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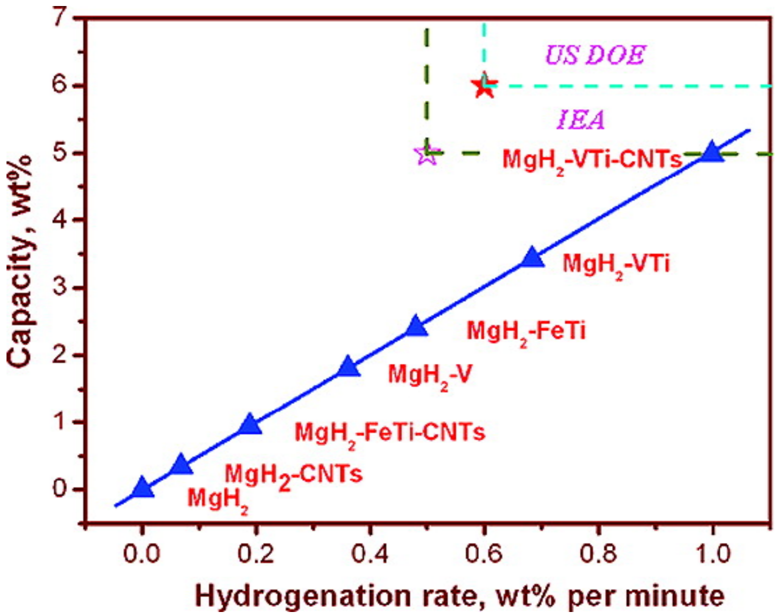

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Metallic and Carbon Nanotube-Catalyzed Coupling of Hydrogenation in Magnesium

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Abstract: Synergistic effect of metallic couple and carbon nanotubes on Mg results in an ultrafast kinetics of hydrogenation that overcome a critical barrier of practical use of Mg as hydrogen storage materials. The ultrafast kinetics is attributed to the metal−H atomic interaction at the Mg surface and in the bulk (energy for bonding and releasing) and atomic hydrogen diffusion along the grain boundaries (aggregation of carbon nanotubes) and inside the grains. Hence, a hydrogenation mechanism is presented.

Introduction

A major challenge in realizing the hydrogen economy is the development of efficient and safe storage materials for hydrogen.[1] Magnesium (Mg) and Mg-based alloys have been considered as promising materials that could achieve practical hydrogen storage because of their low cost, high capacity, and excellent reversibility.[2] However, there exists two critical barriers to the practical utilization of these materials: the operational temperature is too high, and the hydrogenation kinetics is slow.[3] To overcome these barriers, tremendous efforts have been devoted in the past decade to developing new strategies, such as nanostructuring,[4] alloying,[5] and the use of catalysts.[6] It has been proven that high-energy ball milling could increase hydrogenation kinetics by reducing the grain size, activating the surface and introducing defects.[7] Additionally, Mg can be alloyed with other metallic elements, such as Ni to enhance the absorption kinetics, albeit at the cost of a partial reduction of gravimetric capacity. Transitional metals such as Fe, Ti, and V can also catalyze the hydrogen dissociation process and thus enhance the hydrogenation kinetics significantly at high temperatures (>573 K).[2,8] Recently, carbon materials, in particular carbon nanotubes, have been demonstrated to have an excellent catalytic effect on hydrogen storage in Mg based alloys by enhancing the hydrogen diffusion in MgH_2-C systems.[9]

In our recent studies,[10] we have demonstrated that the catalytic effects of combined transition metals such as Fe and Ti with carbon nanotubes (CNTs) as mixed dopants lead to significant acceleration of hydrogen dissociation and diffusion in nanostructured magnesium, approaching the goal of rapid hydrogenation kinetics at practically meaningful low temperatures. Notably, the effect is significantly enhanced in comparison with the hydrogenation kinetics promoted by elemental Fe[8a] or Ti[8b] alone. This indicates that the synergistic interaction among metals and carbon nanotubes may be an effective strategy to significantly lower the operating temperature and to increase hydrogenation kinetics. Despite this progress, the hydrogenation kinetics still falls short of the requirements for practical applications.[10a] It is therefore desirable to further explore and develop the synergistic effects of CNTs with other metallic catalysts in order to achieve faster hydrogenation kinetics. It has been shown that V and Ti are both individually effective in promoting the hydrogenation kinetics of Mg based alloys and that V is in fact much more effective than either Fe or Ti

