JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Thermodynamic and Kinetic Destabilization of Magnesium Hydride Using Mg−In Solid Solution Alloys

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Supporting Information

ABSTRACT: Efforts to thermodynamically destabilize magnesium hydride (MgH_2), so that it can be used for practical hydrogen storage applications, have been a difficult challenge that has eluded scientists for decades. This letter reports that MgH_2 can indeed be destabilized by forming solid solution alloys of magnesium with group III and IVB elements, such as indium. Results of this research showed that the equilibrium hydrogen pressure of a Mg−0.1In alloy is 70% higher than that of pure MgH_2. The temperature at 1 bar hydrogen pressure (T_{1bar}) of Mg−0.1In alloy was reduced to 262.9 °C from 278.9 °C, which is the T_{1bar} of pure MgH_2. Furthermore, the kinetic rates of dehydrogenation of Mg−0.1In alloy hydride doped with a titanium intermetallic ($TiMn_2$) catalyst were also significantly improved compared with those of MgH_2.

Among different materials for hydrogen storage, magnesium hydride (MgH_2) is regarded as a promising candidate owing to its high hydrogen capacity (up to 7.6 wt % H_2), reversibility, and low cost.[1,2] However, practical use of MgH_2 for hydrogen storage is largely nonexistent due to two factors: (1) MgH_2 is thermodynamically very stable and (2) kinetic rates of both dehydrogenation and hydrogenation of MgH_2 are too slow.

Over the past several decades, a large amount of effort has been devoted to improving the hydrogen storage properties of MgH_2. A general consensus is that the kinetic rate of hydrogenation of Mg is adequate when Mg is reduced to nanoscale by various mechanical ball milling methods and when it is doped with catalytic additives, such as transition metal intermetallic compounds.[3−5] Although the kinetics of dehydrogenation of MgH_2 can also be significantly improved using catalytic additives and nanosized particles, it is far from being satisfactory from the standpoint of practical applications, because the thermodynamic properties of MgH_2 remains essentially unchanged by the addition of catalysts.[6,7] For instance, it has been reported that catalyzed MgH_2 is able to desorb hydrogen in a temperature range as low as 150−250 °C[8−10] and the rehydrogenation could occur even at room temperature.[10−13] There is little evidence, however, that the catalysts affect the thermodynamics.[10,11] On the basis of the published data,[14] the dissociation equilibrium pressure of MgH_2 is ∼1.0×10^{-4} bar at 120 °C, which is grossly inadequate for practical applications, such as PEM fuel cells, which have a maximum working temperature of 120 °C.

It is not impossible, however, to alter the thermodynamics of magnesium hydride. For example, the reaction enthalpy of Mg can be reduced by alloying Mg with Ni to form an intermetallic compound of Mg_2Ni. The dehydrogenation reaction of Mg_2NiH_4 hydride has an enthalpy of 64.9 kJ/(mol·H_2). The drawback of Mg_2NiH_4 is that its hydrogen storage capacity is only 3.6 wt %.[15] Other intermetallic compounds of Mg that can store hydrogen include: $Mg_{17}Al_{12}$, Mg_2Al_3, Mg_2Si, Mg_2Cu, and Mg_2Ge, among others. Although the reaction enthalpies of these intermetallic compounds with hydrogen are all lower than those of Mg, they all suffer a significant penalty, i.e., the loss of hydrogen capacity.

An alternative to the use of intermetallic compounds is to use solid solution alloys to alter the thermodynamics of MgH_2. Liang[16] reported that thermodynamic properties could be altered by mechanically alloying Mg with Zn, Al, Ag, Ga, Cd, and In. They concluded that cadmium and indium provided the best effects on thermodynamics by forming a solid solution with Mg. Furthermore, Zhong et al. also confirmed that Mg−In solid solution had a decreased reaction enthalpy compared to pure Mg.[17] However, despite these reports, there are very few investigations[6,17] that focus on Mg solid solutions. In particular, there is no report on the kinetic behavior of Mg solid solution alloys or whether it could be improved by the use of transition metal catalysts. In this communication, we report that MgH_2 can indeed be destabilized by forming Mg−In solid solution alloys and the Mg−In alloys can be catalyzed by being doped with $TiMn_2$. In this work, both the temperature and kinetic rates of dehydrogenation were improved significantly.

