Enhanced hydrogen storage properties of MgH$_2$ co-catalyzed with NbF$_5$ and single-walled carbon nanotubes

Ye Luo, Ping Wang, Lai-Peng Ma and Hui-Ming Cheng*
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

Received 19 December 2006; revised 5 January 2007; accepted 7 January 2007
Available online 8 February 2007

The hydrogen storage performance of ball-milled MgH$_2$ with 5 wt.% NbF$_5$ + 5 wt.% single-walled carbon nanotubes as additives was investigated. We found that the hydrogen-sorption kinetics of magnesium is markedly improved by these co-additives. At 573 K, this hydride can absorb 6.3 wt.% hydrogen within 30 s. Even at 373 K, 5.2 wt.% of hydrogen can be absorbed within 10 min. This enhanced hydrogen storage performance was also observed to persist during subsequent absorption/desorption cycles.

Keywords: Hydrogen storage; Magnesium; Mechanical milling; Niobium fluoride; Carbon nanotubes

Magnesium hydride is one of the most studied hydrides due to its high hydrogen storage capacity (with a theoretical maximum value of 7.6 wt.%), high abundance and low cost. However, it has not been widely adopted commercially because of its high operating temperature and sluggish sorption kinetics [1,2]. As demonstrated experimentally, addition of catalysts by mechanical milling can accelerate the hydrogen sorption process of MgH$_2$, within thermodynamic limits [3–11]. The catalysts used include transition metals and/or their oxides, hydrogen storage alloys and carbon materials. Among these, transition metal oxides such as Nb$_2$O$_5$ have attracted considerable interest due to their pronounced catalytic effect [12,13].

We recently found that transition metal fluorides also offer a promising choice for a magnesium-based hydrogen storage system. The pronounced catalytic effect on absorption/desorption kinetics, particularly at relatively low temperatures, has been demonstrated in the Mg–NbF$_5$ and Mg–TiF$_3$ systems [14,15]. However, the hydrogen-sorption capacity, as well as the cycling stability, need to be further improved.

Single-walled carbon nanotubes (SWNTs) possess a unique morphology and electronic structure. In several recent studies, it has been shown that SWNTs also have a positive and sustained effect on the sorption rate and capacity, as well as the cycling stability of MgH$_2$ [16]. Interestingly, we found that MgH$_2$ catalyzed with as-prepared SWNTs (containing 40 wt.% of Fe, Co and Ni) exhibits further improved absorption kinetics and lowered desorption temperature compared with MgH$_2$ catalyzed with purified SWNTs [17]. In addition, it was reported that a significantly enhanced sorption kinetics was achieved in the MgH$_2$–FeTi–SWNTs system; this was believed to come from a synergetic catalytic effect between incorporated carbon and titanium [18]. All these findings suggest that co-catalysis with a transition metal compound and SWNTs may be a promising way to further improve the hydrogen-storing properties of MgH$_2$. In the present paper, we report an investigation of the Mg–NbF$_5$–SWNTs system. As expected, the simultaneous addition of fluoride and SWNTs results in a markedly improved hydrogen capacity and sorption kinetics of MgH$_2$.

The SWNTs used were prepared by hydrogen arc discharge method, as detailed in Ref. [19], and were purified using a procedure previously reported in Ref. [20].

The initial MgH$_2$ powder was prepared by ball-milling magnesium powder (purity >99.9%, 300 mesh) under a hydrogen atmosphere with an initial pressure of 4 MPa for 2 h, followed by 5 h hydrogenation at 573 K. The process was repeated three times to achieve a hydrogenation ratio of 85%, which was determined volumetrically. Niobium fluoride (NbF$_5$, 98% purity, Sigma–Aldrich) powder was used as received. Thus-prepared MgH$_2$ was mechanically milled with 5 wt.% NbF$_5$.
and 5 wt.% SWNTs for 2 h under an argon atmosphere using a SPEX 8000 mill. For comparison, MgH$_2$ + 5 wt.% NbF$_5$ was milled under identical conditions. Two hardened steel balls of 12.75 mm and four hardened steel balls of 6.35 mm in diameter were used for milling, and the ball-to-powder weight ratio was about 40:1. All the sample handling was performed in an argon-filled glovebox (MBraun), in which typical water/oxygen levels were below 1 ppm.

The samples were characterized using X-ray diffraction (XRD, Rigaku D/max 2400) with Cu K$_\alpha$ radiation. The hydrogen-storing properties of the samples were examined using an automatic Sieverts apparatus, in which the pressure and temperature data were simultaneously collected to allow for correction of the pressure change caused by the temperature variation. The leakage rate of the system in the pressure holding test (12 MPa hydrogen for 120 h) was lower than $3.1 \times 10^{-8}$ mmol s$^{-1}$. The mass of the sample for every measurement run was around 200 mg. Before measurements, the system was degassed for 1.5 h with the sample cell being heated to 623 K. Absorption/desorption measurements were performed at various temperatures with an initial pressure of 2 MPa and <10 Pa, respectively. The hydrogen storage capacity was calculated after taking all components into account.

Figure 1 presents a systematic comparison on the absorption behavior between the MgH$_2$ samples with NbF$_5$ as the sole additive and with NbF$_5$ + SWNTs as co-additives. It was observed that the simultaneous addition of NbF$_5$ and SWNTs further improves both the absorption rate and capacity of MgH$_2$. At 573 K in Figure 1a, the amount of hydrogen absorbed is increased from 6.0 to 6.3 wt.% within 30 s. At lower temperatures, the improvement in absorption arising upon adding SWNTs becomes more pronounced. As seen in Figure 1b and c, the co-catalyzed sample can absorb an additional 0.5 and 0.8 wt.% hydrogen within 60 min at 473 and 373 K, respectively. When operated at moderate temperature (i.e. 373 K), MgH$_2$ + 5 wt.% NbF$_5$ + 5 wt.% SWNTs could absorb 4.8 wt.% hydrogen in 5 min. This absorption performance is comparable with the best literature results [13].

