



Original Research

Improvement on hydrogen generation properties of $Zr(BH_4)_4 \cdot 8NH_3$ D.F. Wu^{a,b}, L.Z. Ouyang^{a,c,*}, J.M. Huang^a, J.W. Liu^a, H. Wang^a, X.S. Yang^e, H. Shao^{d,**}, M. Zhu^a^a School of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou, 510641, China^b Guangdong Research Institute of Rare Metals, Guangdong Key Laboratory of Rare Earth, Development and Application, Guangzhou, 510651, China^c China-Australia Joint Laboratory for Energy & Environmental Materials, Key Laboratory of Fuel Cell Technology of Guangdong Province, Guangzhou, 510641, China^d Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering (IAPME), University of Macau, Macau SAR, China^e Advanced Manufacturing Technology Research Centre, Department of Industrial and, Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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ABSTRACT

Hydrolysis of $Zr(BH_4)_4 \cdot 8NH_3$ in deionized water can generate high purity hydrogen at room temperature. However, the sluggish hydrolysis kinetics of $Zr(BH_4)_4 \cdot 8NH_3$ hinders its practical use. To improve its hydrogen generation properties, the effects of magnetic stirring, changing hydrolysis solution and tuning the ammonia coordination number on the hydrolysis properties of $Zr(BH_4)_4 \cdot 8NH_3$ were investigated. Results show that both changing hydrolysis solution and tuning the ammonia coordination number can enhance the hydrolysis kinetics. The hydrolysis kinetics properties of $Zr(BH_4)_4 \cdot 8NH_3$ were significantly improved in $MgCl_2$ and $CoCl_2$ solutions. The $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) samples were synthesized by a ball-milling method with different ammonization time (10, 60 and 180 min). Both the hydrolysis kinetics and hydrogen yield of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) were enhanced as the ammonia coordination number (x) decreased. Thus, tuning ammonia coordination number is an effective way to control the hydrolysis properties of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$).

1. Introduction

Hydrogen is regarded as one of the most promising energy carrier in future energy systems [1,2], due to its high energy density, lightweight and green products. To realize large-scale utilization of hydrogen energy, one of the most critical challenges is to develop suitable ways to store hydrogen. In the past decades, researchers have devoted tremendous efforts to develop a safe, lightweight, and economical hydrogen storage material with moderate operating temperatures. Metal based hydrides, complex hydrides, and carbon materials have been widely investigated as potential hydrogen storage materials [3–5], but unfortunately none of them can meet all the requirements for hydrogen storage system.

In recent years, borohydrides have been extensively studied as promising hydrogen storage candidates due to the high hydrogen capacity and adjustable dehydrogenation conditions [6,7]. The main

drawbacks of borohydrides are the high dehydrogenation temperature and the release of toxic boranes. Studies show that forming borohydride ammoniates is a useful way to regulate the dehydrogenation properties of borohydrides [8–10].

A new borohydride ammoniate, $Zr(BH_4)_4 \cdot 8NH_3$ was reported and considered as a potential hydrogen storage material [11]. With the highest ammonia coordination number ($x = 8$), $Zr(BH_4)_4 \cdot 8NH_3$ has high hydrogen capacity (14.1 wt%) and low dehydrogenation temperature (around 130 °C). However, $Zr(BH_4)_4 \cdot 8NH_3$ suffers from releasing ammonia during the dehydrogenation process, which might be due to its high ammonia coordination number. To suppress the release of ammonia, many additives including NH_3BH_3 , $LiBH_4$ and $Mg(BH_4)_2$ have been studied [12,13]. Recently, Wu et al. reported that hydrolysis of $Zr(BH_4)_4 \cdot 8NH_3$ was also an effective way to thoroughly suppress the release of ammonia [14]. $Zr(BH_4)_4 \cdot 8NH_3$ could react with deionized water at room temperature and release about 1067 mL/g H_2 in 240 min,