Magnesium indium solid solution alloys were prepared by ball milling MgH_2 with indium metal powder, followed by an isothermal homogenization heat treatment at 400 °C. Compositions up to 10% of indium was chosen because the solubility of In in Mg at room temperature is approximately

Received: June 15, 2013
Published: July 15, 2013

ACS Publications © 2013 American Chemical Society

dx.doi.org/10.1021/ja4058794 | *J. Am. Chem. Soc.* 2013, 135, 10982−10985

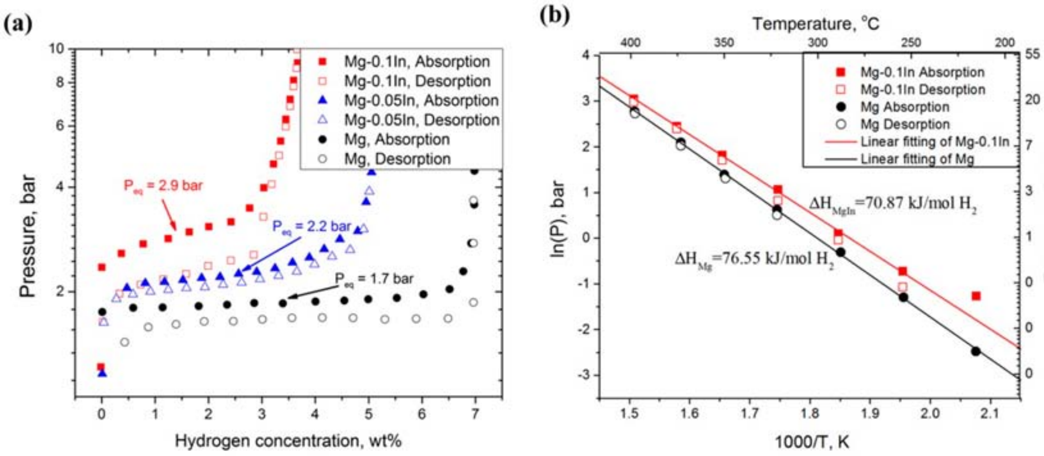

Figure 1. PCI curves (a) comparing Mg−0.05In, Mg−0.1In and Mg at temperature of 300 °C, and van't Hoff plot (b) comparing Mg−0.1In and Mg, detailed experimental data see Figure S1.

11%.[18] This is intended to ensure that Mg−In solid solution will form at dehydrogenated state. Equilibrium pressures (P_{eq}) of the solid solution alloys with 5 atom % (Mg−0.05In) and 10 atom % indium (Mg−0.1In) addition, as well as commercially pure Mg, were measured using a Sievert-type device and the Pressure−Composition-Isotherm (PCI) method, and the results are shown in Figure 1a. It can be seen that P_{eq} values were significantly affected by the amount of indium addition. The P_{eq} of Mg−0.05In at 300 °C increased approximately 0.5 bar and P_{eq} of Mg−0.1In at 300 °C increased by approximately 1.2 bar, or 70%, compared to that of pure Mg. The corresponding van't Hoff plot derived from the P_{eq} data is shown in Figure 1b, indicating that the enthalpy MgH_2 dehydrogenation is reduced to 70.87 kJ/(mol·H_2), significantly lower than that of pure MgH_2, due to the addition of 10 atom % of indium. On the basis of the van't Hoff plot, the temperature for 1 bar P_{eq} of Mg−0.1In is 262.9 °C, which is 16 °C lower than that of pure Mg. Further extrapolation of the van't Hoff plot to low temperature showed that the P_{eq} of Mg−0.1In at 150 °C was almost twice that of pure Mg (0.085 vs 0.047 bar).

