

Influence of lanthanon hydride catalysts on hydrogen storage properties of sodium alanates

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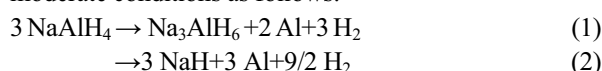
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Abstract: NaAlH₄ complex hydrides doped with lanthanon hydrides were prepared by hydrogenation of the ball-milled NaH/Al+x mol.% RE-H composites (RE=La, Ce; x=2, 4, 6) using NaH and Al powder as raw materials. The influence of lanthanon hydride catalysts on the hydriding and dehydriding behaviors of the as-synthesized composites were investigated. It was found that the composite doped with 2 mol.% LaH_{3.01} displayed the highest hydrogen absorption capacity of 4.78 wt.% and desorption capacity of 4.66 wt.%, respectively. Moreover, the composite doped with 6 mol.% CeH_{2.51} showed the best hydriding/dehydriding reaction kinetics. The proposed catalytic mechanism for reversible hydrogen storage properties of the composite was attributed to the presence of active LaH_{3.01} and CeH_{2.51} particles, which were scattering on the surface of NaH and Al particles, acting as the catalytic active sites for hydrogen diffusion and playing an important catalytic role in the improved hydriding/dehydriding reaction.

Keywords: complex hydride; NaAlH₄; hydrogen storage properties; rare earths; catalyst

To meet the application of hydrogen storage devices for fuel cell, lightweight complex hydrides, such as Mg-based hydride, alanates and borohydrides^[1–3], have been regarded as promising candidate materials. Ti-doped NaAlH₄ as hydrogen storage material was proposed by Bogdanović et al., and it has a theoretical reversible hydrogen storage capacity of 5.6 wt.%^[4–7]. The sodium alanate dehydrogenate and rehydrogenate through a series of decomposition-recombination reactions under moderate conditions as follows:



The two combined reactions give a high theoretical reversible hydrogen storage capacity of 5.6 wt.%; however, the current state-of-the-art reversible hydrogen storage capacity is only around 4.2 wt.% for the transition metal halides-doped NaAlH₄. Moreover, the hydriding/dehydriding reaction kinetics also needs to be improved. The major works of sodium alanates system are trying to explore new kinds of catalysts, modify the microstructure of sodium alanate system by ball milling to reduce the grain size and reaction enthalpy^[8–10].

Rare-earth compounds as catalysts have been widely used in various chemical synthesis reactions and surface modification of materials because of their specific elec-

tron structures. However, they as a kind of dopant for complex metal hydrides are not explored systematically. Only a few counterpart results were reported. Bogdanović et al. reported that, by doping with ScCl₃, PrCl₃ and CeCl₃, the hydrogen storage capacity of NaAlH₄ could be considerably improved, even leading the properties closer to practically useful values^[11]. Lee et al. investigated the de/sorption kinetics and cyclic stability of NaAlH₄ catalyzed with lanthanon oxides, and found that Sm₂O₃ showed the best catalytic performance in both the hydriding kinetics and cyclic stability^[12]. Sun et al. used the lanthanum chlorides and La₂O₃ as catalysts to enhance the dehydriding kinetics of NaAlH₄^[13].

The purpose of this paper is to investigate the catalytic effect of lanthanon hydrides, namely, LaH_{3.01} and CeH_{2.51}, on the hydriding and dehydriding properties of NaAlH₄. The microstructure and hydriding/dehydriding behaviors of the ball-milled (NaH/Al+x mol.% RE-H) composites (RE=La, Ce; x=2, 4, 6) were investigated and reported.

1 Experimental

The starting materials were NaH powder (95%, 74 μm, purchased from Sigma-Aldrich Corp.), Al powder (99%, 74–154 μm), and pure lanthanum and cerium bulks (98%,

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purchased from Rico National Engineering Research Center of Rare-earth Metallurgy & Functional Materials of China) as raw materials of lanthanum hydride and cerium hydride. Then all the operations were carried out in the glove box under pure argon atmosphere. Referring to the hydrogen embrittlement procedure, lanthanum and cerium bulks were intruded into stainless steel vials of planetary ball milling, and ball-milled under 0.6 MPa hydrogen atmosphere at the speed of 500 r/min for 48 h, the milling process was stopped for 2 min after every 10 min of milling to avoid temperature rising during milling. After the catalysts were available, about 3 g sample was prepared each time as follows: NaH, Al and $\text{LaH}_{3.01}$ were weighed in 1:1:0.02/0.04/0.06 three mole ratios, also, NaH, Al and $\text{CeH}_{2.51}$ in 1:1:0.06 mole ratio was weighed. Then the mixtures were introduced into a stainless steel vial together with stainless steel balls. The ball-to-powder mass ratio was 30:1. The vial was then evacuated, and filled with 0.6 MPa supra-pure hydrogen. The milling parameters of the mixtures above were as the same as that of the catalysts.

The hydriding and dehydriding tests of the as-prepared samples (~1 g) were carried out on a Sievert's type apparatus at 120 °C under 12.5 MPa hydrogen pressure during hydrogenation, and at 170 °C against 0.1 MPa during dehydrogenation. The sample was kept at 170 °C under vacuum for 1 h before each hydrogenation.