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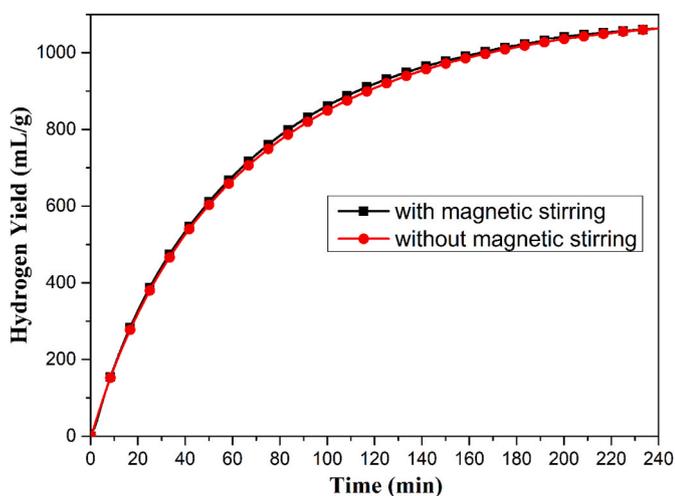


Fig. 1. Hydrogen evolution curves of $Zr(BH_4)_4 \cdot 8NH_3$ with or without magnetic stirring.

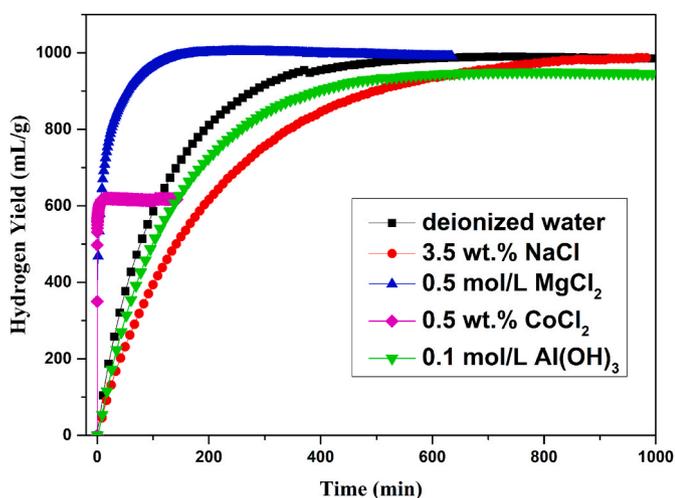
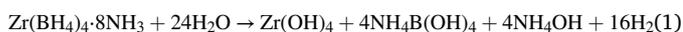


Fig. 2. Hydrogen evolution curves of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions (deionized water, 3.5 wt.% NaCl, 0.5 mol/L $MgCl_2$, 0.5 wt.% $CoCl_2$ and 0.1 mol/L $Al(OH)_3$).

without releasing any toxic diborane or ammonia impurity gases. Furthermore, the hydrolysis mechanism of $Zr(BH_4)_4 \cdot 8NH_3$ was clarified as a three-step process: 1) $Zr(BH_4)_4 \cdot 8NH_3$ reacted with H_2O to form $Zr(BH_4)_4$ and NH_4OH ; and then 2) $Zr(BH_4)_4$ reacted with H_2O to form $Zr(OH)_4$, $B(OH)_3$ and H_2 ; finally, 3) $B(OH)_3$ reacted with NH_4OH to form $NH_4B(OH)_4$. The hydrolysis equation could be summarized as:



By hydrolysis reaction, $Zr(BH_4)_4 \cdot 8NH_3$ could thoroughly suppress the release of ammonia and generate pure hydrogen at room temperature. However, the hydrolysis kinetics of $Zr(BH_4)_4 \cdot 8NH_3$ was sluggish. To improve the hydrolysis kinetics, the effects of magnetic stirring, changing hydrolysis solution and tuning the ammonia coordination number on the hydrolysis properties of $Zr(BH_4)_4 \cdot 8NH_3$ were studied in this work.

2. Experimental

2.1. Preparation

$LiBH_4$ (98%, Sigma-Aldrich), $ZrCl_4$ (99.5%, Alfa Aesar), $NaCl$ (AR,

Aladdin), $MgCl_2$ (99%, Alfa Aesar), $CoCl_2 \cdot 6H_2O$ (AR, Aladdin), $Al(OH)_3$ (AR, Tianjin Damao Chemical Reagent Factory) and NH_3 (99.9%, Guangdong Huate Gas Co.) were used as raw materials.

$Zr(BH_4)_4 \cdot 8NH_3$ was prepared by a ball-milling method. Firstly, $Zr(BH_4)_4$ was synthesized by ball milling $LiBH_4$ and $ZrCl_4$ using a planetary ball mill. Due to its volatility, $Zr(BH_4)_4$ sublimated and deposited on the lid of the ball mill pot during ball milling process. Then, $Zr(BH_4)_4$ was transported into a tube and exposed to ammonia. Finally, $Zr(BH_4)_4 \cdot 8NH_3$ was synthesized as a white powder after ammonization for 8 h. The detailed preparation process was shown in Ref. [11].

$Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) samples were also prepared by a similar ball-milling method, but the ammonization time was reduced to 10, 60 and 180 min. The product powders with different ammonization time (10, 60 and 180 min) were named as S1, S2 and S3, respectively. All handling was operated in a glove box equipped with a recirculation system, which may keep the water and oxygen concentrations below 1 and 5 ppm, respectively.

2.2. Hydrolysis test

The hydrogen generation properties of $Zr(BH_4)_4 \cdot 8NH_3$ in different situations (with magnetic stirring, in different hydrolysis solutions and with different ammonia coordination number) were performed using in our house-made hydrolysis equipment [14]. Around 0.1 g sample was loaded in a 50 mL flask, and then 10 mL hydrolysis solution was injected for hydrolysis. During the process, the generated hydrogen pushed water from Monteggia washing bottle into a beaker, and then the data of exhausting water mass against time were collected. Finally, the hydrogen evolution curves were drawn, and the hydrolysis properties could be evaluated.

2.3. Characterization

The phases of hydrolysis byproducts of $Zr(BH_4)_4 \cdot 8NH_3$ in different situations were indexed by X-ray diffraction (XRD, PANalytical) with $Cu-K\alpha$ radiation. Prior to XRD test, the hydrolysis byproducts were dried by a freeze-drying machine (ALPHA 1–2, GHRIST). All the samples for measurement were loaded on our home-made XRD protective device to protect them from exposure to air.

The SEM pictures of $Zr(BH_4)_4 \cdot xNH_3$ (sample S1, S2 and S3) were studied by field emission scanning electron microscopy (FE-SEM, Zeiss-Supra 40). The chemical bonds of $Zr(BH_4)_4 \cdot xNH_3$ were determined by a Fourier transform infrared spectrometer (FT-IR, NICOLET) using KBr pellets, in the range of $500\text{--}4000\text{ cm}^{-1}$ with 32 scans.

3. Results and discussion

3.1. Hydrogen properties of $Zr(BH_4)_4 \cdot 8NH_3$ with magnetic stirring

Magnetic stirring is one of the most common methods to improve the hydrolysis kinetics. Thus, the effect of magnetic stirring (Model CJJ 78–1, JiTe Experimental Instrument) on the hydrogen properties of $Zr(BH_4)_4 \cdot 8NH_3$ was studied. Fig. 1 presents the hydrogen evolution curves of $Zr(BH_4)_4 \cdot 8NH_3$ with or without magnetic stirring. Results show that magnetic stirring had little improvement to enhance the hydrolysis kinetics. Hence, it can be assumed that the decomposition of $Zr(BH_4)_4 \cdot 8NH_3$ is the rate-limiting step in the hydrolysis process of $Zr(BH_4)_4 \cdot 8NH_3$. In other word, the decomposition rate of $Zr(BH_4)_4 \cdot 8NH_3$ is a key factor affecting the hydrolysis performance. Changing the hydrolysis solution or tuning the ammonia coordination number of $Zr(BH_4)_4 \cdot 8NH_3$ may enhance the decomposition rate of $Zr(BH_4)_4 \cdot 8NH_3$, and then improve its hydrolysis kinetics.

3.2. Hydrolysis properties of $Zr(BH_4)_4 \cdot 8NH_3$ in different solutions

To verify the effects of changing the hydrolysis solution, the

Table 1

Hydrolysis performance data of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions (deionized water, 3.5 wt% NaCl, 0.5 mol/L $MgCl_2$, 0.5 wt% $CoCl_2$ and 0.1 mol/L $Al(OH)_3$).

Hydrolysis solution	Hydrogen yield in 10 min (mL/g H_2)	Hydrogen yield in 30 min (mL/g H_2)	Hydrolysis time (min)	Final hydrogen yield (mL/g H_2)
Deionized water	99	245	600	1000
3.5 wt% NaCl	53	152	800	1000
0.5 mol/L $MgCl_2$	669	821	120	1000
0.5 wt% $CoCl_2$	600	600	<2	600
0.1 mol/L $Al(OH)_3$	63	196	600	980

hydrolysis properties of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions (deionized water, NaCl, $MgCl_2$, $CoCl_2$ and $Al(OH)_3$) were studied. Among these solutions, NaCl, $MgCl_2$ and $CoCl_2$ are common additives to improve the hydrolysis properties of MgH_2 and $NaBH_4$, and $Al(OH)_3$ is an amphoteric hydroxide that may affect the pH in the hydrolysis solution.

