Research Article

Synthesis of Renewable Energy Materials, Sodium Aluminum Hydride by Grignard Reagent of Al

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The research on hydrogen generation and application has attracted widespread attention around the world. This paper is to demonstrate that sodium aluminum hydride can be synthesized under simple and mild reaction condition. Being activated through organics, aluminum powder reacts with hydrogen and sodium hydride to produce sodium aluminum hydride under atmospheric pressure. The properties and composition of the sample were characterized by FTIR, XRD, SEM, and so forth. The results showed that the product through this synthesis method is sodium aluminum hydride, and it has higher purity, perfect crystal character, better stability, and good hydrogen storage property. The reaction mechanism is also discussed in detail.

1. Introduction

Hydrogen is considered as one of the most important energy carriers for future energy vectors because of the higher energy storage density, environmental friendliness, and broadened sources [1]. Complex metal hydride composites in the form of ABH_4 , where A is an alkali metal and B is a group III element, have been widely studied in solution as proton acceptors to enhance H_2 adsorption abilities. $NaAlH_4$ is different from any other metal hydrides and borohydrides with similar structures since it is capable of reversibly storing H_2 after doping with transition metals (e.g., Ti, Fe, or Zr) [2, 3]. $NaAlH_4$ is one of the most useful solid hydrogen storage materials [4]. It could be produced by many methods such as liquid-phase synthesis method [5, 6], solid-phase synthesis method [7], and milling synthesis [8]. However, all these synthesis methods have some disadvantages [4, 9], like lower yield rate, higher consumption of raw material, higher temperature and higher pressure, and so forth [10], which make them difficult for industrial production.

This paper will describe a simple and efficient method to synthesize sodium aluminum hydride under moderate condition. The synthesis could be split into two steps. First, aluminum powder is activated by organics to produce activated aluminum. Secondly, the activated aluminum reacts

with hydrogen and sodium hydride to produce final product [11]. The raw material for this synthesis method is easy to get, and the utilization of the raw material and yield rate are really high. All these features of the synthesis demonstrate that this method is promising for the industrialization of sodium aluminum hydride [12, 13]. It is established that hydrogen storage material sodium alanate can be obtained from low cost starting materials [4].

2. Experimental

2.1. Reagents and Materials. Aluminum powder (granularity, 200, purchased from Beijing Chemical Reagent Factory) was dried in a vacuum oven. Anhydrous aluminum chloride (purchased from Tianjin Chemical Reagent Factory) and iodine (purchased from Zhengzhou Chemical Reagent Factory) were sealed and stored in a dark environment as the initiator. In addition, commercial NaH (purity 60%, purchased from Aladdin) was stored under N_2 atmosphere to prevent oxygen/moisture exposure. Toluene and tetrahydrofuran (THF) (AR, purchased from Tianli Chemical Reagent Co. Ltd.) were distilled over sodium metal under N_2 atmosphere to remove water. H_2 (purity 99.999%, purchased from Taiyuan Industrial Gases Factory) was removed moisture through a scrubber, as the purpose of a protective and reaction

gas. Several freeze-pump-thaw cycles were performed for halogenated hydrocarbons (AR, purchased from Tianjin Chemical Reagent Factory) to remove trace amounts of O_2 and water.

2.2. Synthesis Method. All reactions were carried out under anhydrous and oxygen-free environment (hydrogen circumstance). Since there are some impurities in aluminum powder and NaH surface wrapping in mineral oil, their dosage should be slightly more than the theoretical value. Aluminum powder 2 g, exact amounts of anhydrous aluminum chloride and iodine, and freshly sealed halogenated hydrocarbons 8 mL were added to a 250 mL of three-neck flask after replacement repeatedly with H_2 . The mixture was heated to $40^\circ C$ and refluxed in hydrogen stream with stirring. About 25 minutes later, the reaction has been initiated; as a result, aluminum powder is activated to form an organic aluminum reagent intermediates and active aluminum.

One hour later, 3.5 g NaH and 30 mL of toluene (as the dispersant) were put into the flask. The mixture was heated to $85^\circ C$ and refluxed with stirring for 6 h before it was cooled down to room temperature. After separation and crystallization, the gray powder was dried in vacuo at $60^\circ C$ for 12 h.

