hall process and the cost of recycled NaBO_2 will be reduced to 2 dollar/Kg in future [11, 15, 16]. It is necessary to develop highly efficient catalyst for the hydrolysis of Al and NaBH_4 . In this study, Co_2B and lithium metal were milled with Al to form Al-Li- Co_2B composite. The Al-Li- Co_2B / NaBH_4 system was designed as hydrogen generation materials, which exhibited good generation performance because of the effect of Co_2B and Li. The different parameters of hydrogen generation and relative microstructure analysis were performed for the design of hydrogen generation materials in the future.

2. EXPERIMENTAL METHODS

2.1. Sample preparation

Al powder (99.9% purity, approximately 10 μm particle size), Li plate (99.9% purity, about 1 mm), cobalt salt (99.9% purity) and NaBH_4 (95% purity) were purchased from a Mike reagent company in Hangzhou city of P. R. China. Co_2B was prepared via the reaction of cobalt salt and sodium boron hydride in water at 298 K and dried at 333 K. The molar ratio of cobalt salt and sodium boron hydride was limited at 1.05. The powders of Al, Li and Co_2B were weighed and placed in 50 mL stainless steel jars. The ball-to-mixture weight ratio was 26 to 1. Milling for 10 h was performed in a QM-3SPO4 planetary ball miller at 450 r/min unless otherwise indicated.

2.2. Measurement of hydrolysis kinetics

Hydrogen generation tests were carried out in a sealed reactor attached to a condenser and a graduated cylinder at 298 K and 1 atm. The Al-Li- Co_2B / NaBH_4 system was 0.4 g and the system was pressed into tablets in a stainless steel mould (10 μm diameter) under 5 tons of pressure before the hydrolysis reaction. The Al-Li- Co_2B / NaBH_4 system mass ratio was set at 1:1 unless otherwise stated. The detailed hydrolysis conditions were introduced in our pervious studies [16]. The hydrolysis experiments were carried out at 323 K unless otherwise stated. All hydrolysis experiments were repeated three times and the results were averaged. The hydrogen yield was calculated as the percentage of the generated hydrogen amount to the theoretic hydrogen value.

