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Article

Effects of graphitic carbon nitride on the dehydrogenation of ammonia borane

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ABSTRACT

By ball milling carbon nitride (C_3N_4) and ammonia borane (AB), the AB- C_3N_4 system was successfully synthesized. It is shown that the dehydrogenation temperature of the AB- C_3N_4 system was obviously decreased. However, the concentration of byproduct ammonia was much higher than that of pristine AB. Thus, $LiBH_4$ -modified C_3N_4 (LC_3N_4) was produced and employed to synthesize a AB- LC_3N_4 system. The dehydrogenation of the AB- LC_3N_4 system was investigated using X-ray diffraction, temperature-programmed desorption-mass spectrometry, thermogravimetry-differential thermal analysis, and nuclear magnetic resonance. The results show that the dehydrogenation temperatures of the AB- LC_3N_4 systems were reduced to a lower region compared with pristine AB. Moreover, byproduct borazine and the induction period were significantly suppressed. After $LiBH_4$ modification on C_3N_4 , the other byproduct ammonia was also reduced in the dehydrogenation process. Dynamic analysis and NMR characterization results show that the decomposition mechanism of AB- LC_3N_4 still follows the self-decomposition of AB, which is induced by the formation of $NH_3BH_2NH_3BH_4$.

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1. Introduction

With the rapid development of global economy, the increasingly scarce fossil resource cannot meet the growing needs for energy. Due to the advantages of cleaning, abundance, high energy, and high efficiency, hydrogen as an energy carrier has been highly expected. However, developing highly efficient onboard hydrogen storage systems, as well as providing safe and reliable hydrogen sources for the vehicle fuel cell, is one of the bottlenecks on restricting the industrial application of hydrogen. It was found that the most effective and safest method for onboard hydrogen storage is to store the hydrogen

in solid media, such as physical adsorption [1], metal hydride [2], and chemical hydride materials [3], etc. Ammonia borane (AB) has been paid great attention due to its high weight density (19.6 wt%) and volume density (145 g/L) of hydrogen [4]. However, the disadvantages of this material are dehydrogenation at high temperature, producing poison byproducts (such as ammonia, borane, and borazine ($N_3B_3H_6$)), as well as sample foaming after dehydrogenation [4,5]. Based on these disadvantages, modifications on AB were made from the following aspects: dispersing AB into the support with large surface area [6], using transition metal catalysts to catalyze the dehydrogenation [7,8], thermal decomposition in an ionic liquid [9], and

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dehydrogenation catalyzed by acid-base catalysts [10]. These methods have certain positive effects on the dehydrogenation of AB, either decreasing the dehydrogenation temperature or suppressing the production of by-products. Even though, none of these methods could absolutely overcome the entire shortcomings. Neiner et al. [11] found that AB modified with nano boron nitride (BN) can significantly decrease the dehydrogenation temperature, obviously reduce the induction period, and lower the exothermicity of hydrogen release. However, they also found that byproduct borazine increased obviously during dehydrogenation. Feaver et al. [12] dispersed AB into porous carbon cryogel to obtain a coherent carbon cryogel-ammonia borane composite, which significantly reduced the dehydrogenation temperature and activation energy during hydrogen release. Zhao et al. [13] synthesized a novel water-resistant material by confining AB in poly(methyl acrylate) (PMA). It efficiently lowered the dehydrogenation temperature and suppressed the production of borazine. Therefore, we can conclude that C- and N-based materials can efficiently promote the dehydrogenation of AB.

In this paper, we synthesized carbon nitride (C_3N_4) and modified AB with C_3N_4 . It is shown that adding C_3N_4 can reduce the dehydrogenation temperature, accelerate the dehydrogenation rate, and suppress the generation of byproduct borazine. However, the NH_3 concentration slightly increases during hydrogen release in C_3N_4 -modified AB. Therefore, we further modified C_3N_4 with $LiBH_4$ and found that this can efficiently reduce the concentration of ammonia during dehydrogenation.

2. Experimental

2.1. Preparation of AB, C_3N_4 , and $xAB-yLC_3N_4$ composite system

AB was synthesized using the method in the literature [14]. C_3N_4 was prepared by modifying the method in Ref. [15]. Cyanamide (98%, Alfa-Aesar, 2 g) was heated under nitrogen flow up to 350 °C keeping for 3 h, and then the temperature was increased to 390 °C keeping for 4 h, then continually increased to 550 °C keeping for 4 h, and then cooled at room temperature. All the heating rates were 1 °C/min. The as-obtained yellow solid was C_3N_4 .

For the preparation of the AB and $LiBH_4$ -modified C_3N_4 composite, 123 mg $LiBH_4$ and 1.23 g C_3N_4 were mixed and milled in a Planetary Ball Mills (Retsch, PM400) for 5 h (200 r/min). The mixture was treated under argon atmosphere at 300 °C for 2 h. The obtained $LiBH_4$ -modified C_3N_4 was named LC_3N_4 . Three $xAB-yLC_3N_4$ composite samples were obtained by milling the mixture of AB and LC_3N_4 with mass ratios ($x:y$) of 2:1, 1:1, and 1:2, respectively, for 24 h.

