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Evolution of the active species and catalytic mechanism of Ti doped NaAlH₄ for hydrogen storage

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ABSTRACT

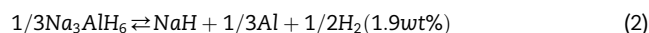
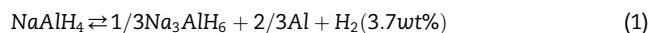
The catalytic mechanism of Ti doped NaAlH₄ for hydrogen storage remains unconfirmed. Here, we investigated the evolution of active species in Ti doped NaAlH₄ system by XRD, XPS and TEM. The results reveal that the evolution of the Ti addition in doped NaAlH₄ is Ti³⁺ → amorphous Ti⁰ → Al–Ti species → Al₃Ti intermetallic. TEM results show that the average particle size of the Al–Ti species and Al₃Ti intermetallic is about 30 nm, and Ti element is uniformly distributed in Al matrix. In further, we discussed the catalytic mechanism and role of active species in Ti doped NaAlH₄ system according to experimental and theoretical calculation. The rehydrogenation process of Ti doped NaAlH₄ system can be divided into three steps: (1) H₂ dissociation, (2) H atom spillover and alanes (Al_xH_y) formation and (3) complex hydrides formation. The addition of Ti can catalyze the process of H₂ dissociation, H atom spillover and formation of alanes. More importantly, the current work may provide a general approach to investigate the catalytic mechanism of other doped complex hydrides for hydrogen storage system.

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Introduction

Hydrogen is considered as a promising alternative energy carrier which can potentially facilitate the transition from fossil fuels to clean energy because it is the most abundant element in the universe, contains the highest energy density per unit mass and low environmental impact [1–3]. However, one of the most difficult remaining technological issues for using hydrogen is to develop hydrogen storage system [4–6]. In recent decades, numerous investigations have been devoted to design and synthesis hydrogen storage materials. Complex hydrides (such as NaAlH₄, LiAlH₄ and LiBH₄) were initially considered not suitable as hydrogen storage materials

due to their poor thermodynamics, kinetics, and reversibility [7–9]. In 1997, a systematic study by Bogdanovic [10] showed that Ti-catalyzed-NaAlH₄ exhibited good reversible hydrogen storage properties at moderate temperatures according to the following two-step reactions:



After Bogdanovic's pioneering work, a wide variety of studies demonstrated that transition-metal catalysts in IIIB (Sc, Y, La and Ce), IVB (Ti, Zr and Hf) and VB (V, Cr and Ta) can enhance the kinetics and reversibility of NaAlH₄ for hydrogen storage [11–17]. Among of them, Ti based catalysts (such as

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TiF₃, TiCl₃, TiO₂ and K₂TiF₆) were proved to be the most effective catalyst [18–21]. In addition, nanoconfinement was another alternative method to improve the kinetics of NaAlH₄, which was generally achieved by confining NaAlH₄ into nanoporous scaffolds by melt infiltration at high hydrogen pressure, using the nanoporous materials such as mesoporous carbon (MC) [22,23], silica (SBA-15) [24], and metal-organic frameworks (MOF) [25,26].

However, the catalytic mechanism of Ti-catalyzed-NaAlH₄ remains unconfirmed [27]. An obvious question to ask when trying to determine the mechanism of the catalytic activity of titanium is: where is the Ti in the doped material and how it can catalyze the hydrogen storage process? The possible active species in Ti-doped NaAlH₄ are Ti⁰, TiH_x (x = 1, 2), Ti–Al phase or Ti oxide. Up to now, a wide variety of experimental techniques and theory calculations have been employed to study the state of Ti in catalyzed- NaAlH₄ system including Synchrotron X-ray diffraction [28,29], X-ray spectroscopy (XPS) [30,31], scanning electron microscope/transmission electron microscope (SEM/TEM) [32–34] and extended X-ray fine structure (EXAFS) [35,36]. Several catalytic mechanisms have been proposed for Ti-catalyzed NaAlH₄ system, such as hydrogen pump/spillover mechanism [37,38], alane mobile species [39,40], nucleation/phase growth [41] and zipper model [42].