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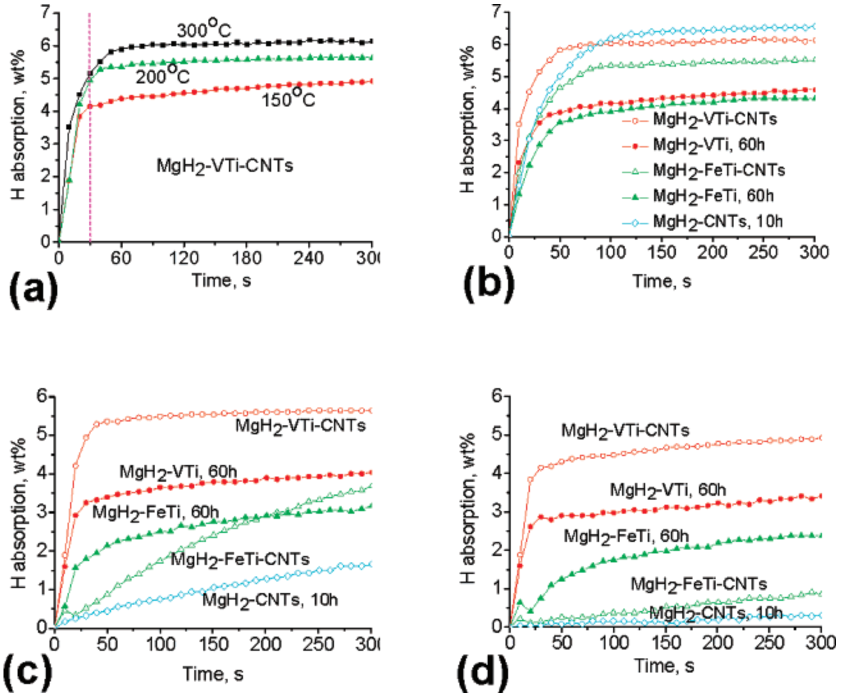

Figure 1. Hydrogen absorption of catalyst-enhanced samples under a hydrogen pressure of 2 MPa. (a) MgH_2−VTi−CNT system at temperatures of 300, 200, and 150 °C. A comparison of VTi, FeTi, CNT, FeTi, and CNT incorporated Mg systems is also shown at 300 (b), 200 (c), and 150 °C (d), respectively.

alone.[8a,11] For this reason, we anticipate that a combination of V−Ti may prove to be more effective in enhancing the hydrogenation kinetics at low temperatures. In this paper, we demonstrate a new MgH_2−VTi−CNT system that exhibits ultrafast hydrogenation kinetics with a high capacity. A possible hydrogenation mechanism is proposed in terms of the synergistic catalytic effects of transition metals and CNTs, especially highlighting the different roles of V as compared with the previously studied case of Fe.

Experimental Procedures

All experiments and handling were carried out in a glovebox with an argon atmosphere to prevent possible Mg oxidation. A MgH_2−VTi−CNT sample was prepared by first milling MgH_2−5.0 wt % (V + Ti) in 60 h, followed by adding 5 wt % CNTs with further milling for 10 h, in a Spex 8000 ball mill. The hydrogen storage capability of the resultant samples was measured by a custom-made automatic Sieverts apparatus. The measurements were carried out by first desorbing the hydrogen in an as-prepared sample at 350 °C for 4 h under vacuum, followed by absorption under three different temperatures (300, 200, and 150 °C, respectively) under a hydrogen pressure of 2 MPa. The energetic profile is calculated by *ab initio* Density Functional Theory (DFT) method.

