

Effect of Synthesis Parameters on the Hydrogen Desorption of MgH_2/C composite Prepared Using Organo-magnesium

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Abstract— The MgH_2/C composite can be synthesized through decomposition of an organo-magnesium precursor under hydrogen pressure. Samples were synthesized at 250°C for 30 min, 2h and 4 h under 2MPa hydrogen pressure, respectively. XRD patterns of the MgH_2/C composite exhibit pure MgH_2 phase with tetragonal structure. Morphology of the MgH_2/C composite exhibits porous nanostructure and shape of resultant particles varies with the synthesis time. TPD spectra of a sample synthesized at 250°C for 4h shows remarkable decrease in onset hydrogen release temperature. MgH_2/C composite prepared by using organo-magnesium precursor decomposes ($T_{\text{max}}=325^\circ\text{C}$) at relatively lower temperature than the MgH_2/C prepared by ball-milling ($T_{\text{max}}=380^\circ\text{C}$).

Keywords—composite material, hydrogen storage, organo-magnesium, TPD measurement

I. INTRODUCTION

Hydrogen is one of the most attractive energy carriers due to its high energy density and zero or low carbon emission properties. One of the major obstacles to utilize the hydrogen as an energy carrier is storage. Hydrogen can be stored as compressed hydrogen gas, liquid hydrogen and solid state hydrogen to deliver energy for fuel-cell applications. Storing hydrogen in gas and liquid state is more energy intensive and costly than the solid state hydrogen storage. Magnesium hydride (MgH_2) is a potential candidate for solid state hydrogen storage due to its abundance and non-toxic nature. Its high theoretical gravimetric capacity of 7.6 wt %, low density and reversibility ($\text{MgH}_2 \leftrightarrow \text{Mg}$) attract considerable attention to use this material for hydrogen storage. Despite all of above mentioned MgH_2 advantages, its hydrogen adsorption/desorption performances at standard conditions are still significantly poor. The high binding energy between magnesium and hydrogen ($74.7 \text{ kJ mol}^{-1} \text{ H}_2$) requires high temperature activation at above 300°C to break the (Mg-H) bond to release hydrogen[1]. Studies have shown that hydrogen adsorption/desorption properties of

MgH_2 could be enhanced by mechanical milling [2, 3], transition metal catalysts addition[4-6] and chemical modification [7]. The MgH_2 particles prepared by mechanical milling resulted in improved characteristics due to the formation of small grain size [3] and crystal defects that create more nucleation sites for MgH_2 phase[6]. Unstable $\gamma\text{-MgH}_2$ phase formed during prolonged milling has shown beneficial catalytic effect on hydrogen absorption kinetics[8]. Although, MgH_2 with enhanced hydrogen storage performances can be produced by the mechanical milling, its large scale application remains uncertain due to long production time and surface impurities. Addition of various catalysts including Pd, Ni, Nb, Fe, Ti and V was found to improve hydrogen adsorption kinetics of MgH_2 . The catalysts promote dissociation/recombination of hydrogen thereby resulting in fast hydrogen adsorption/desorption. Chemical modification achieved by reacting the MgH_2 with Si [7], LiBH_4 [9, 10] Al[11] and Ni[12] was also found to improve dehydrogenation/hydrogenation properties. Upon dehydrogenation, compounds such as MgSi_2 , Li_xMg_y , MgAl and Mg_2Ni were formed which decreased formation enthalpies of hydride phase. However the addition of catalysts often reduces the overall hydrogen capacity of MgH_2 due to the added weight of metal catalyst. Carbon materials have also shown favourable effect for the hydrogenation steps. Addition of graphite, fullerene and carbon nanotubes to the MgH_2 resulted in a low decomposition temperature and fast adsorption rates[13]. Compared with amorphous carbon materials crystalline graphite significantly reduced the desorption temperature of MgH_2 [14]. Despite of intensive studies and improved results achieved by

