

Hydrogen sorption properties of Ti-Zr hydride doped NaAlH₄

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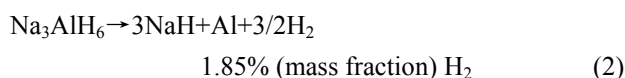
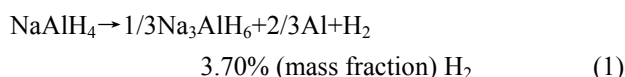
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Abstract: The as-prepared Ti-Zr hydride powder is used as dopant to improve hydrogen storage properties of NaAlH₄ upon mechanical milling under argon atmosphere. The as-milled sample is investigated by X-ray diffraction(XRD), scanning electron microscopy(SEM) and Sievert's technology test. It is observed that Ti-Zr hydride doped NaAlH₄ discharges 2.7% and 4.0% (mass fraction) of hydrogen in 40 min and 11 h at 160 °C, respectively, and keeps its reversible dehydrogenation capacity at 4.0% (mass fraction) after 10 hydrogenation/dehydrogenation cycles. These results show the Ti-Zr hydride doped NaAlH₄ has good reversible hydrogen storage capacity and kinetics. XRD and SEM investigations also show that the doped Ti-Zr hydride uniformly distributes in NaAlH₄ substrate and keeps stable during the hydrogenation/dehydrogenation cycle, indicating that Ti-Zr hydride plays the main surface-catalytic role on improving reversible hydrogen storage properties of NaAlH₄.

Key words: hydrogen storage materials; sodium alanates; Ti-Zr hydride dopant

1 Introduction

Sodium alanate, NaAlH₄, is a potential hydrogen storage candidate with a hydrogen content of 5.55% (mass fraction). This compound slowly decomposes in a two-step reaction:



These reactions take place slowly at 210 °C and 250 °C, respectively, moreover, they are irreversible. In 1997, Bogdanovic and Schwickardi reported that the elimination of hydrogen from solid NaAlH₄ could be markedly accelerated and rendered reversion under moderate conditions of doping hydride with a few molar percent of Ti or/and Zr organ[1]. Following this breakthrough, many intensifying efforts were done to utilize the NaAlH₄ as a practical hydrogen storage materials[2–4]. Further investigations showed that doped Ti and Zr compound are useful for increasing kinetics of reactions (1) and (2), respectively[5]. However, the doping process results in the formation of sodium

by-product and some gas impurities, degrading the reversible hydrogen storage capacity and thermal cycling stability of NaAlH₄[6]. To avoid forming the sodium by-product, WANG et al[7–8] bring the nano-titanium powder into NaAlH₄ by mechanically ball-milling to get the Ti hydride powder doped NaAlH₄ composite, which exhibits good hydrogenation/dehydrogenation capacity and kinetics.

In order to bring the advantages of Ti and Zr on improving kinetics of reactions (1) and (2) respectively and do not involve the by-products, gas impurities in the doping process, for the first time, the authors selected a Ti-Zr hydride as doping compound to improve hydrogen storage properties of NaAlH₄, and used ball milling method to prepare it due to the Ti-Zr hydride is brittle and easy to be crushed into small powder and be uniformly distributed into NaAlH₄ substrate. The aim of the present paper is to investigate the hydrogen storage properties of NaAlH₄ doped by this novel Ti-Zr hydride, and also to study the catalytic mechanism of Ti-Zr hydride doped NaAlH₄.

2 Experimental

Ti-Zr alloy was prepared by magnetic levitation

melting under Ar protection, the sample was turned over and remelted for homogeneity. The purity of raw material Ti and Zr is $>99.9\%$ (mass fraction). Then alloy was crushed into 1.7 mm pats and sealed into stainless steel reactor. The alloy was vacuumed at $550\text{ }^{\circ}\text{C}$ for 0.5 h, and then cooled to room temperature and bring into 3.5 MPa hydrogen to generate Ti-Zr hydride. Lastly, the Ti-Zr hydride and grinding balls with ratio of 1:10 were sealed into stainless steel vial to ball mill for 5 h by SPEX8000 mill. The average particle size of the as-milled powder is less than $5\text{ }\mu\text{m}$.