X-ray diffraction (XRD, Rigaku D/Max PC2500) was performed for investigating the crystal structure of the samples. Surface morphology of the samples was studied by scanning electron microscopy (SEM, HITACHI S-570) with an energy dispersive analysis for X-rays (EDS).

2 Results and discussion

Fig. 1 shows the XRD patterns of lanthanon hydrides prepared by ball-milling pure lanthanide metal for 48 h under a hydrogen atmosphere of 0.6 MPa. It is found that after ball-milling for 48 h, lanthanum and cerium change to $\text{LaH}_{3.01}$ and $\text{CeH}_{2.51}$ lanthanon hydrides, which are non-stoichiometric compounds.

The SEM images of lanthanon hydrides prepared by

ball-milling are presented in Fig. 2. The as-prepared lanthanon hydrides are composed of many submicrometer spherical particles and a few planar particles. Particularly, the average particle size of $\text{LaH}_{3.01}$ is smaller than that of $\text{CeH}_{2.51}$, but the particle distribution of $\text{LaH}_{3.01}$ is less homogeneous than that of $\text{CeH}_{2.51}$.

The hydriding/dehydriding curves of the samples doped with different concentrations of $\text{LaH}_{3.01}$ in 5 cycles are shown in Fig. 3. We found that all samples are activated in the 2nd cycle and perform the best hydriding and dehydriding kinetics. The highest hydriding capacity of NaH/Al+x mol.% $\text{LaH}_{3.01}$ composites (x=2, 4, 6) is 4.78 wt.%, 3.71 wt.% and 3.68 wt.%, respectively. Under the same temperature and hydrogenation condition, the hydriding rate of NaH/Al+6 mol.% $\text{LaH}_{3.01}$ composite is faster than others. With the concentration of catalyst increasing, the dehydriding capacities decrease accordingly. The maximum dehydriding capacities of NaH/Al+x mol.% $\text{LaH}_{3.01}$ (x=2, 4, 6) are 4.66 wt.%, 3.82 wt.% and 3.38 wt.%, respectively. Moreover, the hydriding/dehydriding kinetics of composite are dependent on the concentration of catalyst. For example, the NaH/Al+2 mol.% $\text{LaH}_{3.01}$ composite absorbs 1.70 wt.% H_2 in 30 min. Moreover, the NaH/Al+6 mol.% $\text{LaH}_{3.01}$ composite exhibits the best hydriding kinetics, and it absorbs 2.63 wt.% H_2 in the same period, as shown in Fig. 4. This re-

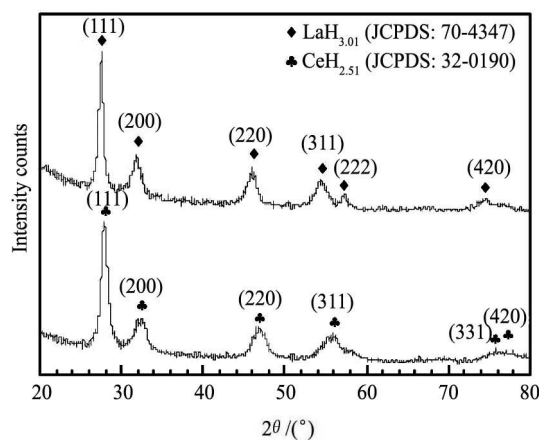


Fig. 1 XRD patterns of lanthanon hydrides prepared by ball-milling under hydrogen atmosphere for 48 h

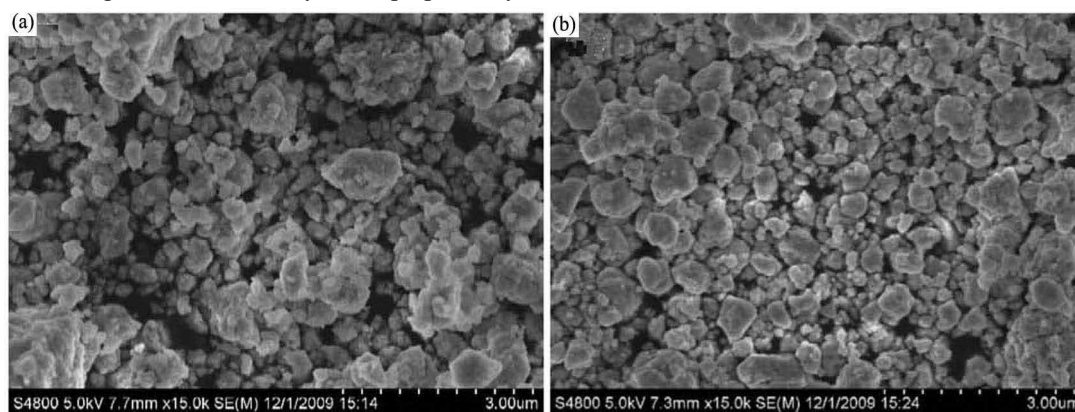


Fig. 2 SEM images of $\text{LaH}_{3.01}$ (a) and $\text{CeH}_{2.51}$ (b) prepared by ball-milling under hydrogen atmosphere for 48 h

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