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Improvement in hydrogen sorption kinetics of MgH_2 with Nb hydride catalyst

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Abstract

Nanocrystalline MgH_2 with fine and evenly dispersed Nb hydride was prepared by ball milling a mixture of MgH_2 and 1 mol.% NbF_5. This NbH-catalyzed MgH_2 desorbed 6.3 wt.% H_2 in 15 min and absorbed more than 90% of its initial hydrogen capacity within 5 min at 573 K. Moreover, this fast sorption kinetics was maintained after 10 cycles. Based on X-ray diffraction and transmission electron microscopy/energy-dispersive spectroscopy analyses, it is suggested that NbF_5 melts during high-energy ball milling and this promotes the formation of extremely fine, film-like Nb hydride preferentially along the grain boundaries of nanocrystalline MgH_2 by a liquid/solid reaction. This unique nanostructured Nb hydride is believed to suppress the grain growth of MgH_2 quite effectively and thus maintain its initial catalytic effect throughout repeated hydrogenation–dehydrogenation cycles.

Keywords: Hydrogen storage; Hydrides; Mechanical milling; Transmission electron microscopy; Catalyst

1. Introduction

The hydrogen storage capacity of MgH_2, 7.6 wt.%, is almost four times higher than those of conventional room temperature interstitial hydrogen storage alloys such as AB_5, AB and AB_2 systems. In addition, MgH_2 does not contain expensive raw materials and is relatively safe to handle compared to other alkali metal and complex metal hydrides. However, the equilibrium dehydrogenation temperature is high, 560 K under 1 bar of hydrogen, and the sorption kinetics is unacceptably slow. These are the main obstacles to overcome before MgH_2 can be seriously considered as a practical materials for high-capacity solid-state hydrogen storage systems.

It has recently been reported [1–6] that some transition metal oxides show a significant improvement in the kinetics of both the dehydrogenation and hydrogenation reaction of MgH_2. In addition, the required milling time to achieve very fast sorption kinetics could be significantly reduced from a few days down to less than an hour or so by using Nb_2O_5 nanoparticles instead of ordinary micron-sized Nb_2O_5 powder [7]. Recently, Hanada et al. [8] reported that the amount of hydrogen absorption reaches up to about 4.5 wt.% at room temperature within 15 s for Mg catalyzed with mesoporous Nb_2O_5 (pore size 3.2 nm). It has also been proposed [9,10] that the actual catalytic effect has to be due either to metallic Nb or Mg–Nb composite oxides with probable oxygen deficiency formed during the first dehydrogenation/hydrogenation cycle as Nb_2O_5 is certainly not thermodynamically stable in the presence of free Mg.

It is now well known that Ti chlorides are very good catalysts for $NaAlH_4$ [11,12]. However, there is still a dispute

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on the actual chemical form of the catalyst and its exact role during dehydrogenation–hydrogenation cycling. One hypothesis is that the actual chemical form is titanium hydride on Ti–Al alloy surfaces formed during mechanical milling and/or heating, which acts as the real catalyst since it has a strong catalytic effect on decomposition of hydrogen molecules into atomic hydrogen and vice versa [13–15]. It will therefore be interesting to see if there is a similar effect on the sorption reactions of MgH_2 with Nb hydrides.

Since it is almost certain that there exists oxide (or hydroxide) layers on any Nb or Nb hydride particles, these are not proper starting materials. Moreover, the finer the particle size, the higher the oxygen level. To verify unambiguously the catalytic action of Nb hydride on the sorption kinetics of MgH_2, one has to use quite fine particles without surface oxide. We have recently found [16] that the addition of NbF_5 significantly improves the sorption kinetics of MgH_2 and that it would be an ideal additive to confirm whether or not extremely fine and surface oxide-free Nb hydrides formed in situ during ball milling and/or hydrogenation processes will act as an effective catalyst. In the present study, we have investigated the effect of NbF_5 addition on the dehydrogenation and hydrogenation kinetics as well as the cycle performance of commercial MgH_2 powder. We have also investigated changes in microstructure after cycling. We also present a plausible explanation, deduced from the results of X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses, as to why MgH_2 ball milled with NbF_5 shows extremely good sorption kinetics compared with other Nb compounds.