2.2. Dehydrogenation performance test of AB, C_3N_4 , and $xAB-yLC_3N_4$

A homemade temperature-programmed desorption-mass spectrometry (TPD-MS) combined system was employed to detect dehydrogenation of AB and $xAB-yLC_3N_4$. The sample was heated under argon at 2 °C/min up to 400 °C. The gaseous

products from the dehydrogenation of AB and $xAB-yLC_3N_4$ were detected by an on-line mass spectrometer.

Volumetric release measurements of hydrogen desorption from samples were performed on a homemade apparatus. In a glove box, a certain amount of AB or $xAB-yLC_3N_4$ was weighted on the bottom of the reactor and sealed. The reactor was then put in a pre-heated furnace at 75 °C. At the same time, the pressure sensor was turned on to detect the dehydrogenation process. The volume of hydrogen desorption was calculated based on the ideal gas equation.

After dehydrogenation, the gases were slowly imported to a prepared dilute sulphuric acid solution. By recording the variation of conductivity of the dilute sulphuric acid solution and the quantity of imported gases, the concentration of NH_3 in the produced gases can be calculated.

2.3. Characterization of AB, C_3N_4 , and $xAB-yLC_3N_4$

The crystal structures of AB, C_3N_4 , and $xAB-yLC_3N_4$ were obtained on a PANalytical X-ray diffractometer (XRD) with Cu K_α radiation (40 kV, 40 mA) in the range of 5°–80°.

Thermogravimetry-differential thermal analysis (TG-DTA) measurements were conducted on an STA449C thermal analyzer (Netzsch). The samples were heated under purified argon at 2 °C/min up to 400 °C.

^{11}B and ^{13}C MAS NMR measurements were carried out on a Bruker Avance 500 NMR spectrometer (11.7 T) with a frequency of 160.5 and 125.76 MHz, respectively. $LiBH_4$ and glycine were used as chemical shift references.

3. Results and discussion

3.1. Dehydrogenation performance test and characterization

The synthesized AB and C_3N_4 were mixed with the mass ratio of 1:1 and milled to obtain an AB- C_3N_4 sample. Figure 1 shows the TPD-MS spectra of pristine AB and AB- C_3N_4 . It can be seen that there are two steps for the dehydrogenation of AB

Fig. 1. TPD-MS curves of pristine AB and AB- C_3N_4 samples.

from room temperature to 250 °C. The peak temperatures of desorption from AB are 112 and 160 °C, respectively, which are consistent with the literature [4,5]. However, the dehydrogenation temperature of AB-C₃N₄ in the first step decreases to 105 °C, suggesting that adding C₃N₄ can obviously promote the dehydrogenation of AB. In the second step, the peak of dehydrogenation becomes broad and centers at 152 °C. This broadening is probably caused by the formation of different decomposition products during AB-C₃N₄ dehydrogenation in the first step. It is worth noting that adding C₃N₄ obviously suppressed the generation of byproduct borazine, which is harmful to fuel cells. However, the content of another byproduct, NH₃, increased obviously. There might be a certain amount of -NH₂ or -NH groups in synthesized C₃N₄. During the interaction, these groups replace NH₃ in AB, which results in the increased NH₃ content in the system. The elemental analysis results show that the composition of synthesized C₃N₄ is C₃N_{5.4}H_{0.2}. The N-H vibrating peak at 3070–3310 cm⁻¹ was also observed in the FT-IR spectrum of C₃N₄, which further confirms the existence of -NH₂ or -NH groups.

It was reported that hydride or borohydride can interact with amide, so that NH₃ concentration can be reduced in gas productions during amide decomposition by adding hydride or borohydride [3,16]. In order to decrease the NH₃ concentration in the dehydrogenation of AB-C₃N₄, we first synthesized LC₃N₄ by modifying C₃N₄ with LiBH₄. LC₃N₄ was then composited with AB through ball milling to obtain xAB-yLC₃N₄ with three different AB to LC₃N₄ mass ratios, 2:1, 1:1, and 1:2, named as 2AB-1LC₃N₄, 1AB-1LC₃N₄, and 1AB-2LC₃N₄, respectively.

Figure 2 displays the XRD patterns of all the synthesized materials. There is a weak peak at 13.2° shown in the XRD spectrum of C₃N₄. The strongest peak is at 27.2°, which is attributed to the (002) reflection of *g*-C₃N₄ [17]. The characteristic diffraction of AB appears in both of 1AB-1LC₃N₄ and 2AB-1LC₃N₄, which demonstrates that AB exists in the composites after ball milling. With reducing the content of AB, the intensity of the corresponding peak gradually decreased. Interestingly, it is found that around 1.2 equivalent gas/AB are released from 1AB-2LC₃N₄ after ball milling. The gas is mainly consisted of hydrogen and a small amount of B₂H₆ confirmed

Fig. 2. XRD patterns of the as-prepared C₃N₄, pristine AB, 2AB-1LC₃N₄, 1AB-1LC₃N₄, and 1AB-2LC₃N₄ samples.

Fig. 3. TPD-MS curves of pristine AB, 2AB-1LC₃N₄, 1AB-1LC₃N₄, and 1AB-2LC₃N₄ samples.

by MS. While, no gas was detected in the two other samples. All the reflections disappeared in the XRD spectrum of sample 1AB-2LC₃N₄, which means that it presents amorphous state.