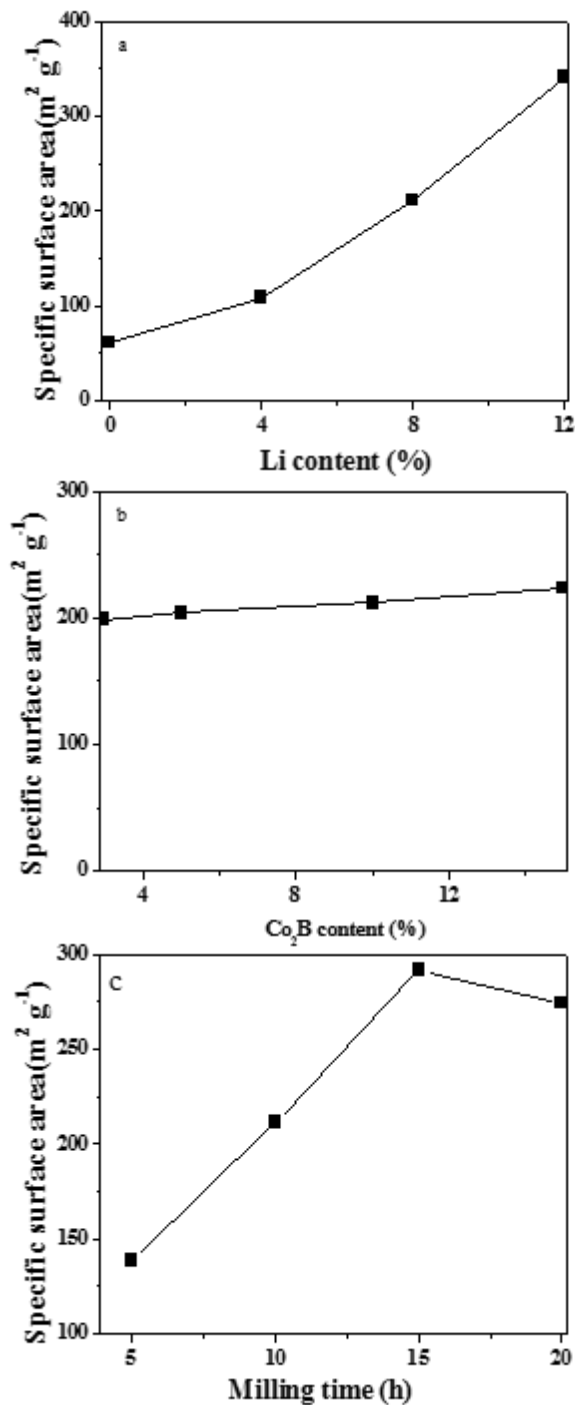


Figure 3. Effects of composition design and milling time on specific surface area changes of Al-Li- Co_2B composite. a, Li content; b, Co_2B content; c, milling time.

2.3. Microstructure analysis

Powder X-ray diffraction patterns of the prepared samples were collected using an X-ray diffractometer (Thermo ARL X'TRA, Switzerland). Scanning electron microscopy observations were

measured with a JSM-5610LV (JEOL Co.) equipped with an IN-CA energy-dispersive X-ray spectrometer. The Brunauer–Emmett–Teller surface area was determined with a surface area analyzer (Micromeritics, ASAP2020) using N_2 as adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of Al-Li- Co_2B composite

Fig. 1 shows the XRD patterns of Co_2B , Al-Li- Co_2B composite. Co_2B (JCPDS-03-0878) has no significant peaks, reflecting amorphous structures formation through the reaction of cobalt salt and NaBH_4 . Peaks of AlLi (JCPDS-10-0018) and Al (JCPDS-03-0932) are identified in the XRD patterns of Al-Li- Co_2B composite, showing only AlLi alloy formation in the milled Al-Li- Co_2B composite. The morphologies of Al, Co_2B , and Al-Li- Co_2B composite are depicted in Fig. 2. Initial Al powder presents irregular several tens of μm columns, and Co_2B shows rough and irregular particles with sizes less than 100 nm, as illustrated in Figs. 2a and 2b. However, the milled Al-Li- Co_2B composite exhibits significant fine particles, ranging from 1 to 5 μm , as depicted in Figs. 3c and 3d. Some fine particles are also observed to be cumulated together with fresh defects and deformation. The distinct changes are attributed to mechanical milling [17, 18], and the formation of AlLi alloy stimulates the decrease in particle size.

Fig. 3 shows the effects of composition design and milling time on the specific surface area changes in the Al-Li- Co_2B composite. The detailed composition design of Al-Li- Co_2B composite is shown in Table 1. The specific surface area exhibits various trends. The specific surface area significantly increases with the increase in lithium content. Lithium metal demonstrates low melting temperature and good ductility. It easily disperses on the aluminum surface and forms AlLi alloy in the milling process. Alloying is the key factor for the increase in the specific surface area of Al-Li- Co_2B composite. For the effect of Co_2B , the specific surface area slightly increases with Co_2B content. The Co_2B particle exhibits a particle size of less than 100 nm and a larger specific surface area than micrometer Al powder. In addition, the nanostructure Co_2B distributes on the Al surface and prevents the combination of Al-Al atoms to some degree. Milling time is another important factor in signifi-

Table 1. Composition design of Al-Li- Co_2B / NaBH_4 system.