2. Experimental procedure

NbF_5 (98%) and MgH_2 (98%) were purchased from Aldrich and Alfa Asear, respectively. One gram of MgH_2 containing 1 mol.% of NbF_5 was charged with 10 7.9 mm diameter Cr-steel balls into a 70 ml hardened steel vial and milled for 15 min with a SPEX-8000 vibratory mill. Special care was taken to prevent inhomogeneous dispersion of catalyst and suppress uneven milling of MgH_2 due to the comparatively short milling time and inevitable gravitational segregation. Except for milling, the sample was handled entirely in a glovebox under argon atmosphere. Both the oxygen and water vapor levels inside the glovebox were kept below 1 ppm.

The thermal decomposition behavior of the milled sample was evaluated using a Netzsch 204 F1 Phoenix differential scanning calorimeter (DSC). Inside the glovebox, about 5 mg of the sample was sealed into an aluminum pan with a lid and three pin holes were made just before starting the measurements. The heating and the argon (99.9999%) flow rates were $5\ K\ min^{-1}$ and $50\ ml\ min^{-1}$, respectively. The dehydrogenation and hydrogenation kinetics as well as the cycling performance were measured with a Netzsch 204 HP Phoenix high-pressure DSC equipped with a high-pressure dynamic gas flow and a vacuum control system. It was heated at $5\ K\ min^{-1}$ to 623 K under flowing argon at $50\ ml\ min^{-1}$. Once the dehydrogenation reaction was complete, the temperature was reduced to 573 K and 99.9999% H_2 was introduced immediately after the DSC chamber had been evacuated. During hydrogenation step, the dynamic pressure and flow rate of hydrogen were maintained at 10 bar and $50\ ml\ min^{-1}$, respectively. When the hydrogenation reaction ended, the chamber was evacuated and argon was introduced again at $50\ ml\ min^{-1}$ under 1 bar. These hydrogenation–dehydrogenation steps were repeated up to 10 cycles and the sample was cooled to room temperature under 10 bar of hydrogen. From this experimental sequence, the cycle performance of sorption kinetics and the relative degradation of hydrogen storage capacity could be evaluated simultaneously. The actual hydrogen storage capacities of the as-milled samples were measured using a Netzsch 209 F1 thermogravimeter (TG) coupled with a Netzsch 403 C mass spectrometer.

The phase composition of the as-milled sample was measured by a Bruker D8 Advance XRD with Cu Kα radiation. A special airtight sample holder was used to prevent any possible reactions between the sample and air during XRD measurement. The chemistry, morphology and dispersion of catalysts as well as the microstructure of both the as-milled sample and the hydrogenated sample after the 11th hydrogenation were characterized using a FEI Techni G^2 TEM with energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

When 1 mol.% of NbF_5 was added to as-received MgH_2, the decomposition start temperature decreased by more than 423 K compared to MgH_2 without catalyst. MgH_2 starts to decompose at about 433 K and the process is complete at 593 K – the temperature at which uncatalyzed MgH_2 begins to decompose. This result is as good as or even better than those of MgH_2 with Nb_2O_5 nanoparticles [7]. It should be mentioned, however, that the decrease in decomposition temperature of MgH_2 with NbF_5 is not because the thermodynamics of MgH_2 has changed but because the reaction kinetics is significantly improved such that MgH_2 decomposes under a near-equilibrium condition. In fact, hydrogen partial pressure inside the DSC cell was much lower than 1 bar due to the dynamic argon flow. It should also be noted that the decomposition temperature range for NbF_5-added MgH_2 is much wider than that of uncatalyzed MgH_2.

The amount of hydrogen desorbed from MgH_2 with 1 mol.% NbF_5 was 6.3 wt.%, while uncatalyzed MgH_2 produced 7.0 wt.% H_2. The start and finish temperatures of the decomposition reaction recorded by TG (Fig. 2) agree very well with those from DSC (Fig. 1). There may be several reasons for the lower than expected hydrogen content of as-received MgH_2. These include MgO and free Mg impurities in commercial MgH_2 raw material confirmed by XRD (not included here), partial decomposition of