The dehydrogenation performance of the samples was detected by TPD-MS, which are shown in Fig. 3. In the first step, dehydrogenation temperature of AB, 2AB-1LC₃N₄, and 1AB-1LC₃N₄ is 112, 105, and 101 °C, respectively. It is obvious that the dehydrogenation temperature decreases with increasing the content of LC₃N₄. In addition, after modification by LiBH₄, it is strengthened for C₃N₄ promoting the dehydrogenation of AB. It is worth mentioning that the addition of LC₃N₄ also suppressed the generation of byproduct borazine. In the TPD-MS spectrum of 1AB-2LC₃N₄, the signal of dehydrogenation almost disappeared, which is attributed to the hydrogen release during the ball milling process. Most importantly, compared with AB-C₃N₄, the content of NH₃ produced during the dehydrogenation of 1AB-1LC₃N₄ and 2AB-1LC₃N₄ decreased significantly.

To detect the quantity of dehydrogenation, volumetric hydrogen release measurements were carried out at 75 °C (shown in Fig. 4). We found that the decomposition of AB at 75 °C has to experience an induction period and release 0.9 equivalents H₂/AB within 12 h, which is in good agreement with the DADB induction mechanism in AB self-decomposition [18]. Because hydrogen was released during the ball milling process, only a small amount of hydrogen was detected in the dehydrogenation of 1AB-2LC₃N₄ at 75 °C. In 1AB-1LC₃N₄ and 2AB-1LC₃N₄ systems, the induction period and dehydrogenation time were obviously shortened. It took 5.6 h for AB to release 0.6 equivalents H₂/AB, while to release the same amount of hydrogen, only 4.5 h and 3.4 h were needed for 1AB-1LC₃N₄

Fig. 4. Volumetric hydrogen release measurements at 75 °C on the pristine AB, 2AB-1LC₃N₄, 1AB-1LC₃N₄, and 1AB-2LC₃N₄ samples.

and 2AB-1LC₃N₄, respectively. Although adding LC₃N₄ can efficiently shorten the induction time during AB dehydrogenation, it is clear that the hydrogen release of α AB- γ LC₃N₄ is keeping S type of curve. It means that the decomposition of α AB- γ LC₃N₄ may still follow the DADB induction mechanism in the self-decomposition of AB. In addition, as shown in Table 1, the concentrations of NH₃ in 1AB-1LC₃N₄ and 2AB-1LC₃N₄ systems are 1.13% and 2.59%, respectively, which are higher than that in AB but greatly lower than that in the AB-C₃N₄ system.

Figure 5 displays TG-DTA profiles of the samples. As shown, the first endothermic peak of AB is caused by the melting of AB. The second exothermic peak is conducted to hydrogen release of AB. The dehydrogenation temperature is 109 °C, which is identical with the results of TPD. When AB was treated at 180 °C, the mass loss is about 49.1%, whereas 2AB-1LC₃N₄ and 1AB-1LC₃N₄ lost around 20.1% and 11.9% in mass, respectively. If calculated based on AB, the mass of 2AB-1LC₃N₄ and 1AB-1LC₃N₄ lost 30.1% and 23.8%, respectively. This means although more NH₃ was produced in the α AB- γ LC₃N₄ system, this system suppressed other byproducts (such as borazine) more efficiently. It is worth noting that no endothermic peak of AB melting was detected in 2AB-1LC₃N₄ and 1AB-1LC₃N₄ systems. Because adding LC₃N₄ can decrease the dehydrogenation temperature of AB, the dehydrogenation temperatures of 2AB-1LC₃N₄ and 1AB-1LC₃N₄ may be below the melting pointing, which damages the crystal structure of AB before melting.

After decomposition, AB turns to be an amorphous material. Any structure information from an XRD pattern cannot be obtained. Thus, this paper characterized and modified AB using NMR technique. Figure 6 and Figure 7 display the ¹¹B and ¹³C MAS NMR spectra of all the samples before and after decomposition. As shown in Fig. 6, the resonance at -26.7 is the typical signal of BH₃ in AB [19]. After modification by LiBH₄, two B species in C₃N₄ appeared, with the chemical shift of 16.9 and

Fig. 5. TG-DTA curves of pristine AB, 2AB-1LC₃N₄, and 1AB-1LC₃N₄ samples.

-0.4. The former is attributed to *sp*²-BN₃ or BN₂H species. The latter is probably related to N-B-C species formed by the interaction of LiBH₄ and C₃N₄. In the spectra of ball milled 2AB-1LC₃N₄ and 1AB-1LC₃N₄ systems, besides a BH₃ signal, the characteristic resonance of BH₄⁻ was also detected at -41.5, which is probably produced from decomposition of AB induced by LC₃N₄. After hydrogen release at 75 °C, a small amount of BH₃ still existed in AB. In addition, new resonances at -36.5 and -10.1 appeared, corresponding to BH₄ and BH₂, respectively, which can be attributed to the formation of DADB [20]. It is worth noting that the chemical shift of BH₄, formed by AB dehydrogenation, is around -36.5, which is different from the 2AB-1LC₃N₄ and 1AB-1LC₃N₄ systems (shown in Fig. 6). In the ¹¹B MAS NMR spectrum of 2AB-1LC₃N₄ after hydrogen release at 75 °C, the peaks at -22.2, -40.4, and -35.5 can be observed, which are related to the residual of BH₃, BH₄ from LC₃N₄ in-

Fig. 6. ¹¹B MAS NMR spectra of LC₃N₄, pristine AB, 2AB-1LC₃N₄, 1AB-1LC₃N₄, and 1AB-2LC₃N₄ samples and the dehydrogenated samples at 75 °C.