The gray solid was dissolved in a mixed solvent of toluene and tetrahydrofuran, and then insoluble matter was filtered off. The solvent was removed from the filtrate under reducing atmosphere, and the resulting white solid was dried in vacuo at $80^\circ C$ for 12 h.

2.3. Characterization. All powder X-ray diffraction experiments were performed on a Rigaku Ultima IV diffractometer equipped with a Cu-K α source operated at 40 kV, 44 mA, and 1.76 kW with the step size of 5° in the scanning range of the diffraction angle $20^\circ \leq 2\theta \leq 80^\circ$ and a scintillation counter detector. The samples were confirmed by comparison with the appropriate pattern from the International Center for Diffraction Database (ICDD) crystallographic database. All Fourier transform infrared (FTIR) spectroscopic measurements were made on a Shimadzu model FTIR-8400S spectrometer equipped with an attenuated total reflectance (ATR) attachment. The sample morphologies were characterized with SEM on an Hitachi model Su-1500. Online Mass Spectrometry analysis was performed using PFEIFFER Omni Star.

3. Results and Discussion

3.1. Infrared Spectroscopy Analysis. The absorption peak of $[AlH_4]^-$ corresponding to Al-H bond stretching was usually used to determine sodium aluminum hydride. As shown in Figures 1(a) and 1(b), there are Al-H bond characteristic peaks that appear in the vicinity of 1660 cm^{-1} and 710 cm^{-1} . Figure 1(c) is the intermediate from reaction started about an hour; there is a clear characteristic peak of aluminum alkyl in the vicinity of 1250 cm^{-1} , 1040 cm^{-1} , and 650 cm^{-1} . It indicates the formation of alkyl-aluminum. It can also be seen from the figure that the purity of the sample is improved

FIGURE 1: FTIR spectra of the sample: (a) sample after recrystallization, (b) sample after completion of the reaction, and (c) intermediate from reaction started about an hour.

TABLE 1: Analysis data of the sample elemental composition.

Element	Theoretical value		Actual measured value	
	Content (%)	Atomic ratio	Content (%)	Atomic ratio
Na	42.59	1.00	42.63	1.03
Al	50.00	1.00	49.74	0.99
H	7.41	4.00	7.36	4.06

after recrystallization, with a significant reduction of impurity peak. By comparing this is consistent with previous results reported in the literature [14, 15]. This indicates that the product has the presence of $NaAlH_4$.

3.2. Elemental Analysis of Samples. H elemental analysis was performed using Germany ELTRA ONH-2000 elemental analyzer. Al elemental analysis was performed using anti-titration according to GB/T 5121.13-2008. Metallic sodium content was measured by Prodigy Full Spectrum Direct Reading ICP emission spectrometer (Leeman Labs, US), and the sample analysis results are listed in Table 1. It can be seen that the actual measured value of these three elements is close to the theoretical value, and the contents of different element are approximately consistent with the theoretical values. The melting point of the sample is between $182^\circ C$ – $185^\circ C$. It has a melting process, it is a range, not a specific temperature point. In other words, it started to melt from $182^\circ C$, and melted completely at $185^\circ C$. Combining the results of the elemental analysis indicates that the molecular of our product is $NaAlH_4$.

3.3. X-Ray Diffraction Analysis. Figure 2 shows the diffractograms of the synthesized samples and the sample after recrystallization. The characteristic peaks of those samples are clearly discernible and consistent with the JCPDF index-card 22-1337 [16]. Based on this result as well as those of FTIR and elemental analysis, it can be conclude that the final product prepared by this method is $NaAlH_4$. It has a monoclinic crystal structure (cell parameters: $a = b = 5.02\text{ \AA}$, $c = 11.31\text{ \AA}$) and I41/a (88) space group. These results are consistent with other studies on the same $NaAlH_4$ and

FIGURE 2: XRD patterns of (a) products after recrystallization and (b) products after completion of the reaction.

similar ones (despite being synthesized by different methods and at higher temperatures). It can also be seen from the figure that there are impurities present in the sample before recrystallization. In other words, the purity of the product is improved after recrystallization.