Mg−0.1In solid solution alloy was then catalyzed by adding 3 molar percent of $TiMn_2$ using the high energy ball milling process under 150 bar pressure of hydrogen. Figure 2 compares the kinetic behavior of uncatalyzed and catalyzed Mg−0.1In alloy during both hydrogenation and dehydrogenation reactions, showing that the rates of the reaction of Mg-0.1In with hydrogen can be accelerated in the presence of a small amount of $TiMn_2$ as a catalyst. Two other samples, namely pure MgH_2 and MgH_2 with 3 atom % $TiMn_2$, were prepared for comparison, using the same milling parameters. The thermogravimetric analysis (TGA) dehydrogenation curves of all four samples are given in Figure 3a, which demonstrates that the dehydrogenation temperature of the catalyzed Mg−0.1In was significantly reduced in comparison with the other samples. The weight loss (i.e., releasing of hydrogen) started at approximately 100 °C, a remarkably low temperature for Mg-based hydrides to dehydrogenate. Furthermore, isothermal TGA tests were carried out at temperatures of 120 and 150 °C, as shown in Figure 3b. This chart confirms that hydrogen can be released, although at a rather slow rate, from the catalyzed Mg−0.1In alloy hydride at 120 °C. When the isothermal experiment was performed at an elevated temperature of 150 °C, the dehydrogenation was accelerated significantly, resulting in full dehydrogenation of the sample within 3 h.

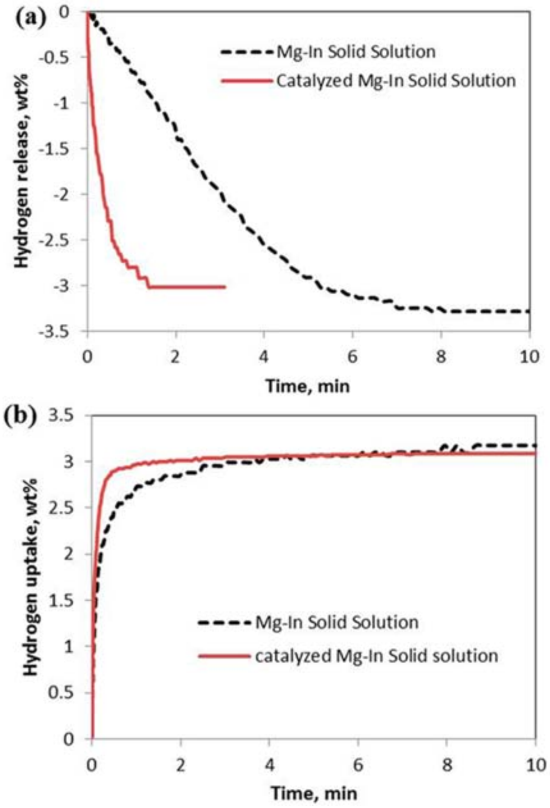

Figure 2. PCT desorption and absorption kinetics of the uncatalyzed and catalyzed Mg−0.1In, performed isothermally at 300 °C (573 K).

To the best of our knowledge, this is the first report showing the ability of an Mg-based hydride to be fully discharged in a temperature range as low as 120−150 °C. Our previous study[10] showed that $TiMn_2$ catalyst has a phenomenal catalytic effect on the Mg−H_2 reactions, although it has no effect on the P_{eq} of Mg. Additionally, we now recognize the significant impact of indium additions on the thermodynamic behavior of Mg. It is therefore believed that indium could at least partially destabilize MgH_2. The Mg−0.1In alloy hydride that was not catalyzed using $TiMn_2$, however, did not show such a decrease of the