Table 1

NH₃ concentration in the gaseous products after dehydrogenation at 75 °C on the samples.

Sample	Pristine AB	2AB-1LC ₃ N ₄	1AB-1LC ₃ N ₄	1AB-1C ₃ N ₄
c(NH ₃)/%	0.14	2.59	1.13	5.51

Fig. 7. ^{13}C MAS NMR spectra of C_3N_4 , LC_3N_4 , 1AB-2 LC_3N_4 , 1AB-1 LC_3N_4 , and 2AB-1 LC_3N_4 samples and the dehydrogenated samples at 75 °C.

duced AB decomposition, and BH_4 from AB self-decomposition, respectively. The broad peak in the range from -26 to 30 is probably due to the signals of BH_3 , BH_2 , BH (sp^3), BN_2H (sp^2) or BN_3 (sp^2), and N-B-C species [21]. Because hydrogen release happened during ball milling, we got similar spectra of 1AB-2 LC_3N_4 before and after treatment at 75 °C, which is also similar to the spectrum of 1AB-1 LC_3N_4 after dehydrogenation at 75 °C, with the signals at -40.3 (BH_4), -22.8 (BH_3), -1.2 (N-B-C), and 17.8 (BN_2H or BN_3). In addition, high baseline in the range from 30 to -30 can be observed in these three spectra, which might be due to the existence of BH and BH_2 species produced by AB decomposition. Because BH_4 and BH_2 species were observed in the productions of hydrogen release, we can deduce that the decomposition of $x\text{AB}\cdot y\text{LC}_3\text{N}_4$ may still follow the DADB induction mechanism, which is consistent with the aforementioned S type hydrogen release curve.

The ^{13}C MAS NMR spectrum of C_3N_4 (Fig. 7) exhibits two signals centered at 157 and 165 , which are attributed to $\text{CN}_2(\text{NH}_x)$ (boundary of the loop) and CN_3 (inner of the loop), respectively [21]. These typical signals are also observed in the ^{13}C MAS NMR spectra of LC_3N_4 samples. Compared with C_3N_4 , the intensity of the peak at 157 increased. This indicates that due to the effect of LiBH_4 , the boundary carbon species in C_3N_4 enhanced. Partial condensed rings in C_3N_4 were probably split to single ring by LiBH_4 . In addition, there are several signals in the range of 23 – 83 shown in the spectrum of the LC_3N_4 sample, which are attributed to sp^3 -hybridized carbon atoms. After the condensed rings in C_3N_4 split, the carbon atoms turned from CN_3 (sp^2 -hybridized) to CN_3H (sp^3 -hybridized) through further hydrogenation. In the ^{13}C MAS NMR spectra of 2AB-1 LC_3N_4 , 1AB-1 LC_3N_4 , and 1AB-2 LC_3N_4 before and after dehydrogenation, the characteristic peaks at 157 and 165 also exist. With the processing of dehydrogenation, the intensity of the peak at 165 obviously decreased, while that at 157 increased. This demonstrates that AB caused C_3N_4 to change from condensed ring to single ring species, which results in the increase of carbon species on the boundary of the loop.

Fig. 8. Kissinger plots of the pristine AB (1), 2AB-1 LC_3N_4 (2), and 1AB-1 LC_3N_4 (3) samples at different heating rates.

3.2. Kinetic analyses

To obtain the information about the dehydrogenation kinetics of AB and modified AB, this paper performed differential thermal analysis (DTA) at different heating rates to get the temperature at the maximum reaction rate. The pre-exponential factor and the activation energy E_a of AB, 1AB-1 LC_3N_4 , and 2AB-1 LC_3N_4 can be determined based on the Kissinger equation:

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p \quad (1)$$

where β is the heating rate, T_p is the temperature at which the maximum reaction rate peaks, and R is the gas constant. Within the small range of temperature variation, E_a and A are assumed to be constant. The dependence of $\ln(\beta/T_p^2)$ vs $1/T_p$ was plotted in Fig. 8. After simulation, a straight line was obtained, in which the slope represents $-E_a/R$, and the intercept is $\ln(AR/E_a)$. Then, E_a and A can be calculated. Then the specific rate constant k at a given temperature can be determined by the Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (2)$$

Table 2 presents E_a , A , and k (at 75 °C) for each sample. It is clear that the activation energy of the first dehydrogenation step remains the same, which indicates that the mechanism of $x\text{AB}\cdot y\text{LC}_3\text{N}_4$ hydrogen release may be the same as that of AB self-decomposition. It is consistent with the dehydrogenation curve and NMR results. This demonstrates that adding LC_3N_4 can induce AB to quickly produce DADB at low temperature, which then induces the decomposition of AB. Thus, the induction period of AB decomposition is shortened. According to the Arrhenius equation, the reaction rates of 2AB-1 LC_3N_4 and 1AB-1 LC_3N_4 in the first dehydrogenation step at 75 °C are 1.8 and 2.3 times that of AB. It is obvious that the hydrogen release rate is enhanced.

Table 2

E_a , A , and k (at 75 °C) calculated from the Kissinger equation and Arrhenius equation.