Results and Discussion

Hydrogen Absorption. Figure 1 shows the hydrogen absorption kinetic curves measured for the MgH_2−VTi−CNT sample (Figure 1a) and their comparisons with Mg−CNTs, Mg−VTi, Mg−FeTi, and Mg−FeTi−CNTs (Figure 1b−d) at absorption temperatures of 300, 200, and 150 °C. As can be seen from Figure 1a, the Mg−VTi−CNT sample can absorb 4.2 and 5.0 wt % hydrogen in only 30 s at 150 and 200 °C, respectively, indicating that the sample exhibits ultrafast hydrogen absorption kinetics. It is also interesting to note that, after 5 min of hydrogen absorption, the hydrogen storage capacity of this sample reached 5.1 and 5.8 wt %, respectively at 150 and 200 °C. This demonstrates that the synergistic effects of the transition metals VTi and CNTs dramatically increase the hydrogenation kinetics as well as its capacity, especially at a temperature as low as 150 °C, which is critically important for practical hydrogen storage applications. The comparison in the hydrogenation kinetics and capacity of the five samples (Figure 1b−d) reveals several phenomena as follows: (1) Transition metals significantly enhance the hydrogenation kinetics but have little impact on the maximum capacity. (2) The transition metals and CNTs have synergistic effects on the hydrogenation. (3) Combinations of transition metals are more efficient in enhancing the hydrogenation kinetics than the additive components individually. (4) V is much more effective than Fe as a catalyst. And (5) the Mg−VTi−CNTs system exhibits superior properties in both capacity and kinetics; most notably it shows extremely fast kinetics at a practically significant low temperature of 150 °C.

Activation Energy. To further study the hydrogenation kinetics, the activation energy (E_A) for hydrogenation was determined. Figure 2 shows the Arrhenius-type plots for the above five samples, together with MgH_2−5%V (milled for 100 h)[11] and MgH_2 (milled for 10 h) samples for comparison, where k is the hydrogenation kinetic rate derived from the measured kinetic curves (tangent of the curves in Figure 1). The values of E_A for these samples are given in Table 1, which clearly shows the following: (1) All additives milled with Mg increased the hydrogenation kinetics (reducing E_A). (2) CNTs enhanced the kinetics of Mg (E_A reduced from 109 to 75.6 kJ/mol) but did not have any effect on the kinetics of the Mg−VTi system (same E_A) and in fact slowed the kinetics of the Mg−FeTi

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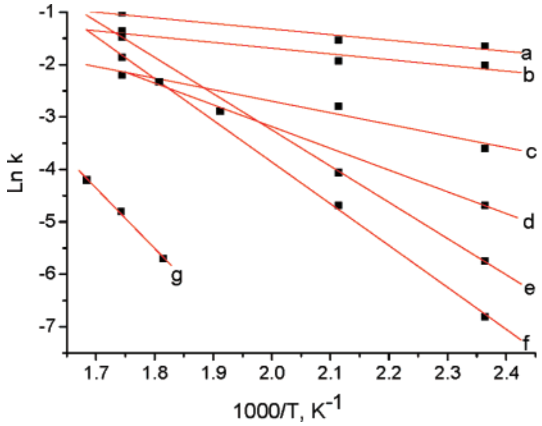

Figure 2. Arrhenius plots of the absorption rate for the samples: (a) MgH_2-VTi milling 60 h + CNTs milling 10 h; (b) MgH_2-VTi milling 60 h; (c) MgH_2-FeTi milling 60 h; (d) MgH_2-V milling 100 h;[11] (e) MgH_2-FeTi milling 60 h + CNTs; (f) MgH_2 + CNTs milling 10 h; and MgH_2 milling 10 h; respectively.

