



Effects of TiCl_3 , TiO_2 , ZrCl_4 , and ZrO_2 on Hydrogen Desorption of MgH_2 and Its Reversibility

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A thorough investigation on hydrogen desorption of MgH_2 and its reversibility with the focus on effects of a catalyst (TiCl_3 , TiO_2 , ZrCl_4 , and ZrO_2) were reported. The experiments were carried out using a Sievert's type apparatus. The reaction kinetics and the phase transformation behaviours were examined using a differential scanning calorimeter (DSC) and an X-ray diffractometer (XRD). It was found that the catalysts play an important role in facilitating smaller MgH_2 crystallite size formation during ball-milling and accelerating hydride formation during the subsequent hydrogen absorption cycles resulting in the hydrogen desorption and reversibility enhancement of MgH_2 . Doping with ZrCl_4 resulted in the smallest MgH_2 crystallite size. That, in turn, resulted in the lowest hydrogen desorption temperature and the highest amount of released hydrogen in the first desorption. However, TiO_2 was identified as the best catalyst because doping with TiO_2 provided the highest amount of reversible hydrogen (~10% capacity drop from initial cycle).

1. Introduction

Hydrogen is regarded as the most promising alternative energy source because it is abundance and produces virtually water as a product from fuel cells. However, to use hydrogen as a fuel for vehicles, it requires a very compact and safe storage system (Conte et al., 2004). As compared with traditional hydrogen storage, e.g. compressed hydrogen gas and liquid hydrogen, solid-state hydrides are preferable because it has high gravimetric and volumetric hydrogen densities, and it is also reversible at appropriate conditions (Schüthel et al., 2004). This statement is in agreement as reported by Züttel (2004). David (2005) also reported that the solid-state hydrides or metal hydrides are the most important characteristics of materials for hydrogen storage. Magnesium hydride (MgH_2) is one of potential solid-state hydride materials because it can reversibly store 7.6 wt% H_2 and has relatively high volumetric hydrogen density ($106 \text{ kg H}_2 \text{ m}^{-3}$) with reasonable cost (Lu et al., 2009). However, it releases hydrogen at a high temperature and possesses slow hydrogen desorption and absorption kinetics (Sakintuna et al., 2007).

Typical methods to destabilize MgH_2 for hydrogen desorption are ball-milling and doping with catalyst (Xie et al., 2009). Ball-milling is the simplest method that would potentially reduce crystallite size of MgH_2 , increase defects, and decrease hydrogen diffusion distance within MgH_2 bulk (Fátayet al., 2005). These results in the faster hydrogen desorption kinetics and higher amount of desorbed hydrogen. Oelerichet al. (2001a) revealed that the catalyst doping would also enhance the hydrogen dissociation and diffusion in MgH_2 by synergically accelerating the desorption kinetics. And the effects of catalyst doping are confirmed by Hanada et al. (2006) and Varin et al. (2011).

There are many types and forms of a catalyst such as transition metal and transition metal compound of oxides and chlorides. Their effects on the hydrogen storage improvement of MgH_2 were reported by several research groups. For the use of a transition metal catalyst, Liang et al. (1999) found that doping 5 mol% 3d-transition metals nanocomposite (Ti, V, Mn, Fe, and Ni) did not change the enthalpy and the entropy of formation of MgH_2 , but it dramatically reduced the activation energy or increased the reaction kinetics of MgH_2 . MgH_2 doped with Ti exhibited the most rapid absorption kinetics. Zaluska et al. (1999)

also reported some enhancement of hydrogen storage properties by transition metal doping in the ball-milled MgH_2 . The doping of 5 wt% Zr significantly reduced the hydrogen desorption temperature of MgH_2 , while the doping of 8 wt% V markedly enhanced the hydrogen absorption kinetics. In the case of transition metal compounds, Malka et al. (2010) found that the lowest desorbed temperature was achieved by doping MgH_2 with either 7 wt% TiCl_3 or ZrF_4 and different metal compounds, e.g. chloride and halide, provide different desorption temperatures.

Typically, a transition metal compound catalyst (e.g. oxide and nitride of a transition metal) poses better catalytic activity than a transition metal catalyst due to their smaller particle sizes and higher surface areas (Barhordarian et al., 2003). In addition, the transition metal compound catalyst has multiple valence states, which provides larger catalytic effects. Oelerich et al. (2001b) found that MgH_2 doped with V_2O_5 yielded the fastest hydrogen desorption, followed by the doping of VN, VC, and V. Furthermore, the doping of V did not show any kinetics improvement. Bhat et al. (2006) showed that doping a catalyst resulted in significant particle size reduction, and MgH_2 doped with NbCl_5 and CaF_2 showed better catalytic activity than doping with Nb_2O_5 . However, to our knowledge, the reversibility of such MgH_2 doped with transition metal compounds has not yet been reported.

