Available online at www.sciencedirect.com
ScienceDirect

Journal of Energy Chemistry 23(2014)726–731

JOURNAL OF ENERGY CHEMISTRY
www.elsevier.com/journals/
journal-of-energy-chemistry/2095-4956
www.elsevier.com/locate/jngc

# Synergetic effects of $NaAlH_4$-$TiF_3$ co-additive on dehydriding reaction of $Mg(AlH_4)_2$

Ying Wang, Li Li, Fangyuan Qiu, Cuihua An, Yijing Wang*, Lifang Jiao, Huatang Yuan

*Institute of New Energy Material Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Key Laboratory of Advanced Energy Materials Chemistry (MOE), Nankai University, Tianjin 300071, China*

[ Manuscript received March 11, 2014; revised April 29, 2014 ]

**Abstract**

The effects of $NaAlH_4$, $TiF_3$ and $NaAlH_4$-$TiF_3$ co-additive on dehydriding reaction of $Mg(AlH_4)_2$ are systematically investigated. The onset dehydrogenation temperature of the co-doped $Mg(AlH_4)_2$ composites decreased to 74 °C, which is about 59 °C lower than that of pure $Mg(AlH_4)_2$. The dehydrogenation kinetics of $NaAlH_4$-$TiF_3$ co-doped $Mg(AlH_4)_2$ sample was also improved, which released about 94% hydrogen within 48 min, but no visible hydrogen was released from pure $Mg(AlH_4)_2$ under the same conditions. The activation energy of co-doped $Mg(AlH_4)_2$ was 85.6 $kJ\cdot mol^{-1}$, which was significantly lower than that of additive-free $Mg(AlH_4)_2$ sample. The synergetic effects of $NaAlH_4$ and $TiF_3$ on the dehydrogenation performance of $Mg(AlH_4)_2$ were confirmed. In addition, a possible catalytic mechanism is discussed, regarding the different roles of $NaAlH_4$ and $TiF_3$ on $Mg(AlH_4)_2$.

**Key words**

hydrogen storage; $Mg(AlH_4)_2$; co-additive; synergetic effects; dehydrogenation properties

## 1. Introduction

Along with the increasing global demand for energy and serious environmental pollution of fossil fuels, considerable efforts have been paid to find renewable and clean energy alternatives [1−4]. Due to its high energy efficiency and environmentally friendly property, hydrogen is considered as an ideal alternative energy carrier [5−8]. However, the widespread implementation of hydrogen appeals for advanced materials that can store and deliver large amounts of hydrogen with fast kinetics at moderate temperature [9]. Since Bogdanović et al. [10,11] first made $NaAlH_4$ reversible under mild conditions, complex metal hydrides have been proposed as promising hydrogen storage mediums [12−16]. Amongst them, $Mg(AlH_4)_2$ has attracted tremendous researches for its high theoretical $H_2$ capacity (9.3 wt%), non-toxicity to environment and commercial favorable properties.

$Mg(AlH_4)_2$ was successfully synthesized by Wiberg and Bauer [17] via solvent mediated metathesis method in 1950. Thermal analyses confirmed that $Mg(AlH_4)_2$ dehydrogenated through the following two major reactions [18,19]:

$$Mg(AlH_4)_2 \rightarrow MgH_2 + 2Al + 3H_2 \tag{1}$$

$$MgH_2 + Al \rightarrow Mg_2Al_3 + (Mg, Al)ss + H_2 \tag{2}$$

Generally, the onset dehydrogenation temperature of $Mg(AlH_4)_2$ varies from 115 °C to 200 °C [20−22]. The relatively high decomposition temperature and sluggish dehydrogenation kinetics of $Mg(AlH_4)_2$ have limited its commercial use. Therefore numerous methods have been proposed to overcome these drawbacks. In practice, high energy ball-milling is an effective way to create active sites and defects which play important roles in the dehydrogenation of $Mg(AlH_4)_2$. Another important method is to explore high-performance catalysts or additives [23−25]. Among all the additives, Ti-based compounds are widely used. For example, Amama et al. [26] reported the positive effects of different Ti precursors (Ti, $TiO_2$ and $TiCl_3$) on $LiAlH_4$, which could significantly decrease its decomposition temperature and activation energy. The enhanced destabilization effects of $TiCl_3$ on $Mg(AlH_4)_2$ was found by Fichtner et al. [20]. It was found that the operating temperature of $TiCl_3$ doped $Mg(AlH_4)_2$ was 45 °C lower than that of pure $Mg(AlH_4)_2$. More recently, Liu et al. [21] found that $TiF_4$ could significantly improve the dehydrogenation kinetics of $Mg(AlH_4)_2$. Computation

---

* Corresponding author. Tel/Fax: +86-22-23503639; E-mail: wangyi@nankai.edu.cn

This work was supported by the MOST Project (2010CB631303, 2012AA051901), NSFC (5117108), 111 Project (B12015) and MOE (IRT-13R30).

doi: 10.1016/S2095-4956(14)60205-9

investigations [27] showed that F anion and Ti cation had synergetic effects on the dissociation of hydrogen, which implied that $TiF_3$ may also improve the dehydrogenation properties of $Mg(AlH_4)_2$.

The combination of different hydrides can generally lead to better hydrogen storage properties than their individual competitors. Yang et al. [28] investigated that $Mg(BH_4)_2$-$LiAlH_4$ mixtures had a lower onset dehydrogenation temperature than that of either $Mg(BH_4)_2$ or $LiAlH_4$ alone. Yang et al. [29,30] found that the existence of $NaAlH_4$ could decrease the dehydrogenation temperature of $Mg(AlH_4)_2$ to a lower value. Using in situ synchrotron X-ray diffraction their group further confirmed the destabilization effects of $NaAlH_4$ on $Mg(AlH_4)_2$.