As demonstrated above, the addition of SWNTs produces a positive influence on the hydrogen absorption capacity and hydrogenation rate of MgH$_2$. In terms of desorption, however, SWNTs had a negative effect. Figure 2 shows the hydrogen desorption profiles of the MgH$_2$ + 5 wt.% NbF$_5$, MgH$_2$ + 5 wt.% SWNTs and MgH$_2$ + 5 wt.% NbF$_5$ at 573 K. Both the desorption rate and capacity of the co-catalyzed sample are inferior to that of the sample with NbF$_5$ as the only additive. Currently, the mechanism behind the observed degradation in desorption performance is not yet clear.

The co-catalyzed and singly catalyzed MgH$_2$ samples were further investigated with regard to cycling stability. Figure 3a and b presents the cycling absorption profiles of the two samples, respectively. It was found that the absorption profile of the NbF$_5$ + SWNTs co-catalyzed sample in the 10th cycle is nearly identical to that of first cycle. In contrast, as seen in Figure 3b, the MgH$_2$ + 5 wt.% NbF$_5$ sample suffers from serious capacity loss: only 5 wt.% hydrogen can be obtained after 10 cycles, about 1.5 wt.% lower than that in the first cycle. In Figure 4, the cycling desorption profiles of the two samples are compared. Here, it should be noted that a two-step desorption process (first at 573 K for 1 h, then at 623 K for 2 h) was applied to allow a complete hydrogen discharge from the samples. But only the profiles collected at 573 K with an initial vacuum condition were presented. It was found that both samples need two or three cycles to achieve the maximum desorption kinetics. Then the co-catalyzed sample strongly maintains its desorption performance in subsequent cycles. Its 10th desorption profile is nearly identical to its third one. About 4.5 wt.% hydrogen can be desorbed within 60 min. However, for the MgH$_2$ + 5 wt.% NbF$_5$ sample,
only 3.3 wt.% hydrogen was desorbed within the same period in the 10th cycle. Here, it should be noted that the problematic desorption kinetics arising upon adding SWNTs could be partially alleviated after the first three cycles (as seen in Fig. 4a).

Figure 5 presents the X-ray diffraction patterns of the as-milled MgH$_2$ + 5 wt.% NbF$_5$ + 5 wt.% SWNTs sample as well as those of the dehydrogenated and hydrogenated states after cycling at 573 K. For comparison, the MgH$_2$ + 5 wt.% NbF$_5$ sample milled under identical conditions is also included. It was observed that the diffraction patterns of the two samples in the as-milled state are quite similar. In both cases, the most intense Bragg peaks are identified as tetragonal $\beta$-MgH$_2$ (PDF 12-0697), and a metastable orthorhombic phase $\gamma$-MgH$_2$ (PDF 35-1184) can be observed, which has been previously reported to form upon milling MgH$_2$ [16]. The most intense peaks are from Mg (PDF 35-0821) in the dehydrogenated state of MgH$_2$ + 5 wt.% NbF$_5$ + 5 wt.% SWNTs after cycling and (d) hydrogenated sample of MgH$_2$ + 5 wt.% NbF$_5$ + 5 wt.% SWNTs after cycling.

mainly come from oxygen contamination during XRD examination. MgF$_2$ can be identified in the dehydrogenated/hydrogenated sample, suggesting that MgH$_2$ reacts with NbF$_5$ to produce MgF$_2$ [14]. No diffraction peaks from NbF$_5$ and SWNTs can be detected, which agrees with previous results [14,18].

It has been well established that transition metals may facilitate the dissociation of hydrogen molecules and the recombination of hydrogen atoms into the molecular state. When MgH$_2$ and NbF$_5$ were milled together [14], Nb species with zero and $x^+$ valence states were identified in the as-milled and dehydrogenated states by X-ray photoelectron spectroscopy (XPS). This may account for the observed catalytic effect arising upon adding NbF$_5$. Regarding the positive effect of SWNTs, however, no conclusive explanation can yet be given. Several recent studies reported the catalytic effect of SWNTs on the reversible desorption of Mg, Li–N–H system, etc. It was suggested that SWNTs might simply serve as a mixing agent [18]. Alternatively, it was claimed that the metal catalyst particles incorporated during the process of preparing SWNTs might play a critical role in catalytic enhancement [16,17]. In the present co-catalyzed system, these possibilities may exist. Additionally, the possibility of synergetic catalysis associated with interaction between facile $\pi$-electrons of SWNTs and the 3d-electrons of transition metal cannot be ruled out. Further investigation on the electronic structure of the samples and related materials may throw more light on the possible mechanisms.

Simultaneous addition of 5 wt.% NbF$_5$ and 5 wt.% SWNTs leads to a pronounced improvement in the hydrogen-storing properties of MgH$_2$. Compared with the sample catalyzed by NbF$_5$ alone, MgH$_2$ co-catalyzed with NbF$_5$ + SWNTs has enhanced absorption kinetics and cycling capacity. It can absorb 6.3 wt.% hydrogen in about 30 s and 6.7 wt.% in 60 min at 573 K. Even at 373 K, 5.2 wt.% of hydrogen can be absorbed in 10 min. Additionally, the co-catalyzed sample exhibits improved absorption/desorption cycling stability. The problematic desorption kinetics in the co-catalyzed sample can be partially alleviated by submitting the sample to several cycles of absorption/desorption.

The financial support for this research from the Hundred Talents Project of Chinese Academy of Sciences is gratefully acknowledged.