Table 1. Activation Energy for Hydrogenation of Different Systems

system	activation energy (kJ/mol)	system	activation energy (kJ/mol)
$MgH_2-VTi-CNTs$	10.1	$MgH_2-FeTi-CNTs$	65.5
MgH_2-VTi	10.4	MgH_2-FeTi	21.0
MgH_2-V	39.3	MgH_2-CNTs	75.6
MgH_2	109		

system (E_A increased from 21.0 to 65.5 kJ/mol). (3) The combination of FeTi was more efficient than V alone (E_A 21.0 compared with 39.3 kJ/mol), although V has been reported to be more effective than either Fe or Ti individually.[8a,b,11] The combination of VTi is however much better (E_A 10.4 kJ/mol). The high-resolution transmission electron microscopy (HRTEM) image in Figure 2S (Supporting Information) clearly shows that the structure and grain size of the investigated MgH_2-VTi-CNT sample are similar to those of the previously studied $MgH_2-FeTi-$CNT sample.

Hydrogenation Mechanism. To gain further insight into the reasons underlying these phenomena, we propose the hydrogenation mechanism as follows based on the evidence available to date both from theoretical calculations[12] and experimental observations.[10] The hydrogenation process can be divided into three key steps:

(1) dissociation of hydrogen molecules on the Mg surface;

(2) atomic hydrogen diffusion along the grain boundaries;

(3) atomic interaction of metallic catalyst and H atoms and H release.

In the first step, the hydrogen dissociation necessitates overcoming an energy barrier. The barrier for molecular hydrogen dissociation without any substrates is extremely large, 4.52 eV, indicating the dissociation is impossible under normal conditions.[13] However, according to the molecular orbital theory the energy barrier decreases with a decrease in energy of the valence orbitals, and the orbitals become more contracted when a metal atom is present.[13] We have recently performed *ab initio* Density Functional Theory (DFT) calculations which show that transition metallic catalysts can change the reaction (minimum energy) pathway for the hydrogen dissociation and in some cases eliminate the energy barrier altogether.[12a] When molecular hydrogen approaches Mg atoms on a clean Mg surface, the energy barrier for dissociation is 1.15 eV, requiring ~400 °C for sufficient dissociation to be detectable.[12a] The calculated activation energies for molecular hydrogen dissociation on V and Ti atoms are quite small, 0.201 and 0.103 eV, respectively (as seen in the Supporting Information), making the dissociation of hydrogen with V and Ti practical at a very low temperature. Although we have not performed DFT calculations on the effect of Fe due to the complexity of the electronic structure and magnetic properties, Fe should play a similar role in hydrogen dissociation based on molecular orbital theory,[13] investigations by Song et al.,[8d] and experimental evidence, e.g., shows that $MgH_2-FeTi-$CNTs can absorb a large amount of hydrogen at temperatures as low as 100 °C.[10a]

We now consider the second step, in which CNTs appear to play a key role for hydrogen boundary diffusion. It has been proven experimentally that there exist some residual CNTs with their specific tubular structure besides the amorphous carbon produced after 10 h of ball milling with Mg.[10b] Unlike the atomic C produced during the milling process, which can enter the Mg crystal structure,[12b] the tubular CNTs are most likely aggregated along the grain boundaries inside the Mg particles. Under the milling conditions we conducted our experiments, a typical Mg particle size in diameter is about 500−1000 nm that may contain thousands of grains 10−50 nm in size.[10] Given this physical constitution, the grains in the center of the particle may be effectively inaccessible insofar as hydrogen diffusion is concerned, particularly at lower temperatures as the outer regions of the particles and the grain boundaries become saturated in a hydride-like structure. This appears to be the main reason why hydrogen absorption profiles usually plateau short of the theoretical (stoichiometric) capacity. When residual CNTs with a tubular structure are present at grain boundaries, however, hydrogen diffusion along the grain boundaries may be significantly enhanced, facilitating access to the inner Mg grains even at a low temperature. In this way, more grains within the particles can react with hydrogen atoms to form hydrides thus increasing the hydrogen capacity.