Sample	E_a /(kJ/mol)	A/min^{-1}	k/min^{-1}
AB	117.5	2.30×10^{15}	5.32×10^{-3}
2AB-1 LC_3N_4	117.4	3.88×10^{15}	9.34×10^{-3}
1AB-1 LC_3N_4	118.1	6.34×10^{15}	1.20×10^{-2}

Graphical Abstract

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Effects of graphitic carbon nitride on the dehydrogenation of ammonia borane

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The dehydrogenation temperature of C_3N_4 -modified ammonia borane was reduced to lower region with depression of byproduct and induction period compared with pristine ammonia borane.

4. Conclusions

By modification of synthesized C_3N_4 with $LiBH_4$, LC_3N_4 was obtained and was then used to modify AB to get excellent dehydrogenation materials. This study provides new ideas to improve the dehydrogenation performance of AB. However, a large amount of ammonia was produced during the dehydrogenation of modified AB. Two aspects can be made to optimize the dehydrogenation of AB: (1) optimizing the synthesis method of C_3N_4 to enhance the polymerization degree of C_3N_4 and decrease the number of NH_2 group in C_3N_4 ; (2) adding other type of materials and shielding the NH_2 group in C_3N_4 to suppress the production of ammonia during the decomposition of AB.

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石墨型氮化碳对氨硼烷放氢性能的影响

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摘要: 利用石墨型氮化碳(C_3N_4)和氨硼烷(NH_2BH_3 , AB)球磨制备了AB- C_3N_4 体系, 发现 C_3N_4 的加入使AB放氢反应温度明显降低, 但是副产物氨气浓度有所升高。因此, 利用 $LiBH_4$ 改性的 C_3N_4 (LC_3N_4)同AB球磨合成了AB- LC_3N_4 体系, 并采用X射线衍射、程序

升温脱附-质谱联用、热重-差热分析及核磁共振等技术考察了该体系的脱氢性能。结果表明,由于 LC_3N_4 的加入,AB的放氢反应温度明显降低,放氢反应速率加快,放氢诱导期缩短,同时抑制了副产物无机苯的生成。另外, C_3N_4 的化学修饰也降低了AB- LC_3N_4 放氢过程中生成氨气的浓度。动力学分析和核磁共振结果表明,AB- LC_3N_4 分解过程依然遵循 $\text{NH}_3\text{BH}_2\text{NH}_3\text{BH}_4$ 诱导的氨硼烷自分解机理。

关键词: 氨硼烷; 氮化碳; 脱氢; 硼氢化锂

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1. 前言

随着世界经济的迅速发展,日益紧缺的化石能源已经不能够满足人们对能源与日俱增的需求. 氢能作为来源广、能量高、洁净高效的二次能源,被人们寄予厚望. 然而,开发高效的车载储氢系统,为车载燃料电池提供安全可靠的氢源是制约氢能规模化应用的瓶颈之一. 研究发现,最安全有效的车载储氢方法是将氢气储存于固体介质,比如物理吸附材料^[1]、金属氢化物^[2]和化学氢化物^[3]等材料中. 氨硼烷(NH_3BH_3 , AB)以其较高的储氢质量密度(19.6 wt%)和体积密度(145 g/L)而备受关注^[4],但其放氢温度高,可产生毒副产物(如氨气、硼烷和无机苯等),且材料放氢后体积膨胀^[4,5]. 基于此,研究人员从以下几个方面对其进行了修饰改性: 将AB分散到大比表面积的载体上^[6],或利用过渡金属催化剂催化放氢^[7,8],或在离子液体中热分解^[9],或利用酸碱催化剂催化放氢^[10]. 这些方法对AB放氢性能都有一定的促进作用,或降低了脱氢温度,或抑制了副产物的生成,但没有任何一种改性方法可以完全克服其缺点. Neiner等^[11]利用纳米氮化硼(BN)与AB进行复合,发现其放氢温度显著降低,诱导期明显缩短,放氢热效应减弱,但是放氢气体中副产物无机苯明显增多. 而Feaver等^[12]将AB分散在碳凝胶上,所得复合物有效降低了AB的放氢温度,减小了AB放氢过程中的活化能. Zhao等^[13]将AB包裹到聚丙烯酸甲酯材料中,得到了一种抗水的新材料,并且该材料有效地降低了AB的放氢温度,同时能够抑制副产物无机苯的生成. 由此可见,C基、N基材料可以有效提高AB的放氢性能.

本文自行合成了氮化碳(C_3N_4),并用它对AB进行改性. 结果表明, C_3N_4 的加入不仅降低了AB的脱氢反应温度,加快了脱氢反应速率,而且抑制了杂质气体无机苯的生成,但放氢过程中 NH_3 含量有所增加. 因此,我们利用 LiBH_4 对 C_3N_4 进行了改性,发现改性后的 C_3N_4 可以有

效降低脱氢反应气体中的 NH_3 浓度.

2. 实验部分

2.1. AB, C_3N_4 及 $x\text{AB-yLC}_3\text{N}_4$ 复合体系的制备

按照文献[14]合成AB. C_3N_4 按照改进的文献[15]的方法制备,具体操作如下: 称取2 g单氰胺(98%, Alfa-Aesar),在 N_2 气氛下,从室温以 $1^\circ\text{C}/\text{min}$ 升温到 350°C ,恒温3 h,再经40 min升到 390°C 恒温4 h,再经160 min升到 550°C 恒温4 h,最后自然冷却至室温,收集所得的黄色固体即为 C_3N_4 .