In this work, effects of ball-milling and transition metal compound catalysts, including TiCl_3 , TiO_2 , ZrCl_4 , and ZrO_2 , on the hydrogen desorption temperature, the amount of released hydrogen, and the reversibility of MgH_2 were investigated. Phase transformation, calculated crystallite size, and activation energy of the samples were also reported.

2. Experimental

The starting metal hydride, MgH_2 (90 % and Mg 10 %, Acros Organics), and catalysts, TiCl_3 (prepared by vacuum drying of 12% TiCl_3 solution in hydrochloric acid), TiO_2 (Degussa P25), ZrCl_4 (99.99 %, Sigma Aldrich), and ZrO_2 (98.5 %, Riedel-de Haën), were used without further purification. All sample handlings were done in a glovebox filled with liquid nitrogen to prevent contamination from air and moisture. MgH_2 samples were prepared from a 1:0.03 molar ratio of MgH_2 and a catalyst using a centrifugal ball mill (Retsch S100) at a speed of 300 rpm under nitrogen atmosphere for 5 h. The weight ratio of stainless steel balls (316SS) to powder was 60:1. The hydrogen desorption temperature and capacity as well as the reversibility of the sample were examined in the Sievert's type apparatus.

Approximately, 0.3 g of a milled sample was packed into the stainless steel vial reactor, where two calibrated K-type thermocouples (Cole Parmer) were placed to monitor and control the temperature throughout the desorption. A pressure transducer (Cole Parmer, model 68073-68074) was employed to monitor the pressure change. The hydrogen desorption was carried out from room temperature to 400°C with a heating rate of 2°C min⁻¹ under 0.1 MPa H_2 initial pressure. The temperature was held at 400°C until no pressure change in the system was observed. The released hydrogen in the hydrogen desorption was calculated using the real gas law. It should be pointed out that the amount of a doped catalyst was not taken into account when the amount of released hydrogen was calculated. After the hydrogen desorption, the sample was compressed under 6.0 MPa H_2 and 350°C for 12 h for the hydrogen absorption. Both hydrogen desorption and absorption were repeated to investigate the reversibility of the sample.

Sample identification was performed using a Rigaku X-ray diffractometer (XRD, model DMAX 2200 HV) at room temperature over a range of 25 to 75° with Cu $K\alpha$ radiation (40 kV, 30 mA). The crystallite size of the sample was averaged from the first four highest peak intensities, calculated using the Scherrer equation. The activation energy of the sample was determined from the Kissinger method. The hydrogen desorption temperature at the maximum peak (T_p) of each experiment was measured using a differential scanning calorimeter (DSC 822, Mettler Toledo). About 1.0 mg of a milled sample was placed into an Al crucible. The crucible was heated from 100 to 400 °C using different heating rates of 2, 5, 8, and 10 °C min⁻¹.

3. Results and discussion

Effects of ball-milling and the catalyst on phase transformation and crystallite size of MgH_2 were examined by XRD. As illustrated in Figure 1, MgH_2 appears to be the major phase in all samples. Differences in the height and width of the MgH_2 peaks indicate different quantities and crystallite sizes of MgH_2 after ball-milling and doping with different catalysts. In addition, the XRD pattern of the as-received sample (Figure 1(a)) indicates the presence of Mg and $\text{Mg}(\text{OH})_2$ impurities. The diffraction peaks of these impurities disappear after ball-milling, while there are new MgO peaks observed for all un-doped and doped samples. This would possibly be caused by (i) the decrease in the crystallite sizes of impurities, (ii) the reaction between remaining oxygen and oxide in the system to form thermodynamically stable MgO, and (iii) the decomposition of $\text{Mg}(\text{OH})_2$ to MgO, which corresponds to the report of Hout et al. (2001). They showed

that the high energy produced during ball-milling reduced the decomposition temperature of $\text{Mg}(\text{OH})_2$ to MgO . The MgH_2 peaks after ball-milling (or un-doped MgH_2) are lower and broader than those of the as-

