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Hydrogenation of Nanocrystalline Mg at Room Temperature in the Presence of TiH_2

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Hydrogen as a fuel is one of the most promising energy carriers for a cleaner global environment based on renewable energy. The use of hydrogen requires the development of an efficient and effective method for hydrogen storage that can not only store hydrogen safely but also supply it where needed and when it is needed. Metal hydrides,[1] chemical hydrides,[2] and high surface area adsorbents[3] including carbon and metal−organic frameworks (MOF)[4] have been investigated as hydrogen storage media. Most complex metal hydrides hydrogenate at high temperatures (>250 °C) because of slow kinetics at low temperature that is caused by the high energy barrier of the hydrogenation reactions. In contrast, when high surface area adsorbents such as carbon nanoframeworks and MOFs are used, hydrogen adsorption takes place at low temperature ranges (∼77−200 K) due to weak interactions between the hydrogen molecules and the adsorbant materials. Most of the intermetallic alloys, such as $LaNi_5$[5] (AB_5 type), can absorb hydrogen at room temperature; however, these materials have low hydrogen storage capacities (<2 wt %), which limits their usage to lower energy applications. There is thus a need to continue materials discovery to obtain higher capacities and find better-performing materials for specific applications.

Magnesium and magnesium-based alloys are considered attractive candidates as rechargeable hydrogen storage materials because of their high hydrogen capacities (theoretically up to 7.6 wt %), reversibility and low costs. The reaction of hydrogen with elemental Mg is one of the most widely studied reactions in the field of solid-state hydrogen storage.[6] Typically, the hydrogenation of Mg requires a temperature of 250 °C or higher. Further, the rate of hydrogenation is slow at moderate temperatures (200−300 °C), and it requires rather high temperatures (>400 °C) to achieve complete conversion of Mg to MgH_2 at a reasonable rate.[6d] Although there have been many efforts and significant progress on improving the hydrogen storage properties of magnesium,[6] including a few independently reported studies of Mg hydrogenation at room temperature,[7] the hydrogenation of Mg at or near room temperature remains a phenomenon that is not well understood. Considering its scientific and technological significance, it is important to understand the underpinning mechanisms and kinetics of room-temperature hydrogenation.

In this work, we found that the dehydrogenated nanostructured $MgH_2-0.1TiH_2$ prepared by ultra-high-energy and high-pressure (UHEHP) mechanical milling[8] can uptake a significant amount of hydrogen at room temperature at a reasonable rate. This finding is potentially useful for many applications, including hydrogen storage and hydrogen separation from gas mixtures such as synthetic gas.

The nanostructured material was prepared by milling mixtures of MgH_2 and TiH_2 in a molar ratio of 10:1 using a custom-made UHEHP planetary ball milling machine under 13.8 MPa hydrogen pressure, as previously reported.[9] Before each hydrogenation measurement, the milled sample was heated to 300 °C under vacuum for 2 h to allow complete dehydrogenation of MgH_2. The dehydrogenated samples were then hydrogenated at room temperature (25 °C). Figure 1A shows the isothermal hydrogenation curves of the dehydrogenated samples at room temperature under different hydrogen pressures. It can be observed that the dehydrogenated samples absorbed a significant amount of hydrogen (>50% of total capacity) within 4 h when the hydrogen pressure is higher than 20 bar. Even under much lower hydrogen pressure (<2 bar), the sample can still take up more than 1.5 wt % hydrogen at room temperature. One of the hydrogenated samples was then subjected to a cyclic test as described below.

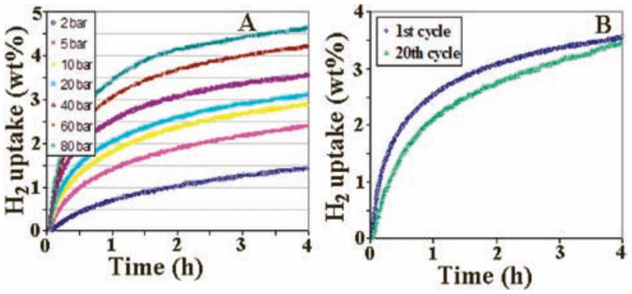

Figure 1. (A) Isothermal hydrogenation profiles of the dehydrogenated $MgH_2-0.1TiH_2$ at room temperature under different hydrogen pressure. (B) Isothermal hydrogenation profiles of the dehydrogenated $MgH_2-0.1TiH_2$ at room temperature under hydrogen pressure of 40 bar; blue curve, 1st cycle; and green curve, 20th cycle.

Cyclic kinetic measurements of dehydrogenation and hydrogenation were carried out using the PCT instrument according to the following procedures: dehydrogenation was performed by keeping the mixture at 300 °C under 1 kPa H_2 for 1 h, while hydrogenation was performed at room temperature for 4 h under a H_2 pressure of about 40 bar, which is substantially higher than the equilibrium pressure. Between the dehydrogenation and hydrogenation of each cycle, a 30-min evacuation process at 300 °C was conducted to ensure the complete dehydrogenation of the sample. Figure 1B shows the hydrogenation curves of the 1st and the 20th cycles from the cyclic measurements. It shows that the kinetics of hydrogenation at room temperature remained almost unchanged from the 1st to the 20th cycle.