在制备AB和 LiBH_4 改性的 C_3N_4 复合体系时,首先分别称取123 mg的 LiBH_4 和1.23 g的 C_3N_4 ,在Retsch PM400型行星式球磨机上球磨5 h (200 r/min),所得混合物在Ar气氛中于 300°C 焙烧2 h,所得产物为 LiBH_4 改性的 C_3N_4 ,记为 LC_3N_4 . 然后,分别称取质量比($x:y$)为2:1, 1:1及1:2的AB和 LC_3N_4 ,球磨24 h即得到三种不同比例的AB- LC_3N_4 样品,记为 $x\text{AB-yLC}_3\text{N}_4$.

2.2. AB, C_3N_4 及 $x\text{AB-yLC}_3\text{N}_4$ 的放氢性能测试

AB及 $x\text{AB-yLC}_3\text{N}_4$ 的程序升温脱附-质谱(TPD-MS)联用实验在自行安装的装置上进行,样品由室温以 $2^\circ\text{C}/\text{min}$ 升至 400°C ,载气为高纯Ar. 采用MS在线检测AB及 $x\text{AB-yLC}_3\text{N}_4$ 脱氢后的气体产物.

AB及 $x\text{AB-yLC}_3\text{N}_4$ 的放氢量测试在自行安装的装置上进行. 在手套箱中将一定量的AB或 $x\text{AB-yLC}_3\text{N}_4$ 装填在反应管底部,将反应管密封后放入预先升至 75°C 的加热炉中,同时开启压力传感器,监测放氢过程. 根据理想气体方程计算放氢量.

放氢结束后,将气体缓慢导入配制的稀硫酸溶液中,通过记录稀硫酸溶液的电导率变化及导入气体的量,即可计算得出所产生气体中的 NH_3 浓度.

2.3. AB, C_3N_4 及 $x\text{AB-yLC}_3\text{N}_4$ 的表征

AB, C_3N_4 及 $x\text{AB-yLC}_3\text{N}_4$ 样品的晶相结构在PANalytical型X射线衍射(XRD)仪上测定,使用Ni过滤

的Cu K_{α} 射线,管电压40 kV,管电流40 mA,扫描范围 5° ~ 80° .热重-差热(TG-DTA)分析在Netzsch公司的STA449C型热分析仪器上进行,从室温以 $2^{\circ}\text{C}/\text{min}$ 升至 400°C ,载气为高纯Ar.魔角旋转核磁共振(MAS NMR)表征在Bruker公司Avance 500型NMR仪器上进行, ^{11}B 及 ^{13}C 均在11.7 T磁场强度下测量,此时 ^{11}B 及 ^{13}C 的核磁共振频率分别为160.5和125.76 MHz,定标参照物分别为 LiBH_4 和甘氨酸.

3. 结果与讨论

3.1. 放氢性能测试及表征

首先将合成的AB和 C_3N_4 按照质量比1:1的比例球磨,试图对AB进行改性.图1为AB和AB- C_3N_4 的TPD-MS谱.可以看出,AB从室温到 250°C 之间分两步进行放氢,分别在112和 160°C ,与文献^[4,5]结果一致;经 C_3N_4 修饰后,AB第一步放氢温度降至 105°C ,表明 C_3N_4 的加入对AB放氢有明显的促进作用.第二步放氢呈现宽化现象,峰温约为 152°C .这可能是由于 C_3N_4 的加入使AB第一步分解产生了不同的分解产物,导致第二步脱氢峰宽化.值得一提的是, C_3N_4 的加入明显抑制了对燃料电池有毒害作用的副产物无机苯的生成;但另外一种副产物 NH_3 的含量明显升高,这可能是因为所合成的 C_3N_4 中含有一定量的 $-\text{NH}_2$ 或 $-\text{NH}$ 基团,在与AB作用时取代了AB中的 NH_3 造成的.所合成的 C_3N_4 的元素分析表明,其组成为 $\text{C}_3\text{N}_{5.4}\text{H}_{0.2}$;同时该样品的FT-IR谱中于 $3070\sim 3310\text{ cm}^{-1}$ 处出现N-H振动峰,进一步证实 $-\text{NH}_2$ 或 $-\text{NH}$ 基团的存在.

研究表明,氢化物、硼氢化物等可以同氨基化合物相互作用,从而减少氨基化合物分解过程中氨的生成^[3,16].为了降低气体产物中的氨浓度,我们首先利用 LiBH_4 修饰 C_3N_4 合成 LC_3N_4 ,再将后者与AB进行球磨复合,合成了三个比例的 $x\text{AB}-y\text{LC}_3\text{N}_4$ 体系.其中AB与 LC_3N_4 的质量比分别为2:1,1:1及1:2,以下分别简写为 $2\text{AB}-1\text{LC}_3\text{N}_4$, $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $1\text{AB}-2\text{LC}_3\text{N}_4$.