either addition of catalysts and/or mechanical milling, hydrogen storage performances of MgH_2 remains impractical. Theoretical studies done by Wagemans *et al.* [15] predicted that decreasing the grain size would result into a less stable MgH_2 that decomposes at relatively low temperature. According to their calculations MgH_2 with crystal size of 0.9 nm would require only 200°C to release hydrogen. Recently, Nielsen *et al.* [16] synthesized nanoparticles of MgH_2 inside nanoporous carbon aerogel scaffold ($D_{\text{pore}}=7$ nm) by using organo-magnesium as a magnesium precursor. Improvement of kinetics and decrease of onset temperature (from 350 to 175°C) for hydrogen desorption was concluded to be due to the particle size reduction. However, only 18 wt % of MgH_2 was incorporated in carbon aerogel scaffold releasing only a maximum hydrogen capacity of 1.4 wt %. Aguey-Zinsou *et al.* [17] also demonstrated that synthesis of 5 nm colloidal magnesium particle size by electrochemical reduction of magnesium salts with Tetrahydrofuran and Tetrabutylammonium bromide (THF+TBA) liquid phase which can release up to 7.6 wt % of hydrogen at temperatures as low as 85°C in 5 hours. It is evident from above that synthesis of MgH_2 still needs to be developed to achieve best hydrogen storage performances. The synthesis route has to be simple, efficient and cost-effective with short production time to allow large scale production of MgH_2 . If one adds a catalyst to MgH_2 storage system, its hydrogen storage capacity decreases dramatically, therefore it is crucial to develop a synthesis route that will not affect the hydrogen capacity. As mentioned above, nanoparticles have proven to overcome thermodynamic as well as kinetic limitations of MgH_2 . Fabrication of MgH_2 nanoparticles by aqueous solution methods are unattainable due to high reactivity of magnesium with water. Synthesis of MgH_2 using organo-magnesium precursors is well known[18], so far no studies have been reported regarding hydrogen storage performances. Since some organo-magnesium precursors are available in liquid form, one can control particle size, particle morphology and porosity of MgH_2 by optimizing synthesis parameters. Controlling desirable powder properties of MgH_2 is very essential as hydrogen storage performances of MgH_2 are greatly dependent on its nanostructure. In this study, we report that highly porous MgH_2/C composite can be synthesised by

using organo-magnesium precursor. Thermal decomposition properties of MgH_2/C composite was studied and compared with the MgH_2/C produced by the conventional ball-milling.

II. EXPERIMENTAL

A. Synthesis of MgH_2/C composite using organo-magnesium precursor

1M dibutyl magnesium (MgBu_2) solution in heptane (Aldrich) was dried in a glove box under argon atmosphere overnight to allow evaporation of heptane. MgBu_2 white precipitate (slurry) was transferred to custom-made Sievert's apparatus (Suzuki-Shokan Co., Ltd) and subjected to a hot 250°C furnace to allow thermal decomposition of MgBu_2 and formation of MgH_2 under 2 MPa hydrogen pressure. In order to optimise the synthesis condition, MgH_2 powders were synthesized at synthesis temperature of 250°C for 30 min, 2h and 4h under 2 MPa hydrogen pressure. For comparison purpose, magnesium (99.98 % Aldrich) was mixed with carbon black at a weight ratio of 90/10 (Mg/C) and milled using planetary ball-milling ("pulverisette 5" Fritsch). The resulting mixture was heated at 350°C under hydrogen pressure (5.5MPa) to obtain MgH_2 phase.

B. Sample characterisation

The crystalline phase of the samples was identified by X-ray diffraction (MiniFlex, Rigaku) analysis with $\text{CoK}\alpha$ radiation. Internal morphology of samples was observed by high-resolution Transmission Electron Microscope (TEM) (200 kV, JOEL). Hydrogen desorption tests were carried out by temperature programmed desorption (TPD) using a measurement setup reported in our previous work[19]. Prior to TPD measurement samples were cycled two times (adsorption at 250°C/desorption at 400°C) in Sievert's apparatus. To determine hydrogen content, the TPD system was calibrated with a known concentration of hydrogen gas before the measurement. Total content of released hydrogen is calculated from the area under the TPD curve.

III. RESULTS AND DISCUSSION

In order to select synthesis temperature, MgBu_2 white precipitate (slurry) was heated from room temperature to 500°C at a heating rate of 5°C in helium flow. Its decomposition curve obtained by TPD-MS is shown in Figure 1. As we can see

during the heating the MgBu_2 decomposed evolving hydrogen, butene, butane and ethane gas. Release of butene, butane and ethane was started at 165°C and reached its maximum peak at around 236°C . Broad peak at around 230°C and sharp peak at 360°C correspond to hydrogen released from MgBu_2 . The sharp peak at 360°C is characteristic to the thermal decomposition of MgH_2 .