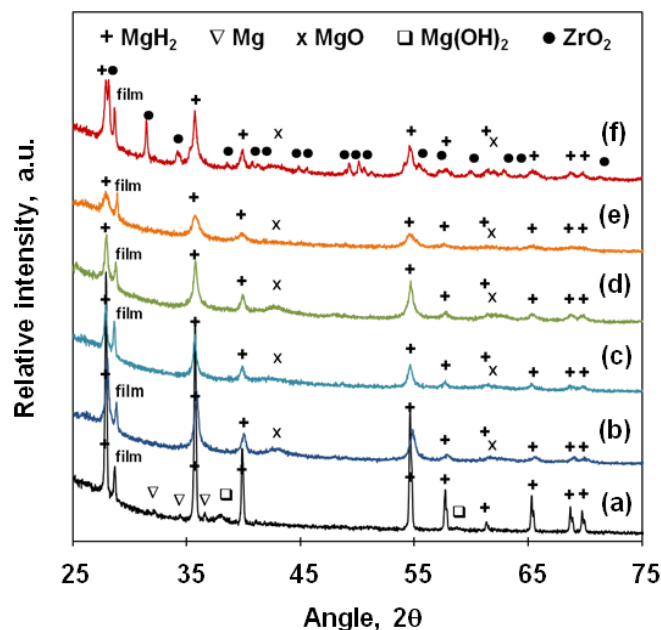


Figure 1: XRD patterns of (a) as-received MgH_2 , (b) un-doped MgH_2 , MgH_2 doped with (c) TiCl_3 , (d) TiO_2 , (e) ZrCl_4 , and (f) ZrO_2 after ball-milling for 5 h

received sample, indicating partial decomposition and reduction in the crystallite size of MgH_2 . The calculated crystallite size using Scherrer equation shows that the size of MgH_2 is reduced from 46.12 to 35.57 nm after ball-milling (Uvarov and Popov, 2007).

Except those of the ZrO_2 doped sample, the XRD patterns of the doped MgH_2 samples (Figures 1(c)-(f)) possess only diffraction peaks of MgH_2 and MgO without those of the catalysts. The calculated MgH_2 crystallite sizes (after ball-milling) of ZrCl_4 , TiO_2 , TiCl_3 , and ZrO_2 doped samples are 20.76, 21.55, 24.06, and 28.12 nm, which are smaller than that of the un-doped sample. This indicates that doping MgH_2 with the catalysts results in smaller MgH_2 crystal formation, and different catalysts seem to reduce the MgH_2 crystallite sizes in different extents.

Hydrogen desorption temperature, amount of desorbed hydrogen, and reversibility of the MgH_2 samples were investigated by using a Sievert's type apparatus over a temperature range of 50-400 °C. The hydrogen desorption profiles in the first to fourth desorption of un-doped MgH_2 and MgH_2 doped with TiCl_3 , TiO_2 , ZrCl_4 , and ZrO_2 after ball-milling for 5 h are shown in Figures 3(a)-(e). The total amounts of released hydrogen and desorption temperatures are compared in Figures 2(b)-(e).

For the first desorption cycle, all samples initially release hydrogen at approximately 100 °C (Figure 3). This low desorption temperature may be possibly from MgH_2 crystal distortion created during ball-milling. A significant release of hydrogen can be noticed at a temperature higher than 300 °C (Figure 2(b)), while doping with catalysts seems to facilitate the release at a lower temperature. It can be clearly seen that the desorption temperature is reduced from 370 °C for the un-doped sample to 325, 335, 340, and 360 °C for the samples doped with ZrCl_4 , TiO_2 , TiCl_3 , and ZrO_2 . Figure 2(b) shows an interesting trend of the desorption temperature as a function of MgH_2 crystallite size, which is consistent with the observation on the hydrogen desorption activation energy. That is MgH_2 doped with ZrCl_4 possesses the smallest crystallite size and the lowest activation energy; hence, it releases hydrogen significantly at the lowest temperature among the investigated MgH_2 samples.

The catalysts seem to increase the total amount of released hydrogen for the first desorption cycle. Figure 2(c) shows that the total amount of desorbed hydrogen of MgH_2 (un-doped sample) is increased from 4.8 to 5.5, 5.4, 5.2, and 5.0 wt% when MgH_2 is doped with ZrCl_4 , TiO_2 , TiCl_3 , and ZrO_2 , but it does not reach the theoretical value of 7.6 wt%. The figure reiterates the correlation between the desorbed hydrogen amount from the first desorption cycle and MgH_2 crystal size as previously observed for the activation energy and desorption temperature. It is believed that one important role of the catalyst on the first

hydrogen desorption cycle is to facilitate smaller hydride crystallite size formation after ball-milling rather than directly accelerate the hydrogen desorption kinetics. As smaller MgH_2 crystal would have relatively low hydrogen desorption barriers, e.g. hydrogen diffusion from core to outer surfaces, hydrogen desorption can then take place at a lower temperature with faster kinetics, and higher released hydrogen.