Fig. 2 exhibits the hydrogen evolution curves of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions (deionized water, 3.5 wt% NaCl, 0.5 mol/L $MgCl_2$, 0.5 wt% $CoCl_2$ and 0.1 mol/L $Al(OH)_3$). As shown in Fig. 2, it

took 600, 120 and 800 min for $Zr(BH_4)_4 \cdot 8NH_3$ to generate 1000 mL/g H_2 in deionized water, $MgCl_2$ and NaCl solutions, respectively. Compared to that in deionized water, the hydrolysis kinetics was significantly improved in $MgCl_2$ solution but became worse in NaCl solution. It took less than 2 min to generate 600 mL/g H_2 in $CoCl_2$ solution. Thus, the hydrolysis rate in $CoCl_2$ solution was quite fast but the hydrogen yield was significantly reduced. Finally, it took 600 min to generate 980 mL/g H_2 in the $Al(OH)_3$ solution, implying both the hydrolysis kinetics and yield got worse. In summary, the hydrolysis kinetic properties of $Zr(BH_4)_4 \cdot 8NH_3$ were improved in the $MgCl_2$ and $CoCl_2$ solutions, however the hydrogen yield was reduced in the $CoCl_2$ solution. The hydrolysis performance data of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions are summarized in Table 1.

To elucidate the hydrolysis mechanisms of $Zr(BH_4)_4 \cdot 8NH_3$ in different hydrolysis solutions, the hydrolysis byproducts were collected and analyzed. Fig. 3 shows the XRD patterns of the hydrolysis byproducts of $Zr(BH_4)_4 \cdot 8NH_3$ in (a) 3.5 wt% NaCl, (b) 0.5 mol/L $MgCl_2$, (c) 0.5 wt% $CoCl_2$ (inset: picture of the hydrolysis byproduct solution) and (d) 0.1 mol/L $Al(OH)_3$ solutions.

As shown in Fig. 3(a) and (b), the hydrolysis byproduct in 3.5 wt% NaCl solution was mainly unreacted NaCl, while the byproduct in 0.5 mol/L $MgCl_2$ solution was composed of $MgCl_2(H_2O)_6$ and $NH_4(Mg(H_2O)_6)Cl_3$. The poor hydrolysis kinetics in NaCl solution may be ascribed to the salt-effect of NaCl. Due to the decomposition of NaCl, the average ionization degree of NH_4OH (intermediate product in the first step of hydrolysis mechanism of $Zr(BH_4)_4 \cdot 8NH_3$) was raised, resulting in higher pH in the solution and worse hydrolysis kinetics. By contrast,