Sample	Al-Li- Co_2B (wt%)			Mass ratio of Al-Li- Co_2B / NaBH_4
	Al	Li	Co_2B	
1	90	0	10	1:1
2	86	4	10	1:2
3	82	8	10	1:1
4	78	12	10	2:1
5	89	8	3	1:1
6	87	8	5	1:1
7	77	8	15	1:1

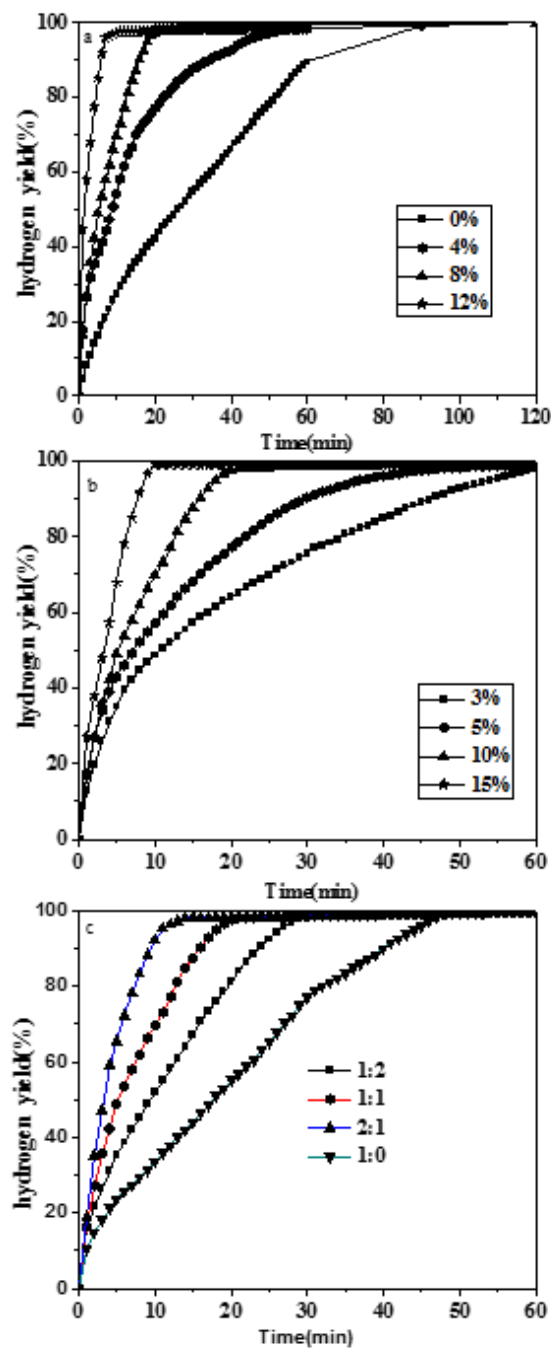


Figure 4. Hydrogen generation curves of Al-Li-Co₂B/NaBH₄ system. a, effect of Li content; b, effect of Co₂B content; c, effect of Al-Li-Co₂B/NaBH₄ mass ratio

cantly increasing the specific surface area of the Al-Li-Co₂B composite. Milling not only influences the formation of AlLi alloy and morphologies of Al-Li-Co₂B composite, but also decreases the grain size. The repeated cold welding and fracturing during milling reduces the particle size from the initial 10 μm to 1–5 μm . The specific surface area increases with milling time increasing from 5 h to 15 h, but it decreases with milling time further increasing from

15 h to 20 h.

3.2. Effect of composition design

The hydrogen generation curves of the Al-Li-Co₂B/NaBH₄ system are shown in Fig. 4 according to the composition design in Table 1. The Al-Li-Co₂B/NaBH₄ system has 100% hydrogen yield within 120 min, and its hydrogen generation rate is altered with parameter changes including Li content, Co₂B content, and Al-Li-Co₂B/NaBH₄ mass ratio. The Al-Li-Co₂B/NaBH₄ system without Li content, that is, sample 1 in Table 1, reaches 100% hydrogen yield at 90 min. The systems with 4 wt.%, 8 wt.%, and 12 wt.% of Li content in Al-Li-Co₂B composite, which correspond to samples 2, 3, and 4 in Table 1, require 60 min, 17 min, and 7 min to arrive at 100% hydrogen yield, respectively, as shown in Fig. 4a. The addition of Li metal, which is an important factor in accelerating Al hydrolysis, has been considered to increase the specific surface area, as shown in Fig. 3. In addition, Li metal easily hydrolyzes in water, and its hydrolysis byproduct LiOH can act as a catalyst for Al hydrolysis.