In our previous work, we have separated the Al₃Ti intermetallic from the NaAlH₄ + 10 mol% TiF₃ by dissolution and filtration using tetrahydrofuran (THF) as solvent [43]. Here, we further investigate the evolution and structure of the active species in Ti doped NaAlH₄ system by XRD, XPS and TEM. Moreover, we propose a new possible catalytic mechanism for Ti-doped NaAlH₄ system and discuss the role of active species.

Experimental and computational

Chemicals

NaAlH₄, TiF₃ and tetrahydrofuran (THF) were purchased from Sigma–Aldrich Corp., All chemicals were of analytical grade and used as received without further purification.

Evolution of the active species

The mixture of NaAlH₄ with 10 mol% TiF₃ was carefully introduced into a stainless steel vessel together with stainless steel balls in an Ar-filled glove box. The milling was carried out at 350 rpm and the ball-to-powder weight ratio was 60:1. A little milled sample was taken out from the stainless steel vessel for characterization after milling 15, 30, 60, 90, 180 and 300 min, respectively. The separation of active species can be achieved by filtration using tetrahydrofuran (THF) as solvent due to the dissolution of NaAlH₄ in THF. For a typical process, 0.5 g milled NaAlH₄ and cycled NaAlH₄ were dissolved in 50 ml THF at room temperature under vigorous stirring, respectively. Then the non-dissolved materials from two samples were obtained through filtration, which were noted as Al–Ti-m and Al–Ti-c, respectively. All steps were carried out in an Ar-filled glove box.

Characterization

The evolution of active species in Ti doped NaAlH₄ system was characterized by Powder X-ray diffraction (XRD, X'Pert-PRO powder X-ray diffractometer) and X-ray photoelectron spectroscopy (XPS, Escalab 250). Transmission electron microscopy (TEM, Tecnai-GF20), high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDX elemental scanning analyses were carried out to investigate the microstructure of the Al–Ti nanostructure. The sample for TEM measurement was suspended in ethanol and supported on a carbon-coated copper grid. The hydrogen desorption/adsorption kinetics and consecutive cycling of samples were performed on an high pressure gas reaction controller (Advanced Materials Corp., USA), and the hydrogen desorption was performed at 160 °C, and the hydrogen adsorption was carried out at 120 °C and p (H₂) = 100 bar for 2 h. The temperature inside the sample cell was measured in the experiments, and the measurement range of pressure sensors used for hydrogen desorption and adsorption cycling test were 0–20 bar and 0–200 bar with accuracy of 0.05%, respectively.

Computational methods

All present calculations are performed with DFT plane wave method utilizing the Cambridge Serial Total Energy Package (CASTEP) [44] in the Materials Studio of Accelry Inc. The ultrasoft pseudopotential [45] in conjunction with the Perdew–Wang (PW91) [46] functional within GGA, was applied in this work. The surfaces were modeled by periodic slabs containing six atomic layers of Al(111) or Ti doped Al(111) separated by a vacuum region of 15 Å. H₂ dissociation and atomic H diffusion were studied in a 2 × 2 unit cell with sixteen metal atoms per layer. The Brillouin zone was sampled with the Monkhorst–Pack grid [47]. The calculations were carried out using the 3 × 3 × 1 Monkhorst–Pack mesh k-points surface calculations, and cutoff energy was set to be 350 eV. The complete linear synchronous transit/quadratic synchronous transit (LST/QST) method was used to locate the transition states (TS) for the H₂ dissociation and H atom diffusion on the surface.

Results and discussion

Hydrogen storage properties of Ti doped NaAlH₄

Fig. 1 shows the hydrogen desorption curves of NaAlH₄ with 10 mol% TiF₃ at 160 °C against vacuum during ten cycles. All hydrogen adsorption were carried out at 120 °C and p (H₂) = 100 bar for 2 h. The curves clearly show that there are two different chemical reaction steps, and the first step corresponding to reaction (1) is faster than the second step. In the first desorption cycle, NaAlH₄ with 10 mol% TiF₃ starts to release hydrogen at about 60 °C, and about 2.3 wt.% hydrogen is released in less than 10 min. While the hydrogen desorption rate falls drastically after 10min and about 3.8 wt.% hydrogen is released at 160 °C in 80 min. This sudden change in hydrogen desorption kinetics reflects the transition from reaction (1) to (2) of NaAlH₄. The hydrogen desorption curves of

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