The third step involves hydrogen−metal interactions to form catalyst-H bonds, e.g., VH_2, TiH_2, and $MgFe_2H_6$,[8d,11,14] and hydrogen diffusion within the individual grains. The stability of these transition metal hydrides is a key factor influencing the hydrogenation kinetics. It has been reported that both TiH_2 and $MgFe_2H_6$ are very stable and not easily desorbed. For example, high temperatures of ~380 °C[15] and above 500 °C[16] are required for the decomposition of such hydrides of TiH_2 and $MgFe_2H_6$, respectively. Although the desorption temperature could be somewhat lowered in the presence of Mg atoms,[17] the requisite temperature is still high (between 200 and 300 °C) in the presence of Fe and Ti together.[10b] The strength of the TiH_2 and $MgFe_2H_6$ interaction most likely can cause the atomic

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hydrogen to “stick” on the distributed Ti in the Mg matrix and, hence, presents a hurdle to the subsequent diffusion into the grain, slowing the overall hydrogenation kinetics. The catalytic roles of Ti and/or Fe appear therefore to involve facilitating the dissociation of molecular hydrogen at the particle surface, but not necessarily the diffusion into the grains.

The situation is, however, quite different when V is present. Although V displays a high affinity for hydride formation,[11b,18] V hydrides may also be decomposed very easily. The reaction ($VH_2 \rightarrow V + 2H$) has been reported to occur at 35 °C[18] and this process could be further enhanced in the presence of Mg atoms.[17] It is reported that the energy barrier for H desorption from a free V surface is only 0.04 eV.[19] Subsequently, the atomic hydrogen transfers to Mg atoms, forming MgH_2 around the V site. V can be regarded as an “atomic hydrogen pump”, which facilitates atomic hydrogen transportation. The Mg−V system shows excellent kinetics at a relevant low temperature.[15] V not only serves as an effective catalyst for hydrogen dissociation (step one above) but also facilitates the atomic hydrogen diffusion in the MgH_2 matrix (step three), providing very fast hydrogenation kinetics even at low temperatures. Hence, the process of hydrogen dissociation is unlikely to be a rate-limiting process in the presence of V.

The possible reason that a combination of V (Fe) and Ti is more effective for hydrogenation than V or Fe itself deserves some further thought. Although Ti will tend to hold H bound, impeding the subsequent hydrogen diffusion, Ti atoms can enter the Mg lattice structure during high-energy milling[12a] as they have a similar atomic size, resulting in deformation of the Mg structure.[20] It is possible that this deformation may result in the presence of some vacancies that are favorable for atomic hydrogen diffusion compared with the undeformed Mg structure.

In light of the above discussions of catalytic mechanisms, it is not surprising that the MgH_2−VTi−CNT system displays much faster kinetics compared with the MgH_2−FeTi−CNTs system as found in this work. With an analysis of the first-order kinetic curve presented in Figure 1, the hydrogenation rate for the MgH_2−VTi−CNT sample at 150 °C can be estimated to be 8.4 wt % H per min, which is ∼40 times than that (0.21 wt % H per min) for MgH_2−FeTi−CNTs. The comparison of different systems and the U.S. Department of Energy (DOE) and International Energy Agent (IEA) targets is plotted in Figure 3, which clearly shows that MgH_2−VTi−CNTs has the largest capacity (5.1 wt %) and fastest kinetics (average 1.0 wt % per min in 5 min) at a low temperature of 150 °C, indicating that the IEA benchmark for hydrogen absorption is attainable.