Co₂B is a good catalyst for NaBH₄ hydrolysis. The increase in Co₂B amount presents the increased active sites, which accelerate the hydrolysis kinetics of NaBH₄. Co₂B may also act as a cathode to Al anode, which improves the electrochemical corrosion of Al. The systems with 3 wt.%, 5 wt.%, 10 wt.%, and 15 wt.% of Co₂B in Al-Li-Co₂B composite, which correspond to samples 3, 5, 6, and 7 in Table 1, require 60 min, 40 min, 17 min, and 8 min to reach 100% hydrogen yield, respectively, as shown in Fig. 4b.

The increase in Li and Co₂B content evidently improves the hydrolysis of Al and NaBH₄. As Al and NaBH₄ have 1360 ml g⁻¹ and 2588 ml g⁻¹ of theoretic hydrogen yield, respectively, the hydrogen generation amount and rate can be regulated by the Al-Li-Co₂B/NaBH₄ mass ratio. Sample 3 in Table 1 is selected to evaluate the hydrogen generation performance of the system with different Al-Li-Co₂B/NaBH₄ mass ratios. The hydrogen yield of up to 100% requires decreased time with the increase in Al-Li-Co₂B/NaBH₄ mass ratio from 1:2 to 1:1 and 2:1. It can be attributed to the similar effect of the increase in Co₂B for NaBH₄ hydrolysis. However, the hydrogen yield of up to 100% requires longer time for Al-Li-Co₂B composite (1:0) than the Al-Li-Co₂B/NaBH₄ system. The results indicate an interaction in the hydrolysis of Al-Li-Co₂B and NaBH₄. The hydrolysis byproduct NaBO₂ presents alkaline, which can act as a catalyst for Al hydrolysis. The increased conductivity from the dissolution of NaBO₂ also accelerates the electrochemical corrosion of Al. By contrast, the hydrolysis byproduct of Al-Li-Co₂B composite may also improve the hydrolysis kinetics of NaBH₄.

Fig. 5 shows the hydrogen generation of NaBH₄ hydrolysis catalyzed by Co₂B or the hydrolysis byproduct of Al-Li-Co₂B composite. 0.02 g Co₂B presents bad catalytic activity for NaBH₄ hydrolysis, and approximately 50% hydrogen yield is achieved at 120 min, as shown in Fig. 5a. The catalytic activity of 0.02 g Co₂B distributed on the surface of the hydrolysis byproduct of Al-Li-Co₂B composite is improved significantly, and 100% hydrogen yield is achieved within 120 min. The hydrolysis byproducts of Al-Li are Al(OH)₃ and LiAl₂(OH)₇·xH₂O, which exhibit low catalytic activity for NaBH₄ hydrolysis but act as catalyst carriers [19]. The results indicate that Co₂B gradually distributed on Al(OH)₃ and LiAl₂(OH)₇·xH₂O is helpful in accelerating the hydrolysis of NaBH₄.