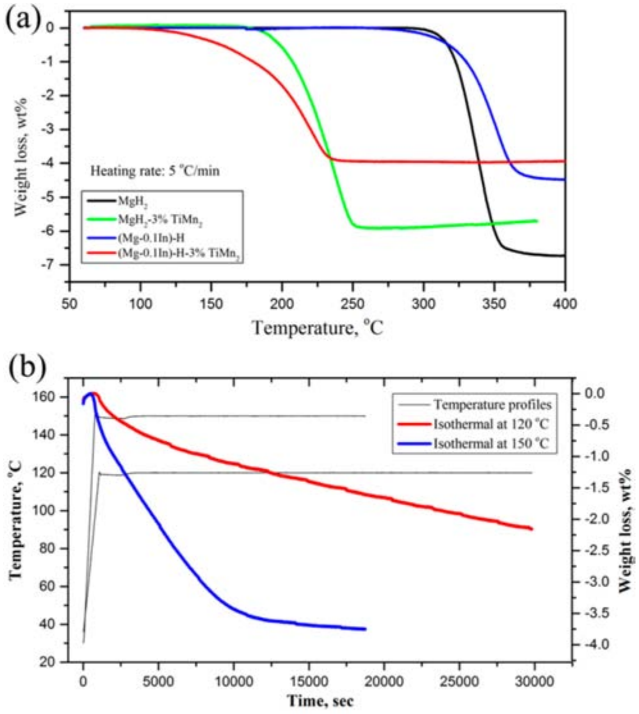

Figure 3. Comparison of TGA curves for (a) MgH_2−0.1In doped by 3 atom % $TiMn_2$ catalysts, MgH_2−0.1In, MgH_2 doped by 3 atom % $TiMn_2$ and as-milled MgH_2, and (b) $TiMn_2$ catalyzed MgH_2−0.1In dehydrogenation curves at 120 and 150 °C.

desorption temperature as compared to the pure MgH_2 sample, suggesting that the alloying with indium alone did not accelerate the kinetics for hydrogen desorption. When the $TiMn_2$ catalyst was used, its effect on decreasing the desorption temperature was drastic. Therefore, the significant improvement of the kinetic behavior of Mg hydride is attributed to the synergistic effect of both indium and $TiMn_2$.

In addition, cyclic dehydrogenation and hydrogenation experiments were performed. A total of 10 cycles (see Figure S2) showed that the catalyzed Mg−0.1In solid solution alloy had not only reversibility, but also good cycle stability. Approximately 3 wt % of hydrogen was reversibly absorbed/desorbed at 200 °C. The hydrogenation reactions were carried out under a hydrogen pressure of ~5 bar, and the dehydrogenation was conducted under a lower pressure of ~0.05 bar. On the basis of the comparison of the kinetics of different cycles (see Figure S3), it can be seen that the kinetic rates remained the same, except that the first dehydrogenation reaction was relatively slow.

Using an in situ synchrotron X-ray diffraction (XRD) technique, the phase transformations of catalyzed Mg−0.1In alloy hydride during dehydrogenation were examined. The wavelength of synchrotron X-ray used was preset to 0.774901 A. The results are shown in Figure 4. Before dehydrogenation, two reactant phases, indium and MgH_2, were identified in the XRD pattern. Besides those two phases, XRD peak of Fe was also observed. This is attributed to contaminations from the sample holder used for the in situ XRD analysis, or from steel balls and/or canister used for high-energy milling.

Figure 4 shows that the XRD peaks of indium, which was added to MgH_2 powder thus present in the as-milled powder, gradually diminished during the dehydrogenation process as the temperature increased. A few points are noted from Figure 4.

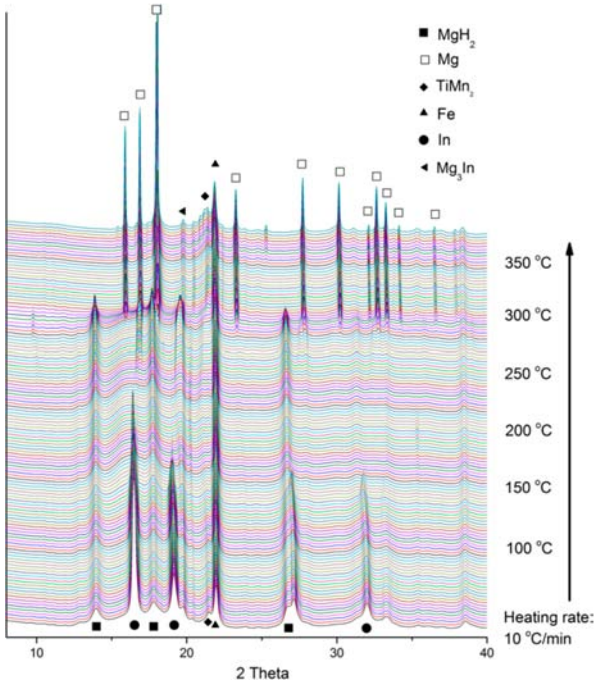

Figure 4. In situ XRD spectra for dehydrogenation reaction of Mg−In−H system, the heating rate is 10 °C/min with experiment running from bottom to top of figure.