3.4. Reaction Mechanism. The reaction mechanism can be described as follows:

At first, aluminum powder is activated in the presence of initiator and the intermediate with a high activity can directly react with hydrogen to form aluminum hydride. The produced AlH_3 then further react with NaH and hydrogen to form final product, NaAlH_4 .

This is confirmed by FTIR and XRD as seen in Figures 1(c), 3, and 4. In Figure 1(c), there is a strong absorption peak at 1640 cm^{-1} , which can be attributed to the Al-H bond vibration absorption [17]. Because in the absence of sodium hydride, therefore it can not be $[\text{AlH}_4]^-$ vibration peak, it should AlH_3 vibration absorption.

To further confirm this reaction mechanism, we also ran some other experiments. Figures 3 and 1(c) show XRD and FTIR of the product without addition of sodium hydride. The results illustrate the generation of different crystal forms of aluminum hydride in the first reaction step. The intermediate obtained at a reaction time of 5 h was detected by XRD and the result is shown in Figure 4. It can be seen that the resulting intermediate contains multiple components including Na_3AlH_6 , AlH_3 , NaH , and NaAlH_4 . This result adds to and provides for our reaction mechanism [18].

FIGURE 3: XRD patterns of mixture obtained after 1 h of reaction.

FIGURE 4: XRD patterns of mixture obtained after 5 h of reaction after adding NaH .

3.5. Scanning Electron Microscopy Analysis. Two scanning electron microscopy (SEM) photomicrographs of the sample surface are depicted in Figure 5. Figure 5(a) shows the microstructure of synthesized NaAlH_4 , where plurality of smaller sized irregular particles and loose structure can be observed on the whole porous surface. This microstructure has large specific surface area; and it is beneficial to improve the capacity of hydrogen storage and release of materials [19]. The sample after recrystallization is shown in Figure 5(b); its surface is smooth but has a lot of voids there, which suggests that there is certain functional materials storage of

FIGURE 5: SEM micrographs of obtained NaAlH_4 before its recrystallization (a) and that after recrystallization (b) for magnified 1000 times.

gas. Based on this phenomenon, compounds with different morphologies can be obtained using this method.

3.6. Performance Analysis of Dehydrogenation. According to the literature [20], the de/hydrogenation reactions of NaAlH_4 take place in three steps as follows:

Online Mass Spectrometry is a gas collection device, in which acquisition gaseous substances are released during heating under the protection of N_2 , so as to get its content. The heating rate of hydrogen online MS is 5°C per minute; the peak of the figure represents hydrogen release.

Figure 6 is the Online Mass Spectrometry of hydrogen from synthesized samples. It can be seen that hydrogen was released during the decomposition of the sample. This result showed that the synthesized sodium aluminum hydride has hydrogen storage capability. There are approximately 3.62 wt% H_2 released at 340°C and 0.35 wt% H_2 releasing at about 100°C , which can be attributed to the decomposition of remnant aluminum hydride [17] and influence of impurities. This shows that the stability to get NaAlH_4 is not good.

Figure 7 shows the Online Mass Spectrometry of hydrogen from samples after recrystallization. By comparing Figures 6 and 7, there is only a hydrogen release peak at 370°C in Figure 7, and its content is about 3.87 wt%. This shows that the sample is more stable after recrystallization and has better purity.

It is concluded that sodium aluminum hydride obtained by this method has a hydrogen storage capacity from Online Mass Spectrometry and SEM. The hydrogen storage capacity is less than those reported in the literature by calculation. As the temperature increases, there will be a release of hydrogen;

FIGURE 6: Online MS of hydrogen from synthesized NaAlH_4 .

FIGURE 7: Online MS of hydrogen after recrystallization from synthesized NaAlH_4 .

this also provides evidence for the stability. In summary, the sample has more stable and more complete polymorph after recrystallization.

4. Conclusions

From the above discussion, it can be concluded that NaAlH_4 was successfully synthesized by a very effective method in this paper. Our preparation way has some advantages including low cost, mild reaction conditions, and high output rate. The synthesized NaAlH_4 has hydrogen storage capacity and more moderate desorption conditions and better stability after recrystallization. All these advantages indicate that our process has potential application for the industrial production of NaAlH_4 . This provides a strong guarantee of the research and development for other hydrogen storage materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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