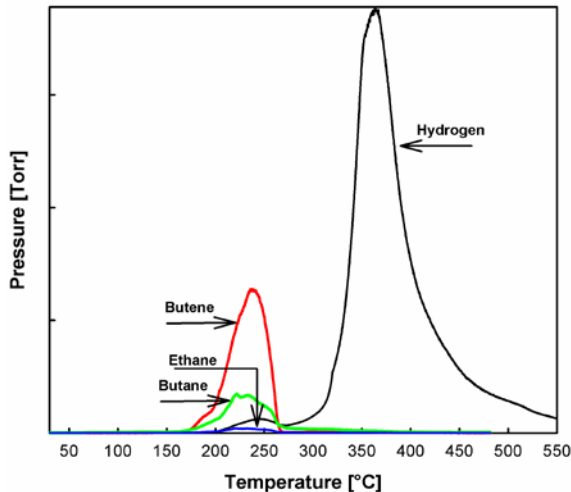


Fig.1 TPD-MS curves of decomposition of MgBu_2 in helium flow measured from room temperature to 500°C at heating rate of $5^\circ\text{C}/\text{min}$

The TPD-MS results indicate that the thermal decomposition of MgBu_2 starts at around 165°C and completes at around 250°C giving products such as alkane, alkene gas and MgH_2 . Wiberg *et. al.* [20] also reported similar thermal decomposition behavior of MgBu_2 . Considering that the thermal decomposition of MgBu_2 would result in additional by-products, it is crucial to know the percentage of MgH_2 phase. To evaluate the percentage of MgH_2 , the MgBu_2 was decomposed at 250°C for 4h under vacuum. The obtained white powder was heated in helium flow from room temperature to 500°C at a heating rate of 5°C min^{-1} and its decomposition behavior was recorded by TPD measurement. The released hydrogen content was 5.3 wt %, which means around 70 wt % of MgH_2 phase can be formed through the thermal decomposition of MgBu_2 and the rest being composed of other impurities. In order to fully convert MgBu_2 to magnesium hydride external hydrogen supply is necessary.

1) Hydrogen desorption properties of porous MgH_2/C composite

As discussed above external hydrogen supply is necessary to fully convert MgBu_2 to MgH_2 phase. In order to identify optimum synthesis time and temperature for the synthesis of MgH_2 the hydrogen pressure of 2 MPa was selected for further study. Figure 2 shows XRD patterns of MgH_2 synthesized at 250°C at various synthesis times.

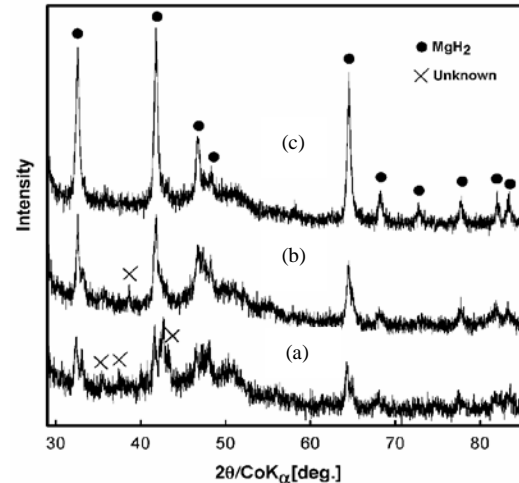
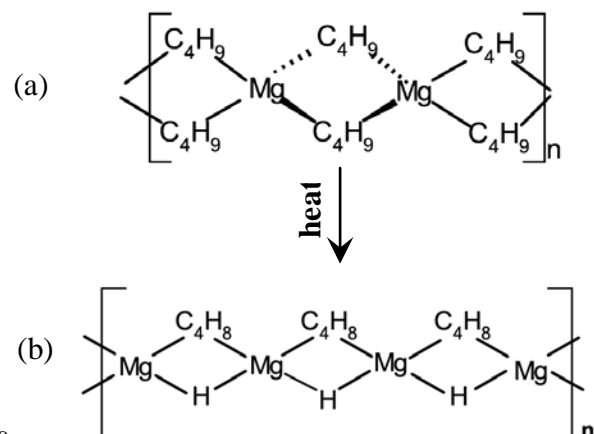


Fig.2 XRD patterns of samples synthesized at 250°C for (a) 30 min, (b) 2h and (c) 4h.

