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Microstructure and desorption properties study of catalyzed NaAlH₄

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1. Introduction

New energy supplier systems are urgently needed to comply with environmental restrictions and decrease the dependence on petroleum. Investigations show that hydrogen is a potential major alternative as an environment friendly energy carrier [1–3]. Among the various forms of hydrogen storage, it is the lightweight complex hydrides, such as NaAlH₄, LiAlH₄ and LiNH₂, have been considered as promising solid-state hydrogen storage materials for on-board fuel cell applications because of their high hydrogen content [4–6]. However, complex hydrides do not reversibly absorb and desorb hydrogen under moderate conditions when an appropriate catalyst is not added. In 1997, it was firstly reported that, under moderate conditions of temperature and pressure, NaAlH₄, Na₃AlH₆ and Na₂LiAlH₆ catalyzed Ti exhibit reversible hydrogen storage characteristics enhance the kinetics of hydrogen sorption reactions [4]. Since then, to improve the hydrogen storage properties of NaAlH₄, achieving the appropriate catalysts has been recognized as a key technology. The catalysts studied have been elemental titanium, TiCl₄, Ti–Zr, Ir/Al₂O₃, HfCl₄, TiF₃ ZrCl₄, et al. [7–11]. Recently, the use of rare-earth compounds as catalysts has excited great interest in improving the hydrogen-storage properties. A series of rare-earth chlorides has been adopted to catalyze the dehydrogenation reaction of NaAlH₄. Isothermal dehydrogenation measurements have proved that these chlorides enhance the dehydrogenation kinetics and lower the decomposition temperature of

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ABSTRACT

NaAlH₄ catalyzed by Ce(SO₄)₂ and LaCl₃ have been studied by PCT (Pressure–Content–Temperature) experiment and SEM (Scanning Electron Microscope) test method. The results show that doping with Ce(SO₄)₂ and LaCl₃ increases markedly the desorption amount of NaAlH₄. In the first desorption stage, NaAlH₄ doped with LaCl₃ display larger amount of hydrogen release than NaAlH₄ doped with Ce(SO₄)₂, while, the desorption rate of the latter is obviously faster than the former. SEM analysis shows that heating could make NaAlH₄ form a kind of porous structure. The further study indicates that different dopants have different effects on the microstructure of NaAlH₄.

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NaAlH₄. The catalytic effect is in the following decreasing order: SmCl₃ > CeCl₃ > TiCl₃ > NdCl₃ > GdCl₃ > LaCl₃ > ErCl₃. The effect of rare-earth elements on hydrogenation/dehydrogenation behavior has been studied by Pukazhselvan et al. [12]. Compared to a Ti catalyst, misch metal is more effective for enhancing the desorption kinetics and rehydrogenation of NaAlH₄.

Furthermore, the results from our study on LaCl₃, Ti, Ni and Co show that rare-earth compounds can improve the hydrogenstorage properties of NaAlH₄ more efficiently than metal catalysts such as Ti, Ni and Co [13].

In this work, $CeCl_3$ and $Ce(SO_4)_2$ additives have been studied. A pressure–composition–temperature (PCT) apparatus has been used to study the process of decomposition of NaAlH₄ and SEM has been used to study the microstructure of NaAlH₄.

2. Experimental details

NaAlH₄(\geq 93 wt% pure) was used as received with no additional purification. Due to the mass of crystal water in Ce(SO₄)₂.4H₂O and CeCl₃.7H₂O, dehydration was carried out before NaAlH₄ was mixed with Ce(SO₄)₂ and CeCl₃ in order to prevent any effect of this crystal water on NaAlH₄. Ce(SO₄)₂.4H₂O and CeCl₃.7H₂O were heated to 160 °C and 150 °C, respectively, and then kept at these temperatures for 4h. All operations on the samples were done under a dry argon atmosphere in a glove box to prevent reaction with moisture and oxygen in the air. NaAlH₄, usually 1 g, was mixed with Ce(SO₄)₂ and LaCl₃ by ball-milling for 30 min at a gyration rate of 400 rpm using a planetary mill. Three hardened-steel vials sealed under argon and containing fourteen steel balls (1 g each) were used. The agate jars were overturned once every 5 min in order to make powder homogeneous mixing. The ball-milled samples were then transferred to 3 ml glass bottles in a glove box under dry argon atmosphere.