The improved hydrogenation kinetics at room temperature can be characterized by calculating the activation energy of the hydrogenation reaction. In this study, the activation energy for hydrogenation of magnesium was calculated according to the Arrhenius equation:

$$E_A = -RT\ln(k/k_0) \qquad (1)$$

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10.1021/ja910944w

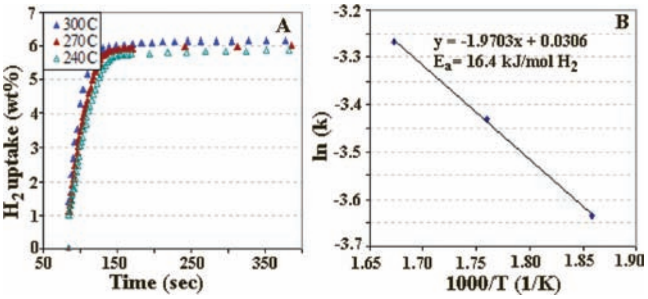

Figure 2. (A) Isothermal hydrogenation curves for the dehydrogenated $MgH_2-0.1TiH_2$ under 2 MPa hydrogen pressure at 240, 270, and 300 °C, respectively. (B) Kissinger plot of the milled $MgH_2-0.1TiH_2$ sample.

where E_A is the activation energy, k is a temperature-dependent reaction rate constant, R is the gas constant, and T is the absolute temperature. The activation energy of the reaction can be determined by measuring the rate constant k at several different temperatures and then plotting ln(k) versus 1/T on the basis of the following equation:[10]

$$d\alpha/dt = kf(\alpha) \qquad (2)$$

where $f(\alpha)$ is a conversion function depending on the reaction mechanism, and α is the reacted fraction. Several solid-state reaction mechanism models were tested, including the nucleation-and-growth, the geometric contraction, the diffusion, and the reaction order models based on different geometries of the particles and different driving forces.[11] The model based on the first-order reaction was selected according to the results of the tests:

$$kt = -\ln(1-\alpha) \qquad (3)$$

Using the data of isothermal hydrogenation at different temperatures (initial hydrogen pressure is 20 bar) as shown in Figure 2A, the activation energy (E_A) for the hydrogenation reaction of magnesium derived from the dehydrogenated nanostructured $MgH_2-0.1TiH_2$ is calculated as 16.4 kJ/mol H_2, as shown in Figure 2B. The k values in Figure 2B were obtained by plotting the data according to eq 3.

The above results demonstrate that the nanostructured $MgH_2-0.1TiH_2$ system is superior to undoped nano- or micrometer-scaled MgH_2 with respect to the hydrogenation properties of magnesium at room temperature.[6] The kinetic improvements can be understood qualitatively on the basis of the effects of nanosize scale and the addition of TiH_2. The hydrogenation of magnesium comprises a number of steps taking place in sequence:[6d] H_2 transport to the surface; H_2 chemisorption and dissociation to H; H diffusion; nucleation and growth of hydride phase. H_2 dissociation is known to be the rate-controlling step since the addition of catalysts for this process increases the kinetics drastically.[6d]

In general, the increased rate of hydrogen absorption of magnesium can be partially understood on the basis of the nanosize scale of the particles, thus the large surface area per unit mass of the material. However, as mentioned earlier, the nanosize factor alone cannot explain the relatively large amount of hydrogen absorbed by magnesium at room temperature, as observed in this study. The addition of TiH_2 had a critical effect.

First, it was observed by using high-resolution TEM that the grain size of the MgH_2-TiH_2 mixture was almost unchanged and TiH_2 was distributed uniformly among the MgH_2 particles during the cyclic measurements.[9] This observation suggests that TiH_2 can act as a grain growth inhibitor that prevents the coarsening of Mg or MgH_2 particles during the dehydriding−hydriding cyclic reactions,[12] preserving the nanoscale effect during the course of the experiments.

Second, based on a theory proposed by Schimmel et al.,[6d] the catalytic effect of TiH_2 can also be understood by viewing TiH_2 as a hydrogen-saturated catalyst in close contact with Mg particles; thus, TiH_2 can act as nucleation and growth centers of the magnesium hydride phase. Furthermore, TiH_2 is usually a nonstoichiometric compound and thus is expected to allow faster diffusion of hydrogen.

As a third possible explanation, it was recently shown that the addition of TiH_2 changes not only the reaction enthalpy but also the reaction entropy of Mg with H_2.[9] Because the entropy value of the H_2 gas is constant, the changes in ΔS can be accounted for by the differences in entropy between $MgH_2-0.1TiH_2$ and MgH_2. The fact that the ΔS as well as ΔH values are different compared to MgH_2 implies that TiH_2 has formed an alloy or solid solution with MgH_2 during the high-energy, high-pressure ball milling. Although we do not have any direct evidence yet, it is feasible that a metastable structure would facilitate diffusion of hydrogen in the solid, as it has been shown by studies on metastable thin films of Mg−Ti systems.[13] Needless to say, further in-depth research is needed to fully understand the effects of TiH_2 in a powder mixture as in this study.

In conclusion, significant uptake of hydrogen by magnesium at room temperature was observed in this study. The magnesium was derived by dehydrogenation of nanostructured $MgH_2-0.1TiH_2$ as prepared by the ultra-high-energy and high-pressure planetary milling technique. This finding is potentially useful in a range of energy applications, including mobile or stationary hydrogen fuel cells, cooling medium in electricity generation, and differential pressure compressors.

Acknowledgment. This research was supported by the U.S. Department of Energy (DOE) under contract no. DE-FC36-05GO15069.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA910944W