Diffraction peaks of all samples can be assigned to MgH_2 phase with tetragonal structure[21]. Sample synthesized at 30 minutes exhibit additional impurities and low crystallinity indicating that the synthesis time is not sufficient to form MgH_2 phase. TEM images of samples synthesised at various times are given in Figure 3. Morphology of samples drastically changes upon changing synthesis time. In order to understand morphology of the formed MgH_2 particles a possible change of molecular structure of MgBu_2 upon heating was considered (Scheme 1).



Scheme 1 Molecular structure of MgBu_2 (a) dibutyl magnesium oligomers and (b) dibutyl magnesium oligomers during β -elimination

According to previous works[20] dialkyl magnesium exhibits highly associated linear structure due to the electron deficiency of magnesium. This often results in the formation of a long chain polymer compounds. If we assume that initial MgBu_2 consists of dibutylmagnesium oligomers bridged with carbon atoms then after a short heating period due to the incomplete decomposition of MgBu_2 , structure is more likely to exhibit well-arranged, connected nanosheets as observed in Figure 3a. Prolonged heating would result to the loss of the carbon bridges and β -elimination reaction and as a result the connected network structure may break and form singular nanosheets (Figure 3b). When the synthesis time was prolonged to 4 hours, the nanosheets were transformed into rod-like structure as a result of particle growth and agglomeration (Figure 3c). Then, it is possible to assume that the resultant porous structure might be formed due to the evolution of gaseous decomposition of precursor

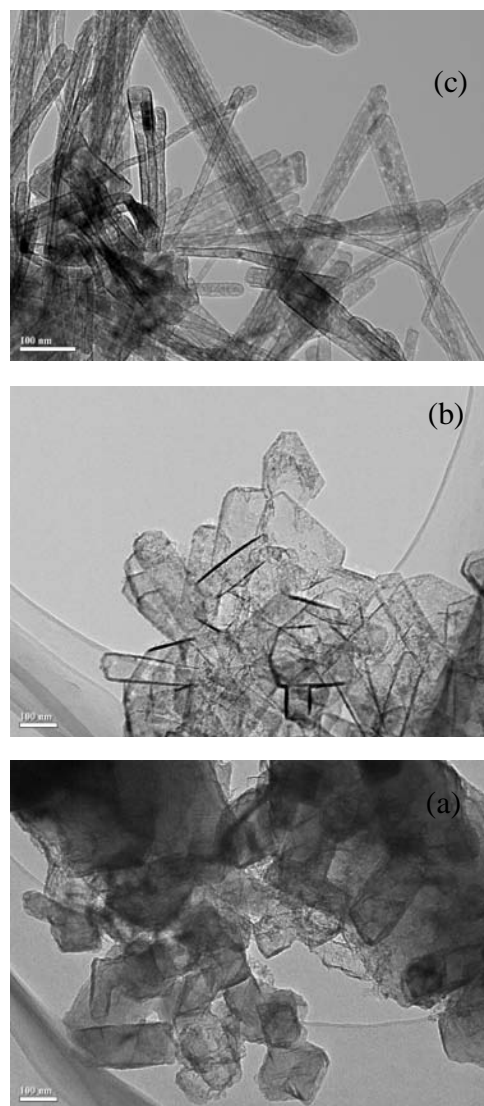


Fig.3 TEM images of samples synthesized at 250°C for (a) 30 min, (b) 2h and (c) 4h.

dibutyl magnesium by-products and simultaneous nucleation of MgH_2 phase.

Effect of synthesis time on the hydrogen desorption temperature was studied by TPD measurement. Samples were synthesised at 250°C for various times (30, 2h and 4h) under hydrogen pressure of 2MPa. As shown in Figure 4 all samples consist of two hydrogen desorption peaks. Sample synthesised in 30 min shows two main peaks at 352°C and 390°C with the onset of hydrogen release as low as 180°C (Figure 4 inset). These two hydrogen desorption peaks shifted towards lower

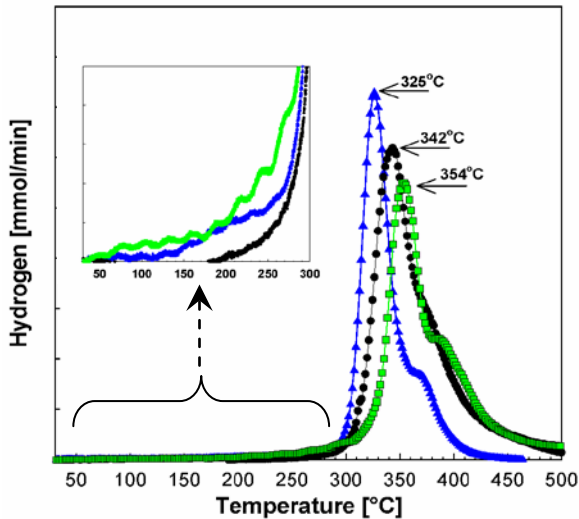


Fig.4 TPD-MS curves of samples(third desorption cycle) synthesized at 250°C for 30 min, 2h and 4h measured from room temperature to 500°C at heating rate of 5°C/min in helium flow.