Hydrogen-desorption experiments were carried out in the PCT apparatus. This can be operated up to 10 MPa and 400 °C. The pressure of hydrogen released in relation to volume was displayed by a pressure transducer. The experimental studies were done using a reactor. The samples doped with Ce(SO₄)₂ and LaCl₃ were heated

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Fig. 1. Relations of dehydrogenation amount and time of NaAlH4 at 200 °C.

in vacuum at a heating rate of $5 \,^{\circ}$ C/min. All the pressure and temperature data were acquired during the heating process, and the dehydrogenation curves were drawn by special software.

The samples for electron microscopy were prepared in the glove box under a dry argon atmosphere. Electron microscopy studies were performed with a D/Max-2500 SEM operated at 40 kV.

3. Results and discussion

3.1. Desorption capacity of NaAlH₄ doped with $Ce(SO_4)_2$

To investigate the catalytic effect of $Ce(SO_4)_2$ and $LaCl_3$ on dehydrogenation capacity of NaAlH₄, the dehydrogenation behavior of NaAlH₄ milled 30 min were characterized by the decomposition curves shown in Fig. 1. NaAlH₄ presents a low desorption kinetics during the first desorption. However, the desorption rate increases dramatically after about 43 min. This sudden change in dehydrogenation kinetica reflects the transition from reaction:

 $NaAlH_4 \rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2$



Fig. 2. Relations of time and amount of hydrogen release of NaAlH₄ doped with 2, 3, 4 and 5 mol% Ce(SO₄)₂.

With the time prolonging, from 60 to 180 min, the desorption rate presents a slow increase again. The dehydrogenation curves provide the information concerning the amount of hydrogen release shows that NaAlH₄ releases only about 0.75 wt% within 180 min.

The measured dehydrogenation capacities of NaAlH₄ doped with Ce(SO₄)₂ under 200 °C are shown as a function of desorption time in Fig. 2. The process of hydrogen release of all samples presents a very marked two-step desorption. The two stages present NaAlH₄ and Na₃AlH₆ decompositions, respectively [14–16]. The amount and the rate of hydrogen release in the first stage are importantly higher than in the second step. In addition, it can be seen that the total amount of hydrogen release of all samples is very near, and, the time of hydrogen release also shows significantly same in the first stage. The desorption amount of NaAlH₄ doped with 4 mol% Ce(SO₄)₂ is larger than other doped samples. The sample doped with 3 mol% Ce(SO₄)₂ has the least amount of



Fig. 3. SEM image of NaAlH₄ doped with 2, 3 and 4 mol% Ce(SO₄)₂ (a) NaAlH₄ doped with 3 mol% Ce(SO₄)₂ heated at 200 °C, (b) NaAlH₄ doped with 4 mol% Ce(SO₄)₂ heated at 200 °C, (c) NaAlH₄ doped with 2 mol% Ce(SO₄)₂ heated at 200 °C, (d) the unheated NaAlH₄ doped with 2 mol% Ce(SO₄)₂.

Table 2

5 mol% LaCl₃

4 30

Table 1

Time, amount and average rate of hydrogen release of $NaAlH_4$ doped with $\text{Ce}(\text{SO}_4)_2$ in the first stage.

Samples	Desorption amount/wt%	Desorption time/min	Average rate/wt%/min
2 mol% Ce(SO ₄) ₂	3.82	15	0.26
3 mol% Ce(SO ₄) ₂	3.76	15	0.25
4 mol% Ce(SO ₄) ₂	3.97	15	0.27
5 mol% Ce(SO ₄) ₂	3.90	15	0.26

hydrogen release about 3.76 wt% (Table 1). However, compared to undoped NaAlH₄, doping increases markedly the amount and the rate of hydrogen release of NaAlH₄.