Considering the fascinating effects of both Ti-based compounds and $NaAlH_4$ on $Mg(AlH_4)_2$, we expect that $NaAlH_4$-$TiF_3$ co-additive will show some significant improvements on $Mg(AlH_4)_2$. In this work, small amounts of $NaAlH_4$ and $TiF_3$ were added into $Mg(AlH_4)_2$ stepwise. And the synergetic effects of $NaAlH_4$ and $TiF_3$ on the desorption properties of $Mg(AlH_4)_2$ were investigated. It also confirmed that $NaAlH_4$ and $TiF_3$ play different roles in the dehydriding reaction of $Mg(AlH_4)_2$.

## 2. Experimental

### *2.1. Synthesis of $Mg(AlH_4)_2$ composites*

Commercially available $NaAlH_4$, $MgCl_2$ and $TiF_3$ were purchased from Alfa Aesar and used as received. $Mg(AlH_4)_2$ was synthesized by a typical metathesis reaction of $MgCl_2 : NaAlH_4 = 2 : 1$ [31]. The mixture was mechanical ball milled for 5 h at the speed of 450 rpm. The ball-to-powder weight ratio was kept at 50 : 1. The $NaAlH_4$ doped sample was prepared by intentionally adding extra 10 mol% $NaAlH_4$ (on the base of $Mg(AlH_4)_2$) in the precursors.

After the high energy ball-milling, 5 mol% $TiF_3$ (on the base of $Mg(AlH_4)_2$) was added into the after-milled powders and further ground for 5 min. For convenience, the compositions of different samples and their names were listed in Table 1. Except the difference of composition, all the samples were prepared under the same conditions. All the handling and transfer were performed in an argon-filled glove box, which was equipped with a circulatory equipment to keep water and oxygen below 10 ppm.

### *2.2. Characterizations*

NaCl is an inevitable by-product during the metathesis reaction. In this paper, all the experiments were done without further isolation of NaCl. So the theoretical hydrogen capacity of this NaCl-contained system was 3.9 wt%.

The structure was identified by X-ray diffraction (XRD, Rigaku MininFlexII, Cu $K_\alpha$ radiation) with a protective para film. The morphology was determined by high-resolution field emission scanning electron microscopy (FESEM, JEOL-JSM7500). The Al-H vibration spectrum was determined by Fourier transform infrared spectroscopy (FTIR, FTIR-650). The dehydrogenation performance was evaluated by temperature-programmed desorption system (TPD, PX200), under an argon flow of 35 mL·min$^{-1}$. The sorption kinetics was performed by a home-made Sievert's apparatus, using volumetric method. Differential scanning calorimeter (DSC, Q20P) was used to analysis the heat effects during the dehydriding reaction.

**Table 1. Samples compositions used in this work**

| Sample | Compositions |
|---|---|
| S1 | $Mg(AlH_4)_2$ |
| S2 | $Mg(AlH_4)_2$-10 mol% $NaAlH_4$ |
| S3 | $Mg(AlH_4)_2$-5 mol% $TiF_3$ |
| S4 | $Mg(AlH_4)_2$-10mol%$NaAlH_4$-5mol%$TiF_3$ |

## 3. Results and discussion

### *3.1. Structure characterization*

XRD equipment was used to determine the structures of the as-synthesized samples. Figure 1 shows that the diffraction peaks of $MgCl_2$ and $NaAlH_4$ were disappeared after the milling. Moreover, the main peaks in all the as-prepared samples could be well distributed to the new phases of $Mg(AlH_4)_2$ and NaCl. Therefore, it is confirmed that the metathesis reaction of $MgCl_2$ and $NaAlH_4$ is complete and $Mg(AlH_4)_2$ is successfully synthesized. In addition, the diffraction peaks of $NaAlH_4$-$TiF_3$ co-doped $Mg(AlH_4)_2$ sample were distinctly enhanced, which implies a better crystallization. It is worth noting that the invisible diffractions of $NaAlH_4$ and $TiF_3$ may attribute to their amorphization caused by the milling and the relative low content (2.6 wt% for 10 mol% $NaAlH_4$ and 2.7 wt% for 5 mol% $TiF_3$).

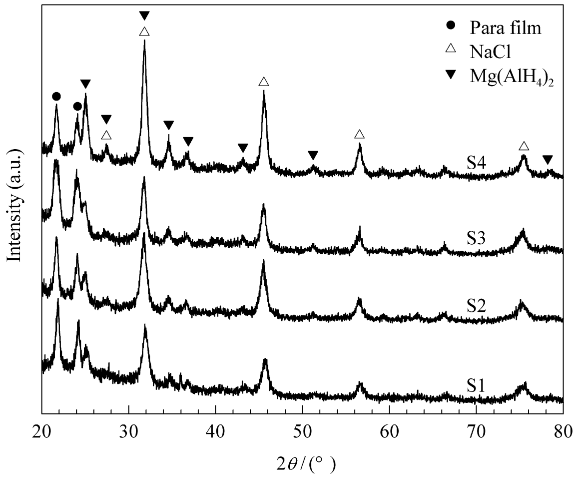

**Figure 1.** XRD patterns of different samples

The FTIR spectroscopy is given in Figure 2. Obviously, the infrared vibration at 3440 cm$^{-1}$ is ascribed to the O−H