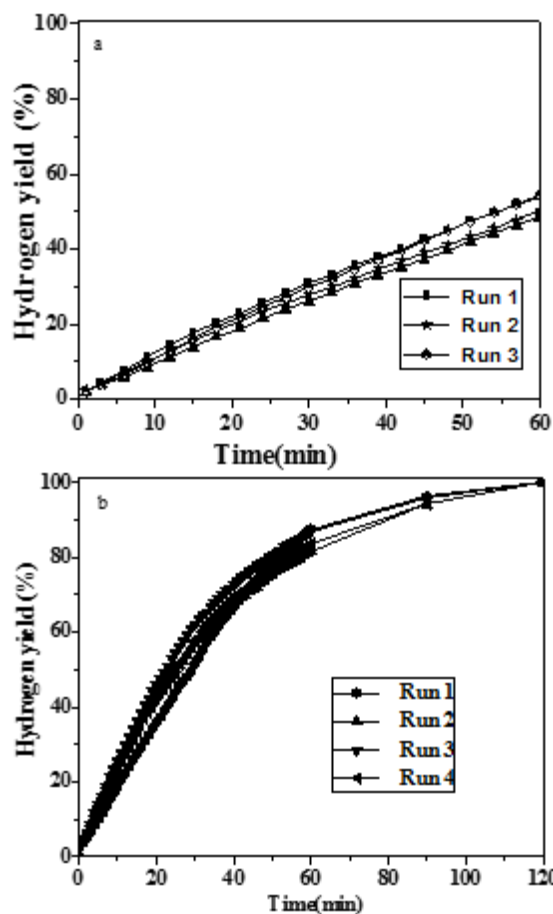


Figure 5. Hydrogen generation curves of NaBH_4 hydrolysis catalyzed by Co_2B (a) or hydrolysis byproducts of $\text{Al-Li-Co}_2\text{B}$ as sample 3 in table 1 (b). Hydrolysis conditions: 0.02 g Co_2B or hydrolysis byproducts of sample 3 including 0.02g Co_2B ; hydrolysis temperature, 323 K; 0.2 g solid-state NaBH_4 and 2 ml water for one run.

3.3. Effect of hydrolysis temperature and milling time

Fig. 6 shows the hydrogen generation curves of $\text{Al-Li-Co}_2\text{B}/\text{NaBH}_4$ system. The hydrogenation rate was collected at different temperatures of 303 K, 313 K, 323 K, and 333 K. The hydrogen generation rate increases, and reaching 100% hydrogen yield needs less time with the increase in temperature. The relative activation energy was calculated to be $17.65 \text{ kJ mol}^{-1}$ based on the highest hydrogen generation rate at different temperatures, as shown in Fig. 6, according to Arrhenius equation and Loser's method [20]. The activation energy is extremely low compared with 53.3 kJ mol^{-1} of Al/NaBH_4 hydrolysis catalyzed by Co nanoparticles and NaAlO_2 solution [21], $37.63 \text{ kJ mol}^{-1}$ of NaBH_4 hydrolysis catalyzed by CoB catalyst supported on carbon nanotubes [9], and $22.57 \text{ kJ mol}^{-1}$ of the Al-Li-Bi-NaCl mixture [22].

Fig. 7 shows the hydrogen generation curves of $\text{Al-Li-Co}_2\text{B}/\text{NaBH}_4$ system with different milling times. The system with 5 h milling time for $\text{Al-Li-Co}_2\text{B}$ obtains 100% hydrogen yield with-

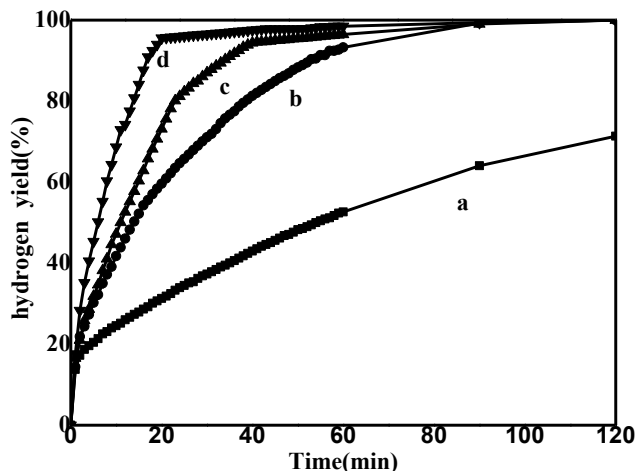


Figure 6. Hydrogen generation curves of $\text{Al-Li-Co}_2\text{B}/\text{NaBH}_4$ system at different temperatures. a, 313 K; b, 323 K; c, 333 K; d, 323 K