图2为所合成样品的XRD谱.可以看出, C_3N_4 在 13.2° 出现一个弱峰,其最强的衍射峰在 27.2° ,与文献报道的 $g\text{-C}_3\text{N}_4(002)$ 晶面的衍射峰吻合^[17]. $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $2\text{AB}-1\text{LC}_3\text{N}_4$ 两个样品都出现了与AB相同位置的衍射峰,说明AB存在于球磨后的复合体系中.但是随着AB比例的减小,其衍射峰也逐渐变弱.有趣的是,将AB与 LC_3N_4 的质量比为1:2的样品进行球磨时,约有1.2 equiv.气体/AB释放出来,经过质谱分析发现,气体主要为 H_2 以

及少量的 B_2H_6 .这种现象在其它两个样品中并未观察到.XRD结果发现, $1\text{AB}-2\text{LC}_3\text{N}_4$ 样品的衍射峰完全消失,呈无定形状态.

之后我们对所合成的样品进行了脱氢性能考察,图3为它们的TPD-MS谱.可以看出,AB, $2\text{AB}-1\text{LC}_3\text{N}_4$ 及 $1\text{AB}-1\text{LC}_3\text{N}_4$ 三种样品第一步放氢温度分别为112,105及 101°C ,即随着 LC_3N_4 掺杂量增加,AB放氢温度降低.经 LiBH_4 修饰后, C_3N_4 对AB脱氢的促进作用增大.需要指出的是, LC_3N_4 的加入同样抑制了无机苯的生成.对于 $1\text{AB}-2\text{LC}_3\text{N}_4$ 体系,第一步放氢峰几乎消失,这与球磨过程中释放 H_2 相关.更重要的是, $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $2\text{AB}-1\text{LC}_3\text{N}_4$ 样品在分解放氢过程中的氨信号均明显低于AB- C_3N_4 .

为了确定各个样品的放氢量, 75°C 时采用体积法测试了放氢性能,结果见图4.可以看出, 75°C 时AB分解存在诱导期,并最终在12 h内释放出0.9 equiv. H_2/AB ,与文献报道的 $\text{NH}_3\text{BH}_2\text{NH}_3\text{BH}_4$ (DADB)诱发氨硼烷分解情况基本吻合^[18].由于 $1\text{AB}-2\text{LC}_3\text{N}_4$ 体系在球磨过程中已放出了 H_2 ,所以在 75°C 放氢性能测试中只检测到少量 H_2 的生成. $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $2\text{AB}-1\text{LC}_3\text{N}_4$ 两个体系在放氢时诱导期及放氢时间均显著缩短:当释放0.6 equiv. H_2/AB 时,AB需5.6 h,而 $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $2\text{AB}-1\text{LC}_3\text{N}_4$ 两个体系分别只需要4.5和3.4 h.虽然 LC_3N_4 有效地缩短了AB放氢的诱导期,但是 $x\text{AB}-y\text{LC}_3\text{N}_4$ 的放氢仍然为一个S型曲线.这说明 $x\text{AB}-y\text{LC}_3\text{N}_4$ 体系分解放氢似乎依然遵循着AB自分解放氢过程中DADB诱导机理.另外,如表1所示, $1\text{AB}-1\text{LC}_3\text{N}_4$ 和 $2\text{AB}-1\text{LC}_3\text{N}_4$ 两个体系中 NH_3 浓度分别为1.13%和2.59%,略高于AB体系,但明显低于AB- C_3N_4 体系.

样品的TG-DTA曲线见图5.可以看出,AB的第一个吸热峰为AB熔化所致,第二个放热峰归属为AB脱氢放热,脱氢峰温为 109°C ,与TPD结果基本吻合.加热到 180°C 时AB失重约为49.1%,而 $2\text{AB}-1\text{LC}_3\text{N}_4$ 和 $1\text{AB}-1\text{LC}_3\text{N}_4$ 分别约为20.1%和11.9%,若按照AB计算,失重量分别为30.1%和23.8%.这表明 LC_3N_4 的掺杂使得 $x\text{AB}-y\text{LC}_3\text{N}_4$ 生成了较多的 NH_3 ,但明显抑制了其它副产物(如挥发性的无机苯)的生成.值得注意的是, $2\text{AB}-1\text{LC}_3\text{N}_4$ 和 $1\text{AB}-1\text{LC}_3\text{N}_4$ 两个体系中未出现AB熔化吸热峰.这可能是因为 LC_3N_4 的加入降低了AB的放氢温度,使其在低于其熔点下分解放氢,从而破坏了AB的晶体结构所致.