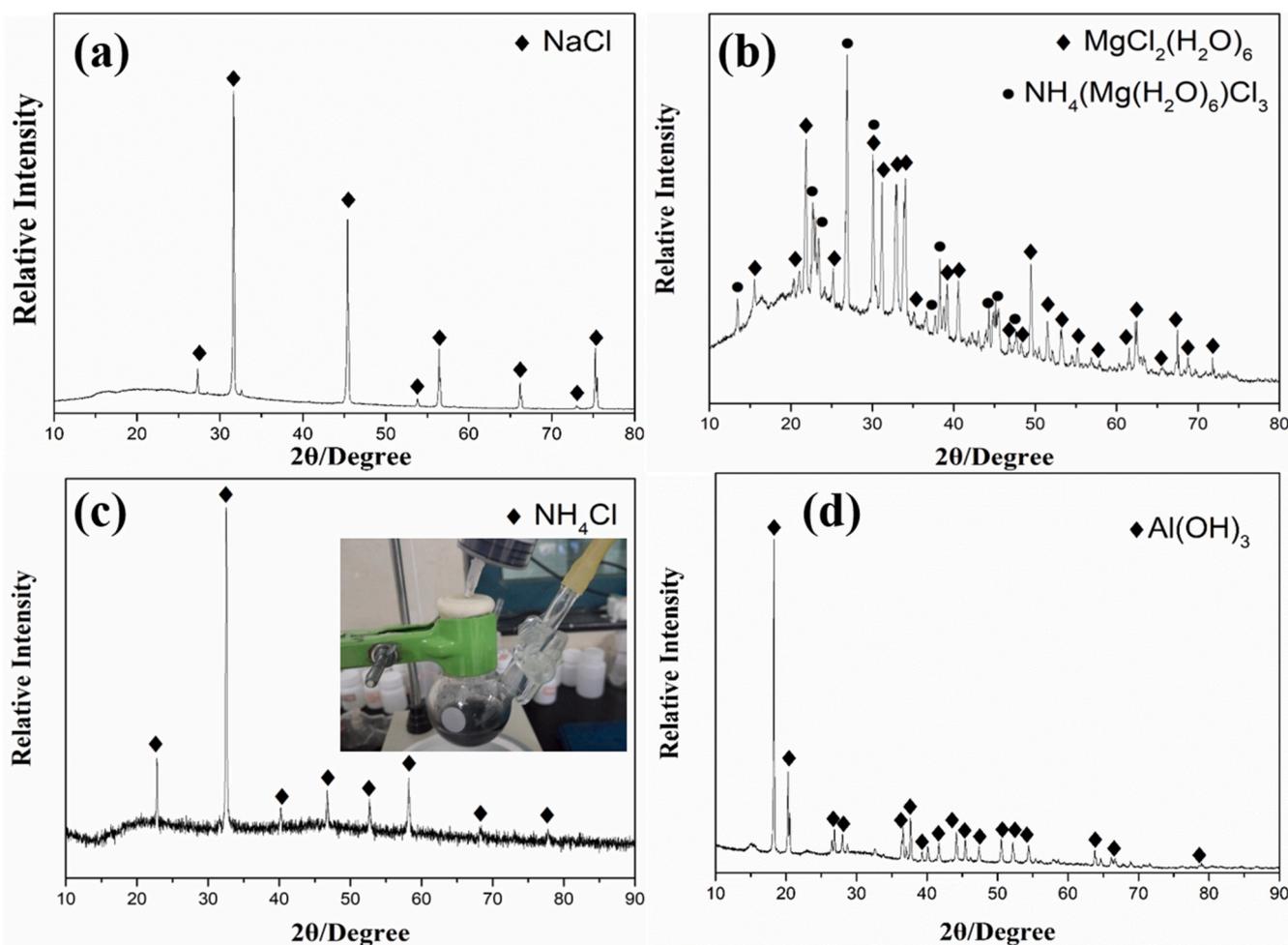


Fig. 3. XRD patterns of the hydrolysis byproducts of $Zr(BH_4)_4 \cdot 8NH_3$ in (a) 3.5 wt% NaCl, (b) 0.5 mol/L $MgCl_2$, (c) 0.5 wt% $CoCl_2$ (inset: picture of the hydrolysis byproduct solution) and (d) 0.1 mol/L $Al(OH)_3$ solutions.

Table 2Theoretical hydrogen yields of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$).

Ammonia coordinate number (x)	8	7	6	5	4	3	2	1
Theoretical hydrogen yield (mL/g H ₂).	1252	1332	1422	1525	1643	1782	1946	2144

particles, consequently the hydrolysis byproduct solution showed a black color. According to its hydrolysis mechanism, the theoretical hydrogen yield of $Zr(BH_4)_4 \cdot 8NH_3$ in $CoCl_2$ solution should be 626 mL/g H₂, which is closed to the observed hydrogen yield, as Fig. 2 shows.

Finally, the hydrolysis byproduct in 0.1 mol/L $Al(OH)_3$ solution was unreacted $Al(OH)_3$, as shown in Fig. 3(d). $Al(OH)_3$ could reduce the pH only in strong alkaline solution (pH > 12), but the pH in hydrolysis solution of $Zr(BH_4)_4 \cdot 8NH_3$ in deionized water was only 10.5 [14]. Thus, $Al(OH)_3$ did not reduce the pH but suppressed the hydrolysis reaction of $Zr(BH_4)_4 \cdot 8NH_3$.

3.3. Hydrolysis properties of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$)

To test the effect of tuning the ammonia coordination number on the hydrolysis performance, $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) were prepared by a ball-milling method with different ammonization time (10, 60 and 180 min), as shown in Fig. 4. The product powders S1, S2 and S3 were determined by XRD (Fig. 5). Results show that S1 was composed of mixture of $Zr(BH_4)_4$ and $Zr(BH_4)_4 \cdot 3NH_3$, while S2 and S3 were $Zr(BH_4)_4 \cdot 3NH_3$ and $Zr(BH_4)_4 \cdot 8NH_3$, respectively. Thus, the ammonia coordinate number (x) of S1, S2 and S3 were $x < 3$, $x = 3$ and $x = 8$, respectively.