Hydrogen Desorption. Hydrogen desorption kinetics data were investigated for MgH_2−VTi−CNTs, MgH_2−FeTi−CNTs, and MgH_2−VTi systems. The desorption profiles are plotted in Figure 4. It is apparent that the MgH_2−VTi−CNT sample displays very good desorption kinetics, desorbing 6 wt % hydrogen (almost all the hydrogen absorbed in this system) within 10 min at 300 °C. Compared with the other two samples, MgH_2−FeTi−CNT and MgH_2−VTi, it can be seen that the pairing of VTi is more effective than FeTi for enhancing the desorption kinetics and that CNTs also enhanced the desorption of hydrogen from Mg. The reasons for this are related to the hydrogenation mechanism discussed above:

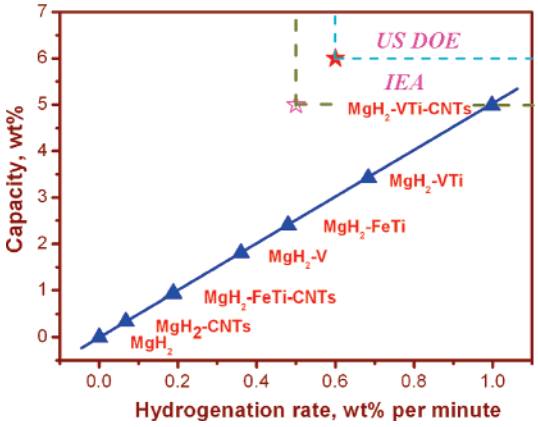

Figure 3. Comparison in maximum capacity and average kinetics in 5 min of hydrogenation for Mg-based nanocomposites at 150 °C.

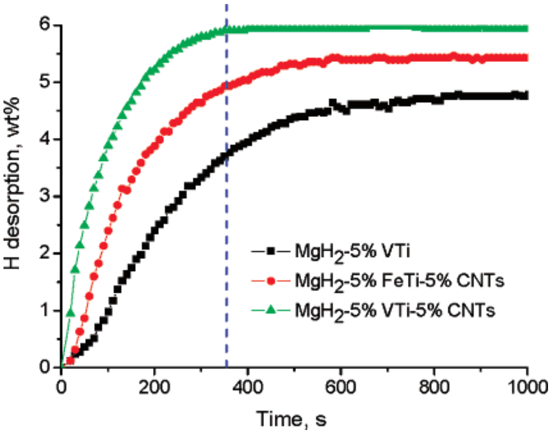

Figure 4. Hydrogen desorption kinetic curves of MgH_2−VTi−CNTs, MgH_2−FeTi−CNTs and MgH_2−VTi systems at 300 °C.

(1) The release of hydrogen atoms from V atoms is much easier because of the much lower energy barrier.[19] The desorption of hydrogen is reverse to the absorption: the hydrogen atoms combined with V on the Mg surface (in the form of VH_x) first dissociated ($VH_x \rightarrow V + xH$) and released. The hydrogen gradient subsequently forced the atomic hydrogen transfer from MH_2 to V.

(2) Thus, CNTs enhanced the desportion kinetics as they facilitated the atomic hydrogen diffusion both inside the Mg grains (with sublayer C atoms[12b]) and along the grain boundaries (with aggregation of residual CNTs[10a]).

However, it should also be noted that the desportion temperature is still relatively high, which hinders the practical applications of Mg-based hydrogen storage materials. Reducing the desportion temperature is a critical challenge as the energy barrier for hydrogen desorption from MgH_2 is very high.[21] Strategies to modify the thermodynamics of Mg-based materials to reduce the desorption energy barrier are clearly to be important topics for further research.[22]

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Conclusions

In conclusion, we demonstrated that transition metals significantly enhance the hydrogen kinetics while CNTs remarkably increase the capacity. V is much more effective than Fe or Ti in enhancing the absorption kinetics; however the combination of two metals proves to be more efficient than a single metal catalyst. A new MgH_2−VTi−CNT system was shown to have ultrafast hydrogenation kinetics and a very large capacity, which is very promising for hydrogen storage applications. A plausible hydrogenation mechanism has been proposed which can explain the important phenomenon of coupled catalytic effects of transitional metals V and Ti, with CNT. The VTi couple and CNT are also found to be effective to enhance the hydrogen desportion from MgH_2.

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Supporting Information Available: Energy profiles for hydrogen dissociation at Mg(0001) surface and HRTEM image of MgH_2−VTi−CNT. This material is available free of charge via the Internet at http://pubs.acs.org.

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