The starting material, NaAlH_4 (purity of 93%, particle size of $43\text{ }\mu\text{m}$) purchased from Acros Organics America was used without purification. The initial material, Ti-Zr hydride doped NaAlH_4 was prepared by ball milling method. Ti-Zr hydride powder was weighted in the molar ratio of NaAlH_4 :Ti-Zr hydride=97:3 in an argon filled glove box. The powders were mixed by ball milling under 0.5 MPa Ar in a high-energy SPEX8000 mill for 5 h with ball-to-powder mass ratio of 4:1. After mixing, a sample of about 0.5 g was transferred to the argon atmosphere glove box of a stainless steel reaction vessel for hydrogen storage properties measurement.

Hydrogenation and dehydrogenation behaviors were measured with a Sivert's type apparatus. Precise pressure measurement and temperature controlling as well were accomplished by using a high-precision pressure transducer and electric oven, respectively. A typical cyclic experiment entailed dehydrogenation at $160\text{ }^{\circ}\text{C}$ and hydrogenation at $120\text{ }^{\circ}\text{C}$ with an initial hydrogen pressure of 0.1 MPa and 9.5 MPa, respectively. Mass of Ti-Zr hydride was taken into calculation of hydrogen capacity of material.

The phase structure and microstructure of sample were characterized by powder X-ray diffraction(XRD, X-pert Pro, $\text{CuK}\alpha$ radiation) and scanning electron microscope (SEM, HITACHIS4800) equipped with an energy dispersive X-ray(EDX) analysis unit.

3 Results and discussion

3.1 Phase structure of sample

Fig.1 shows the XRD patterns for as-milled, dehydrogenated and rehydrogenated Ti-Zr hydride doped NaAlH_4 , respectively. For further analysis, the XRD pattern for as-milled Ti-Zr hydride is also shown in Fig.1(d). It is seen in Fig.1(a) that the main phase is NaAlH_4 , that means NaAlH_4 almost keeps unchangeable during ball milling process. However, as shown in Fig.1(b), after heating to $160\text{ }^{\circ}\text{C}$, the as-milled Ti-Zr hydride doped NaAlH_4 begins to decompose into Al, NaH and a little of Na_3AlH_6 , but no trace of NaAlH_4 can be found, indicating the reaction(1) of NaAlH_4 finished entirely and the reaction(2) is going partly. Subsequently,

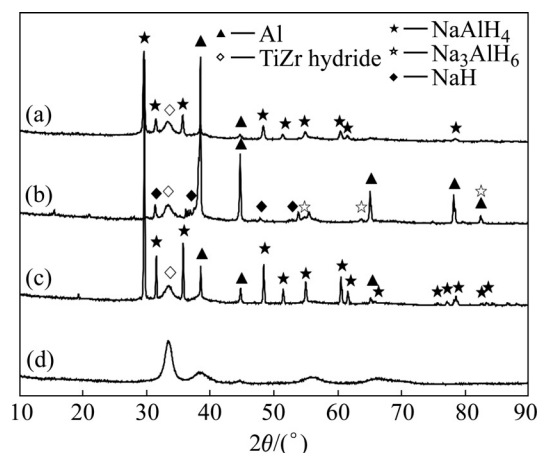


Fig.1 XRD patterns for as-milled state (a), dehydrogenated at $160\text{ }^{\circ}\text{C}$, 0.1 MPa for 11 h (b), hydrogenated at $120\text{ }^{\circ}\text{C}$, 9.5 MPa for 10 h (c) of 3% (mole fraction) Ti-Zr hydride doped NaAlH_4 and as-milled Ti-Zr hydride (d)

after rehydrogenating at $120\text{ }^{\circ}\text{C}$ and 9.5 MPa, except existence of a little amount of Al, NaAlH_4 phases are regenerated, as given in Fig.1(c), indicating a complete restoration of NaAlH_4 from Al, NaH by effect of Ti-Zr hydride dopant, namely that the Ti-Zr hydride doped with NaAlH_4 has a good reversible hydrogenation/dehydrogenation properties.