Fig. 3 gives the SEM image of NaAlH₄ doped with 2, 3 and 4 mol% Ce(SO₄)₂ after desorbed at 200 °C and the unheated NaAlH₄ doped with $2 \mod Ce(SO_4)_2$. It is not difficult to be found that the SEM image of the samples is very similar. The powder article presents a porous structure. Sandrock et al. also found this porous structure when they studied the desorption kinetics of NaAlH₄ and Na₃AlH₆. However, they did not give the interrelated SEM image to further prove their study result. In addition, study from Sandrock et al. [17] also investigated this kind of porous structure. They thought that this kind of porous structure was caused by high heating temperature which exceeding the 182 °C melting temperature of NaAlH₄ and believed that such a porous structure may have distinct advantages relative to limiting particulate migration, packing and expansion, as well as maintaining stable internal gas impedance. However, our study shows that the unheated NaAlH₄ doped with $2 \mod Ce(SO_4)_2$ also presents a kind of porous structure(Fig. 3(d)). So, we think that dopants can also lead to the porous structure of NaAlH₄ except for heating temperature.

3.2. Desorption capacity of NaAlH₄ doped with LaCl₃

Fig. 4 shows the relations of time and amount of hydrogen release of the unheated NaAlH₄ doped with 2, 3, 4 and 5 mol% LaCl₃. The results are very similar to that of NaAlH₄ doped with 2, 3, 4 and 5 mol% Ce(SO₄)₂. The total desorption amount of all doped samples



Fig. 4. Relations of time and amount of hydrogen release of $NaAlH_4$ doped with 2, 3, 4 and 5 mol% LaCl₃.

Time, amount and average rate of hydrogen release of NaAlH ₄ doped with LaCl ₃ in the first stage.				
Samples	Desorption amount/wt%	Desorption time/min	Average rate/wt%/min	
2 mol% LaCl₃	4.00	25	0.16	
3 mol% LaCl₃	4.30	30	0.14	
4 mol% LaCl₃	4.43	32	0.14	

25

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is very near. Examples of desorption curves also show two distinct features: (1) two stages of desorption, both of which are approximately linear with time over much of each desorption range and (2) a pronounced decrease in desorption rate in the second stage. According to Table 2, the sample doped with 4 mol% LaCl₃ presents the largest amount of hydrogen release in the first stage. In addition, it is easy to be seen from the desorption curves that the desorption rate of the sample doped with 5 mol% LaCl₃ is the fastest. Comparatively, the sample doped with 2 mol% LaCl₃ also has the very fast



Fig. 5. SEM image of the unheated NaAlH₄ doped with 2, 3, 4 and 5 mol% LaCl₃. (a) NaAlH₄ doped with 2 mol% LaCl₃, (b) NaAlH₄ doped with 3 mol%LaCl₃, (c) NaAlH₄ doped with 4 mol% LaCl₃, (d) NaAlH₄ doped with 5 mol% LaCl₃.

rate of hydrogen release, however, the desorption amount in the first stage is the least than all doped samples.

Fig. 5 shows the SEM image of NaAlH₄ doped with 2, 3, 4 and 5 mol% LaCl₃ unheated. Unlike NaAlH₄ doped with 2 mol% Ce(SO₄)₂, all samples does not present the porous structure. The particle feature of doped samples is flocculent. The result indicates that dopants have an important effect on microstructure of NaAlH₄. Compared to the samples doped with Ce(SO₄)₂, the desorption amount of samples doped with LaCl₃ in the first stage is higher than the former, while, the desorption rate is obviously slower.

4. Conclusions

In this work, NaAlH₄ catalyzed by Ce(SO₄)₂ and LaCl₃ is prepared using planetary mill and its microstructure and desorption capacity are investigated. The results show that doping with $Ce(SO_4)_2$ and LaCl₃ increases markedly the desorption amount of NaAlH₄. In comparison with $Ce(SO_4)_2$ and $LaCl_3$ catalysts, the samples doped with LaCl₃ display larger amount of hydrogen release in the first stage than the samples doped with $Ce(SO_4)_2$, while, the desorption rate of the latter is obviously faster than the former. In addition, the results from SEM analysis show that heating could make NaAlH₄ form a kind of porous structure. Likewise, doping with $Ce(SO_4)_2$ also can make NaAlH₄ form this kind of porous structure under unheated conditions. However, the microstructure of the samples doped with LaCl₃ presents a flocculent accumulation, and the porous structure is not found. This result proves that different dopants have different effects on the microstructure of NaAlH₄ except for its hydrogen storage capacity.

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