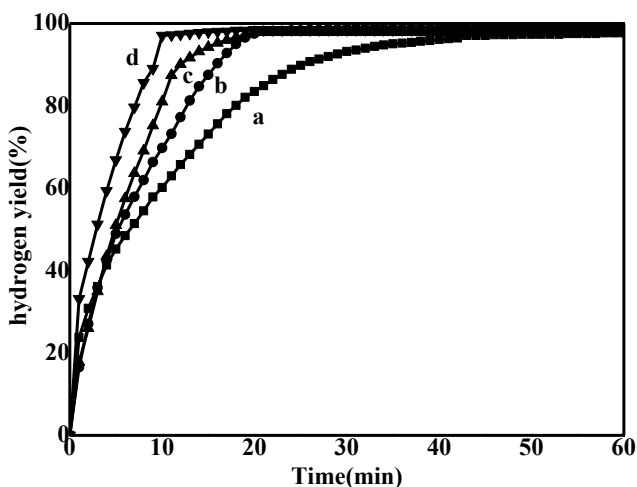


Figure 7. Hydrogen generation curves of $\text{Al-Li-Co}_2\text{B}/\text{NaBH}_4$ system with different milling time. a, 5 h; b, 10 h; c, 15 h; d, 20 h

in 60 min. The hydrogen generation rate of the system significantly increases with the milling time of $\text{Al-Li-Co}_2\text{B}$ composite. The time for hydrogen yield to reach 100% decreases from 40 min to 7 min when milling time for $\text{Al-Li-Co}_2\text{B}$ increases from 5 h to 20 h. The improved hydrogen generation rate is related to the specific surface area of $\text{Al-Li-Co}_2\text{B}$ with different milling times, as shown in Fig. 3. The large specific surface area signifies the large contact surface and high hydrolysis rate of $\text{Al-Li-Co}_2\text{B}/\text{NaBH}_4$ system and water. In addition, small grain size is obtained with long milling time. Fig. 8 shows the XRD patterns of $\text{Al-Li-Co}_2\text{B}$ composite with different milling times. Similar peaks of AlLi , Co_2B , and Al are identified in the XRD patterns of $\text{Al-Li-Co}_2\text{B}$ composite with 5 h, 10 h, 15 h, and 20 h. However, the peaks broaden, particularly at 65° and 78° , reflecting that the grain size decreases as milling time increases. The grain size decreases, and the uniform mixing of $\text{Al-Li-Co}_2\text{B}$

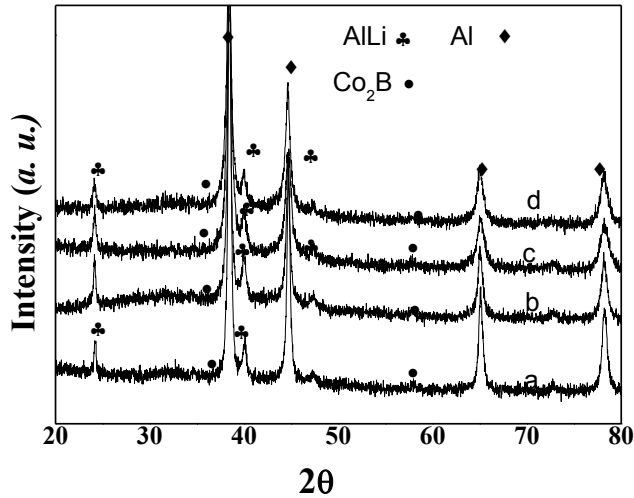


Figure 8. XRD patterns of Al-Li-Co₂B composite with different milling time. a, 5 h; b, 10 h; c, 15 h; d, 20 h