It is seen from Figs.1(a) to (d), the phase structure of Ti-Zr hydride identified by XRD basically keeps unchangeable for the as-milled, dehydrogenated and rehydrogenated samples, respectively.

3.2 Hydrogen storage properties

Fig.2 shows the dehydrogenation kinetics curves for as-milled Ti-Zr hydride doped NaAlH_4 at $160\text{ }^{\circ}\text{C}$, 0.1 MPa condition. The sample can release about 2.7% and 4.0% (mass fraction) hydrogen in 40 min and 10 h, respectively. The characteristics feature of a two-step dehydrogenation reaction in Ti- NaAlH_4 system[9–14] can also be found in the decomposition of Ti-Zr hydride doped NaAlH_4 sample. Different decomposition rates of NaAlH_4 cause its two different dehydrogenation kinetics region, as illustrated in I and II regions of Fig.2, which correspond to the reactions (1) and (2), respectively. It can also be found in Fig.3 that the hydrogen decomposition capacity of the sample remains at more 4.0% (mass fraction) after 10 hydrogenation and/or dehydrogenation cycles, indicating that Ti-Zr hydride doped NaAlH_4 has a remarkable cycling stability. Differing to the traditional metal Ti[7], TiCl_3 or TiH_2 dopants[9], the Ti-Zr hydride dopant not only make Ti-Zr hydride doped NaAlH_4 composite having good kinetic properties in reaction (1) but also enhancing the kinetic properties of reaction (2). That means the element Zr in Ti-Zr hydride dopant also performs important catalytic

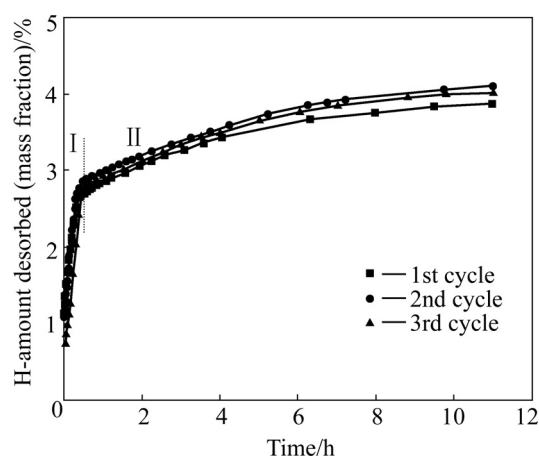


Fig.2 Dehydrogenation kinetics curves for 3% (mole fraction) Ti-Zr hydride doped NaAlH₄ at 160 °C and 0.1 MPa

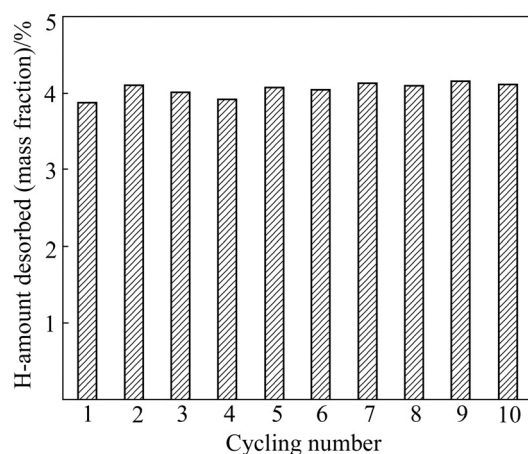


Fig.3 First ten cycles of dehydrogenation kinetics curves for 3% (mole fraction) Ti-Zr hydride doped NaAlH₄ at 160 °C and 0.1 MPa

effect on improving the dehydrogenation kinetics of NaAlH₄.