由于AB放氢分解后生成无定形产物,其XRD谱不

能给出有关结构的信息, 因此本文试图利用NMR技术对AB及修饰后的AB进行表征. 图6和图7分别是各样品在分解前后的 ^{11}B 和 ^{13}C MAS NMR谱. 如图6所示, $\delta = -26.7$ 处的峰是AB中 BH_3 特征峰, 与文献报道^[19]相近. LiBH_4 修饰后的 C_3N_4 在16.9和-0.4出现两个B物种峰, 前者应归属为 sp^2 杂化的 BN_3 或 BN_2H 物种, 而后者可能是 LiBH_4 同 C_3N_4 相互作用形成的N-B-C物种. 在球磨后的2AB-1 LC_3N_4 和1AB-1 LC_3N_4 体系中除了仍保留的 BH_3 特征峰外, 还检测到 BH_4^- 特征峰(-41.5), 它可能为 LC_3N_4 诱导AB作用产生的 BH_4 物种. AB在75 °C放氢后仍然有残留的少量 BH_3 , 同时在-36.5和-10.1处分别产生了新的 BH_4 和 BH_2 特征峰, 这归因于AB自分解过程中产生的DADB^[20]. 值得注意的是, 如图6所示, AB放氢生成的 BH_4 物种在-36.5附近, 不同于2AB-1 LC_3N_4 和1AB-1 LC_3N_4 体系. 在2AB-1 LC_3N_4 75 °C放氢后, 于-22.2, -40.4和-35.5处出现特征峰, 分别归属为剩余的 BH_3 , LC_3N_4 诱导AB产生的 BH_4 以及AB自分解新生成的 BH_4 . 而-26~30的宽峰可能为 BH_3 , BH_2 , $\text{BH}(sp^3)$, $\text{BN}_2\text{H}(sp^2)$ 或 $\text{BN}_3(sp^2)$ 以及N-B-C物种的混合峰^[21]. 因为1AB-2 LC_3N_4 体系在球磨过程中放氢, 所以该体系75 °C处理前后均得到了相似的谱图, 并且同1AB-1 LC_3N_4 75 °C放氢后的基本相同, 即存在-40.3 (BH_4), -22.8 (BH_3), -1.2 (N-B-C)和17.8 (BN_2H 或 BN_3). 此外, 这三条NMR图谱30~30内都具有较高的基线. 这可能是因为样品中仍然含有AB分解后产生的BH及 BH_2 物种. 由于在放氢产物中观察到 BH_4 及 BH_2 物种, 可以推测 $x\text{AB}-y\text{LC}_3\text{N}_4$ 体系在分解过程中仍然遵循DADB诱导机理. 这同前述的S型放氢曲线是一致的.

如图7所示, 所合成的 C_3N_4 有 $\text{CN}_2(\text{NH}_x)$ (环边界)和 CN_3 (环内部)两种C的化学环境, 分别在 $\delta = 157$ 和165具有特征峰, 与文献^[21]结果相近. 在 LC_3N_4 中仍然存在着这两种特征峰, 但是157附近的特征峰有所增强, 说明由于 LiBH_4 的作用, C_3N_4 中边界的碳物种有所增加, 这可能是由于部分 C_3N_4 稠环被 LiBH_4 分裂为单环. 同时 LC_3N_4 样品中生成 $\delta = 23\sim 83$ 处连续的几个特征峰, 可归属为碳的 sp^3 杂化物种. 这很有可能是由于 C_3N_4 的稠环被分裂后, 碳元素再进一步加氢使得 CN_3 (sp^2 杂化)变成 CN_3H ,

(sp^3 杂化). 在2AB-1 LC_3N_4 , 1AB-1 LC_3N_4 和1AB-2 LC_3N_4 分解前后的样品中均存在着157和165的特征峰. 然而随着脱氢的进行, 165附近的特征峰明显减弱, 而157附近的特征峰增强. 这说明AB可以进一步使 C_3N_4 由稠环转变为单环物种, 导致环边界的碳物种增多.

3.2. 动力学测试

为了得到AB及 LC_3N_4 掺杂的AB的脱氢反应动力学数据, 本文在不同升温速率(0.5, 1, 2和3 °C/min)下进行了DTA分析, 以得到反应速率最大值的温度, 然后根据Kissinger方程(见式(1))来确定AB, 1AB-1 LC_3N_4 和2AB-1 LC_3N_4 样品的表观活化能 E_a 和指前因子 A .

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p \quad (1)$$

其中, β , T_p 和 R 分别为升温速率、反应速率最大时的温度和理想气体常数. 在较小的温度变化范围内, 可假定 E_a 和 A 为恒量, 以 $\ln(\beta/T_p^2)$ 对 $1/T_p$ 作图(见图8), 拟合可以得到一条直线, 其斜率为 $-E_a/R$, 截距为 $\ln(AR/E_a)$, 从而得到 E_a 和 A , 然后根据阿伦尼乌斯方程(见式(2))可计算某一温度下的反应速率常数 k .

$$k = A\exp(-E_a/RT) \quad (2)$$

表2归纳了各样品的 E_a , A 和 k 值(75 °C). 可以看出, 第一步热分解反应的 E_a 基本没有变化. 这说明 $x\text{AB}-y\text{LC}_3\text{N}_4$ 分解机理可能依然遵循着AB自分解放氢机理, 与放氢曲线和NMR结果一致. 可见 LC_3N_4 的加入可以诱导AB低温下快速产生DADB, 并进一步诱导AB分解, 从而缩短了AB分解的诱导期. 由阿伦尼乌斯方程算得75 °C时2AB-1 LC_3N_4 和1AB-1 LC_3N_4 样品的第一步脱氢反应速率常数分别是AB脱氢的1.8和2.3倍, 放氢反应速率明显加快.

4. 结论

利用 LiBH_4 对自行合成的 C_3N_4 进行改性得到 LC_3N_4 , 再利用 LC_3N_4 修饰氨硼烷, 得到了放氢性能优异的材料, 这为改善氨硼烷放氢性能提供了一个新的思路. 然而修饰后的氨硼烷放氢过程中有大量副产物 NH_3 生成, 可通过优化 C_3N_4 合成方法, 提高 C_3N_4 的聚合度, 以减少 C_3N_4 中氨基的数量, 或添加其它种类的材料, 来屏蔽 C_3N_4 中的氨基基团, 从而抑制氨硼烷分解放氢过程中氨气.