Hydrogen desorption behaviours in the subsequent desorption cycles of all samples are illustrated in Figures 2(d)-(e) and Figures 3(a)-(e). The results show that all the samples release hydrogen at a slightly lower temperature, while there is no hydrogen desorption at about 100°C . This is an expected result for the reformulated hydride crystal under equilibrium condition without mechanical force applied. Even though the hydrogen desorption temperature of subsequent cycles still follows the initial hydride crystallite size, the amount of desorbed hydrogen shows otherwise. It was found that the total amounts of released hydrogen from MgH_2 doped with TiO_2 and ZrO_2 are significantly higher than those of TiCl_3 and ZrCl_4 doped samples. Nevertheless, all catalyst doped samples still provide higher hydrogen desorption amount than un-doped MgH_2 . It is interesting to further note that even though un-doped MgH_2 has more Mg to re-absorb hydrogen, the total hydrogen desorption amounts from the subsequent cycles of un-doped MgH_2 is the lowest. This evidence suggests that the catalysts also play a role in accelerating the hydride formation during hydrogen re-absorption process. The employed oxide catalysts seem to better catalyze the hydride formation than the chlorides.

In conclusion, the employed catalysts in this study seem to play at least two important roles on hydrogen desorption/adsorption of MgH_2 . The first role is to facilitate smaller MgH_2 crystallite size formation during ball-milling, which helps to expedite the desorption kinetics for all desorption cycles. Besides, the catalysts also play a role in the reversibility of MgH_2 by accelerating hydride formation that enhances the subsequent cycles absorption capability. TiO_2 is identified as the best among the employed catalyst that can provide significant by faster desorption kinetics, lower desorption temperature ($\sim 20 - 35^\circ\text{C}$), and higher hydrogen desorption amount ($\sim 15\%$) than those of the un-doped sample, while still possesses the hydrogen absorption reversibility ($\sim 10\%$ capacity drop from initial cycle).

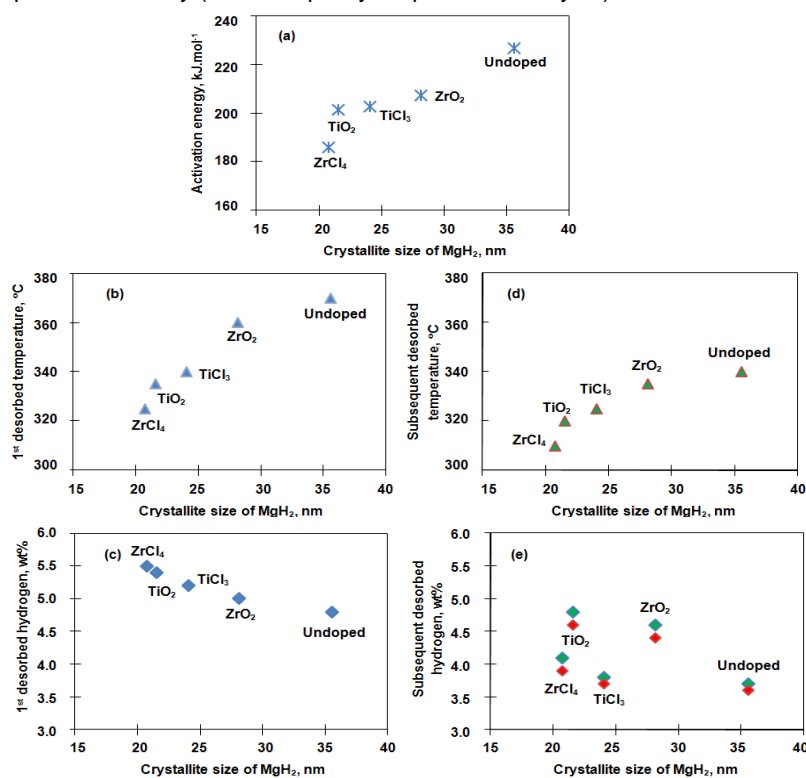


Figure 2: Relationship between crystallite size of MgH_2 and (a) activation energy, (b) desorption temperature, (c) total amount of desorbed hydrogen in the first desorption, (d) desorption temperature, and (e) total amount of desorbed hydrogen in the subsequent desorption