3.3 Catalyzing mechanism

The nature of the active Ti species that catalyzes the reversible hydrogenation/dehydrogenation of NaAlH₄ has been a subject of great interest, speculation, and controversy. Several Ti-containing species, including Al-Ti alloy[15–16], Ti⁰[1,17] and Ti cation with variable valance[11,18] have been speculated as possible candidate of the catalytically active species. However, the direct and convincing identification of this active species has been greatly hindered by the invisibility of Ti-containing species in conventional analytical techniques. However, the analysis of XRD patterns from Figs.1(a)–(c) shows that the phase structure of Ti-Zr hydride basically keeps unchangeable at as-milled, dehydrogenated and rehydrogenated samples states, respectively. To further explore the possible role of Ti-Zr

hydride on improving the kinetic properties of Ti-Zr hydride doped NaAlH₄ composite, the as-milled sample was subjected to SEM and EDS examination. As shown in Fig.4, Ti and Zr are all highly dispersed in as-milled sample matrix. These findings suggest that Ti-Zr hydride should act as surface-localized active species to catalyze the reversible dehydrogenation of NaAlH₄. Moreover, the dispersion degree of the Ti-Zr hydride in NaAlH₄ may greatly influence its decomposition kinetics. Further investigations on this prospect are underway to check the possibility.

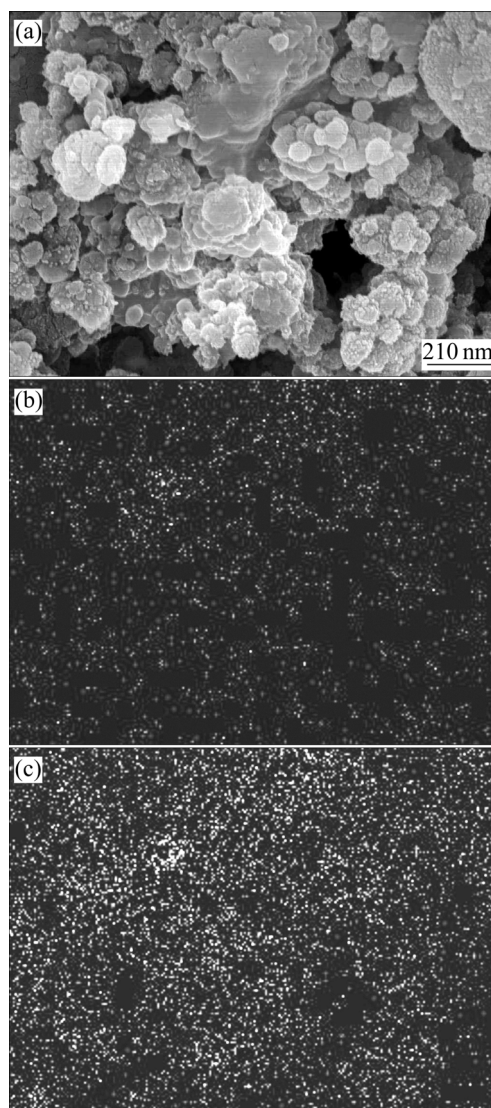


Fig.4 SEM and EDAX maps of Ti, Zr in Ti-Zr hydride doped NaAlH₄: (a) Electronic map; (b) Ti K_{α1}; (c) Zr L_{α1}

4 Conclusions

1) Mechanical milling of NaAlH₄ with the prepared Ti-Zr hydride under argon atmosphere has been found to have good reversible hydrogenation/dehydrogenation properties, the sample releases 2.7% and 4.0% (mass

fraction) hydrogen in 40 min and 11 h at 160 °C, 0.1 MPa, respectively.

2) After 10 hydrogenation/dehydrogenation cycles, the hydrogen decomposition capacity of the sample remains at more 4.0% (mass fraction).

3) The dopant Ti-Zr hydride uniformly distributes in the matrix of NaAlH₄ and keeps its phase unchangeable during the hydrogenation/dehydrogenation cycles, indicating that the surface-catalytic effect of the dopant plays the main role in the reversible hydrogen storage properties of NaAlH₄.

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