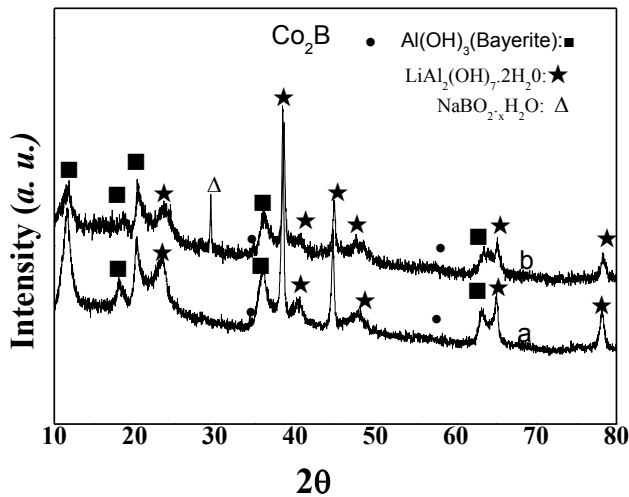


Figure 9. XRD patterns of Al-Li-Co₂B/NaBH₄ system after hydrolysis. a, first hydrolysis; b, successive hydrolysis of NaBH₄

composite presents many paths for the nanostructure formation of AlLi and Co₂B deposited on the Al surface, which can accelerate the hydrolysis of Al and NaBH₄.

3.4. Characterization of Al-Li-Co₂B //NaBH₄ system after hydrolysis

Fig. 9 shows the XRD patterns of Al-Li-Co₂B/NaBH₄ system after hydrolysis. Peaks of Al(OH)₃, LiAl₂(OH)₇·xH₂O and Co₂B are identified in the XRD patterns of the hydrolysis byproduct of Al-Li-Co₂B/NaBH₄ system. The peaks of Al(OH)₃ widen, and the peak at 19° disappears in the XRD patterns of the hydrolysis byproduct of Al-Li-Co₂B/NaBH₄ system after the successive addition of NaBH₄, which is attributed to the dissolution of Al(OH)₃ in the alkaline solution [23]. However, the peaks of LiAl₂(OH)₇·xH₂O lack a significant change after the successive addition of NaBH₄,

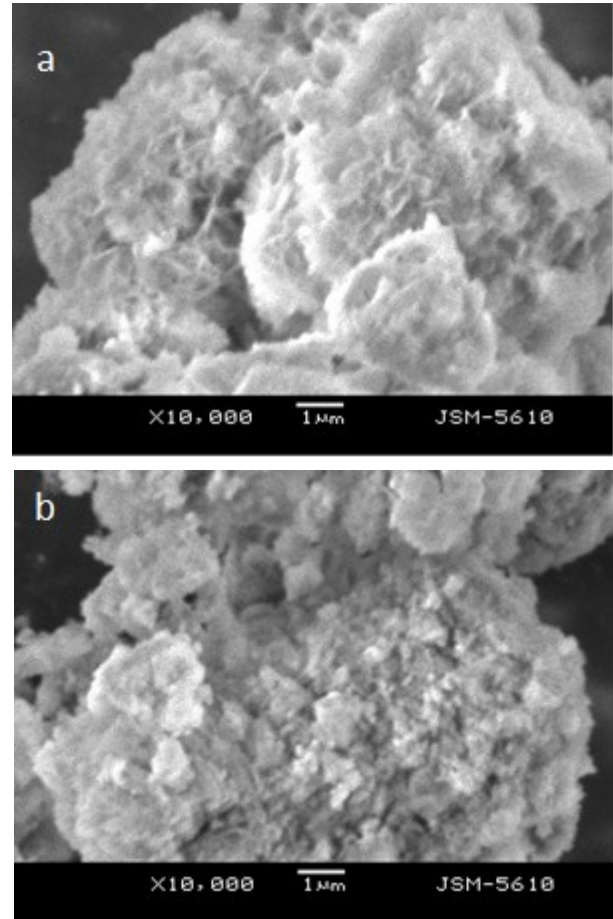


Figure 10. SEM images of Al-Li-Co₂B/NaBH₄ system after hydrolysis. a, first hydrolysis; b, successive hydrolysis of NaBH₄

showing that LiAl₂(OH)₇·xH₂O demonstrates good stability in preventing alkali corrosion. Fig. 10 shows the SEM images of Al-Li-Co₂B /NaBH₄ system after hydrolysis. Cotton-like solids mixed with rod-like solids are observed on the surface of the hydrolysis byproducts of Al-Li-Co₂B/NaBH₄ system. The cotton-like solids significantly disappear, as shown in Fig. 10b, reflecting that the reaction of Al(OH)₃ and the hydrolysis byproduct of NaBH₄ occurs in the hydrolysis process.