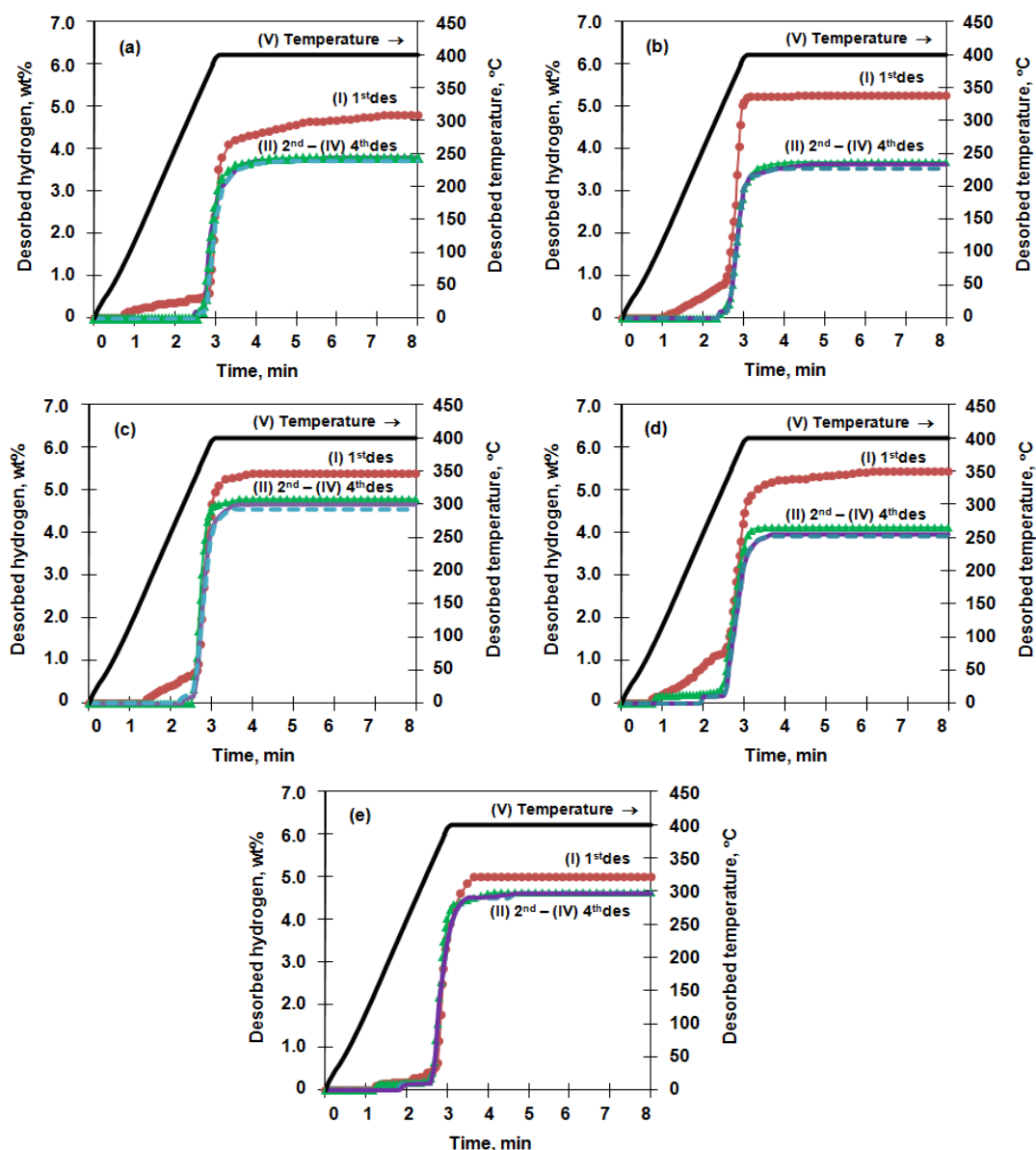


Figure 3: Hydrogen desorption profiles of (a) un-doped MgH_2 , MgH_2 doped with (b) TiCl_3 , (c) TiO_2 , (d) ZrCl_4 , and (e) ZrO_2 after ball-milling for 5 h (I) first, (II) second, (III) third, (IV) fourth desorption, and (IV) desorption temperature

4. Conclusions

In this work, effects of ball-milling and a catalyst (TiCl_3 , TiO_2 , ZrCl_4 , and ZrO_2) on the hydrogen storage properties of MgH_2 were reported. It was found that the employed catalysts can enhance both hydrogen released and reversibility of MgH_2 by facilitating smaller MgH_2 crystallite size formation during ball-milling and accelerating hydride formation during the subsequent hydrogen absorption cycles. Among the employed catalyst, TiO_2 was identified as the best that provided significantly faster desorption kinetics, lower desorption temperature ($\sim 20\text{--}35^\circ\text{C}$), and higher hydrogen desorption amount ($\sim 15\%$) than those of the un-doped sample, while still possessed the hydrogen absorption reversibility ($\sim 10\%$ capacity drop from initial cycle).

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