First, the XRD peaks of indium in the as-milled sample are rather sharp relative to that of MgH_2, despite that the molar ratio between Mg and In is 9:1. This is attributed to the fact that indium metal is very ductile and it retained its metallic crystalline structure after the high energy milling process, while MgH_2 is readily reduced to near amorphous nanoscale structure, which drastically broadens the peaks of MgH_2.[5,10]

Second, at the end of the dehydrogenation, only Mg peaks are present. The gradual disappearance and complete absence of In peak at the end of the dehydrogenation process suggest that it was dissolved in magnesium metal, forming a solid solution of Mg−In.

When the dehydrogenated sample was then rehydrogenated in 10 bar of hydrogen at 300 °C, Figure 5 shows that MgH_2 and

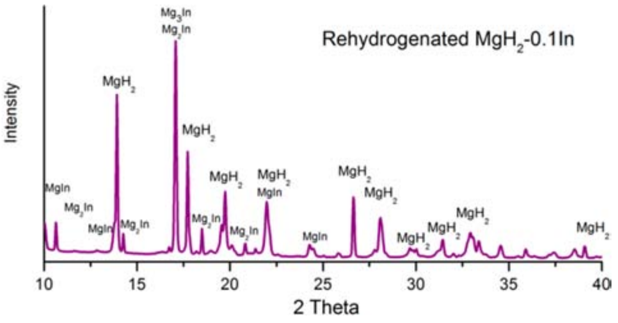

Figure 5. XRD pattern of rehydrogenated MgH_2−10% In.

Mg−In intermetallic phases (β) formed from the Mg−In solid solution. β represents several possible Mg−In intermetallic phases including Mg_3In, Mg_2In and MgIn. This agrees with the hydrogenated Mg−0.05In results from Zhong et al.[17] The repeated cyclic dehydrogenation and hydrogenation experiments suggest the reactions follow the following equation:

$$MgH_2 + \beta \xleftrightarrow{TiMn_2\ catalyst} Mg(In)_{0.1} + H_2\uparrow \quad (1)$$

Equation 1 indicates that in the dehydrogenated state, Mg−In is a solid solution alloy. During the hydrogenation of the solid solution alloy, MgH_2 and Mg−In intermetallic phases (β) disproportionation occurs.

Third, Figure 4 also shows that there is a small amount of Mg−In intermetallic phase present in the dehydrogenated product. This is attributed to the limitation of the kinetics of the reactions. Further research is necessary to assess its impact.

Furthermore, it can be seen that the $TiMn_2$ phase remained constant throughout the entire reaction with no detectable change, which is consistent with other studies that focused on catalysts.[19]

A key point regarding the differences between eq 1 and Mg−H_2 reversible reaction: $MgH_2 \leftrightarrow Mg + H_2\uparrow$, is that the main reactants of both dehydrogenation and hydrogenation reactions remain the same, e.g., MgH_2 vs $MgH_2 + \beta$ on the left of eq 1, and Mg vs $Mg(In)_{0.1}$ on the right of eq 1. These situations offer two logical benefits. First, the reactions retain good reversibility similar to that of pure Mg−H_2 reaction (see Figure S2). The second is that existing well-developed transition metal catalysts would still be effective on the Mg solid solution alloy−hydrogen systems.

On the basis of the results of this research, it is concluded that the thermodynamic equilibrium pressure of magnesium hydride can indeed be increased by forming a solid solution alloy of magnesium with indium. The Mg−0.1In alloy can reversibly absorb and desorb hydrogen. PCI characterizations and the van't Hoff plot showed that the addition of indium provides a significant destabilizing effect on magnesium hydride. The reaction enthalpy of the Mg−0.1In with hydrogen was 70.87 kJ/(mol·H_2), significantly lower than that of the commercially pure MgH_2. The kinetic rates of the dehydrogenation of Mg−0.1In alloy hydride were dramatically improved by incorporating $TiMn_2$ as a catalyst. The catalyzed Mg−0.1In alloy hydride began to dehydrogenate at approximately 100 °C and was fully dehydrogenated at 150 °C within 3 h.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (Grant No. 0933778) and the U.S. Department of Energy (DOE) under contract number DE-AR0000173. The authors also thank Dr. Mark Koopman for proofreading the manuscript and constructive suggestions. J. Lu was supported by the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Award under DOE contract number DE-AC05-06OR23100. Use of the Advanced Photon Source (APS) was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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