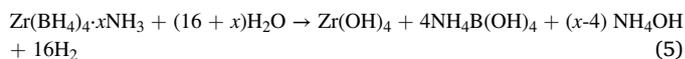
Fig. 6 presents the FT-IR results of S1, S2 and S3. As shown in Fig. 6, S1, S2 and S3 had the same infrared absorption peak positions corresponding to the B–H bonds (stretching: 2180–2470 cm^{-1} ; bending: 1080 cm^{-1}) and N–H bonds (stretching: 2950–3330 cm^{-1} ; bending: 1405 cm^{-1}), indicating that they all had B–H and N–H bonds. However, as the ammonia coordinate number (x) decreased, the shape of infrared absorption peaks became broader.

SEM pictures of $Zr(BH_4)_4 \cdot xNH_3$ (sample S1, S2 and S3) were tested to measure their particle sizes. As Fig. 7 shown, the particle size of $Zr(BH_4)_4 \cdot 8NH_3$ (S3) is about 2–4 μm . The particle sizes of S1 and S2 may be less than S3. However, due to S1 and S2 were very volatility in air, we failed to measure their particle sizes. When S1 and S2 were exposed to the air, they reacted with moisture and produced white smoke immediately.

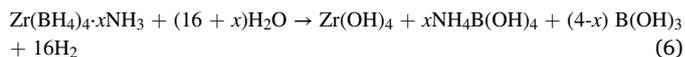
To evaluate the hydrolysis properties of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$), S1, S2 and S3 were hydrolyzed in deionized water at room temperature. Fig. 8 presents the hydrogen evolution curves of S1, S2 and S3. As seen in Fig. 8, the hydrolysis kinetics was significantly improved as the ammonia coordinate number (x) decreased. The hydrogen yields of S1, S2 and S3 in 10 min were 1380, 644, and 222 mL/g H₂, respectively. Interestingly, the final hydrogen yields were also boosted as the ammonia coordinate number (x) decreased. The final hydrogen yields of S1, S2 and S3 were 1495, 1174 and 1054 mL/g H₂, respectively. Thus, tuning the ammonia coordinate number (x) can not only regulate the hydrolysis kinetics but also tailor the hydrogen yield.

The improvements of hydrolysis properties are clarified by the hydrolysis mechanism of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$), as shown in Fig. 9. $Zr(BH_4)_4$ and NH_3 in $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) have different functions in the hydrolysis process: the former provides H^- to form H₂, while the latter combines with water and forms NH_4OH , which can regulate the hydrolysis rate. Consequently, reducing the ammonia coordinate number (x) has two effects: on one side, raising the percentage of $Zr(BH_4)_4$ in $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$), which leads to higher hydrogen yield; on the other side, producing less NH_4OH , which results in more H^+ in solution and faster hydrolysis kinetics. Thus, as the ammonia coordinate number (x) decreased, both the hydrogen yield and the hydrolysis kinetics were improved in the $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) samples.

If $4 = x \leq 8$, then



If $0 < x < 4$, then



Then the theoretical hydrogen yields of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) can be calculated, as shown in Table 2. As the ammonia coordinate number (x) decreased from 8 to 1, the theoretical hydrogen yields remarkably raised from 1252 to 2144 mL/g H₂, which was basically in agreement with the experimental results. In conclusion, tuning the ammonia coordinate number (x) is a useful way to control the hydrolysis properties of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$).

4. Conclusions

The effects of magnetic stirring, changing hydrolysis solution and tuning the ammonia coordination number on the hydrolysis properties of $Zr(BH_4)_4 \cdot 8NH_3$ were investigated. Results show that magnetic stirring had little effect on enhancing the hydrolysis kinetics of $Zr(BH_4)_4 \cdot 8NH_3$. The hydrolysis kinetic properties of $Zr(BH_4)_4 \cdot 8NH_3$ were improved in $MgCl_2$ and $CoCl_2$ solutions, but the hydrogen yield was reduced in the $CoCl_2$ solution. $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) samples were prepared by a ball-milling method with different ammonization time (10, 60 and 180 min). Both the hydrolysis kinetics and hydrogen yield of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$) were significantly improved as the ammonia coordinate number (x) decreased. Thus, tuning ammonia coordination number (x) is an effective way to control the hydrolysis properties of $Zr(BH_4)_4 \cdot xNH_3$ ($x \leq 8$).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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