The hydrolysis of Al-Li-Co₂B/NaBH₄ system can be described as follows. Al, Li, and NaBH₄ can hydrolyze when they come in contact with water. Co₂B and hydrolysis byproduct LiOH stimulate the continuous hydrolysis of Al and NaBH₄. Co₂B acts as a catalyst for NaBH₄ hydrolysis, and its catalytic activity increases because of the nanostructure formation of Co₂B distributed on the hydrolysis byproduct of Al-Li-Co₂B/NaBH₄ system. Alkali from LiOH solution is a catalyst for Al hydrolysis, and the alkali concentration increases because of the continuous addition of the hydrolysis byproduct of NaBH₄. Co₂B also acts as a cathode to Al, and the microgalvanic cell accelerates the electrochemical corrosion of Al because of the increased alkali concentration. Therefore, the increases in Li concentration, Co₂B concentration, and milling time are helpful for Al/NaBH₄ hydrolysis. The detailed preparation/hydrolysis

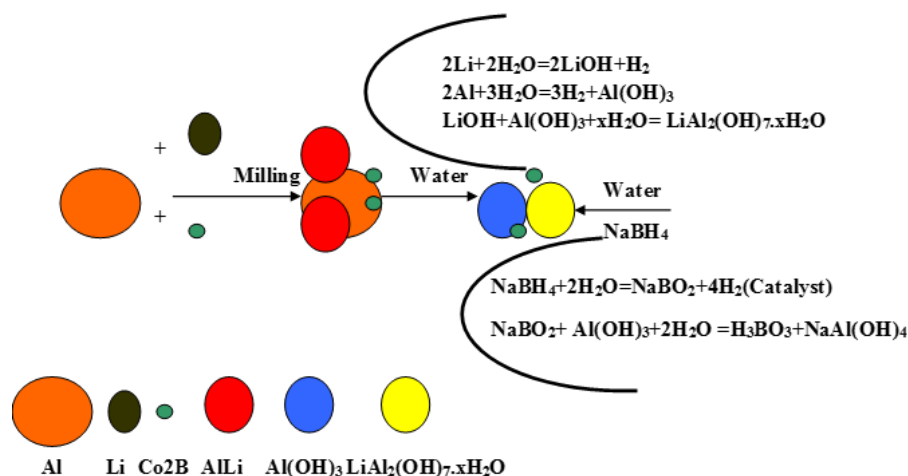


Figure 11. Preparation/hydrolysis schematic diagrams for the Al-Li- $\text{Co}_2\text{B}/\text{NaBH}_4$ system

schematic diagrams for the Al-Li- $\text{Co}_2\text{B}/\text{NaBH}_4$ system can be depicted in Fig. 11.

4. CONCLUSION

The Al-Li- Co_2B composite was prepared through the milling method, and the hydrogen generation performance of Al-Li- $\text{Co}_2\text{B}/\text{NaBH}_4$ system was investigated. Several parameters, including composition designs, hydrolysis conditions, and preparation technologies, were optimized. The hydrogen generation performance of the system improved with the increase in Li concentration, Co_2B concentration, milling time, and hydrolysis temperature. The improvement was attributed to the synergetic effect of LiOH and Co_2B , and their catalytic activity increased because of the synergetic effect of the hydrolysis byproducts of Al/ NaBH_4 system.

5. ACKNOWLEDGMENTS

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