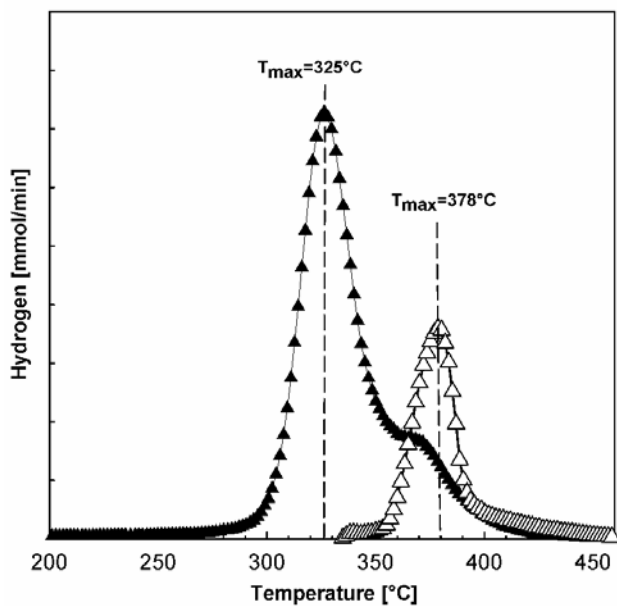


Fig.5 TPD-MS spectra of samples(third desorption cycle) measured from room temperature to 500°C at heating rate of 5°C min⁻¹ in helium flow; (filled black triangle)- MgH₂/C prepared through organo-magnesium decomposition at 220°C for 4h under 2 MPa hydrogen pressure and (unfilled white triangle)- MgH₂/C prepared by ball-milling.

temperatures (by about 25°C) in samples synthesised for 4 hours. Decrease of maximum hydrogen desorption temperature and sharp desorption curves were observed in samples synthesised over long periods (4h).

2) Effect of synthesis methods on hydrogen decomposition properties of MgH₂/C

To compare thermal decomposition properties of ball-milled MgH₂/C with MgH₂/C composite prepared by organo-magnesium precursor, the sample (organo-magnesium) synthesised at 250°C for 4h under 2 MPa hydrogen pressure was selected. Thermal decomposition properties of both ball-milled MgH₂/C and MgH₂/C composite prepared using organo-magnesium precursor were studied by TPD measurement and their results are shown in Figure 5.

The TPD spectra of ball-milled MgH₂/C consist of single desorption peak centered at 378°C, whereas MgH₂/C composite prepared using organo-magnesium precursor exhibits a desorption peak at 325°C. The MgH₂/C composite synthesised through decomposition of organo-magnesium releases hydrogen significantly at lower temperatures than the ball-milled MgH₂/C. The significant difference on their powder morphology is also observed from TEM images as shown in Figure 6. TEM images of ball-milled MgH₂/C exhibits non-uniform structure with agglomerated particles whereas MgH₂/C composite prepared by organo-magnesium precursor consists of porous rod-like structure. The difference in thermal decomposition properties of these two samples can be due to the various morphologies observed by TEM.

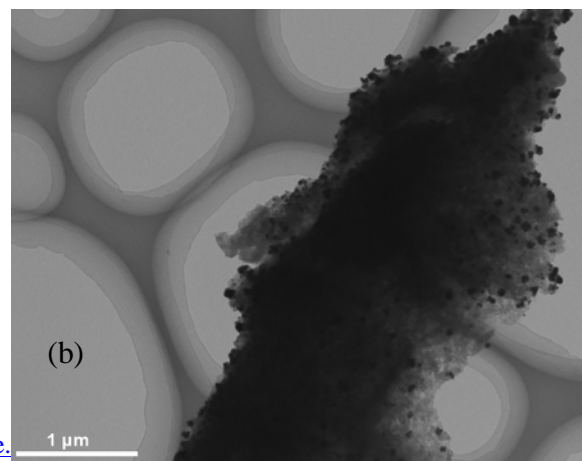
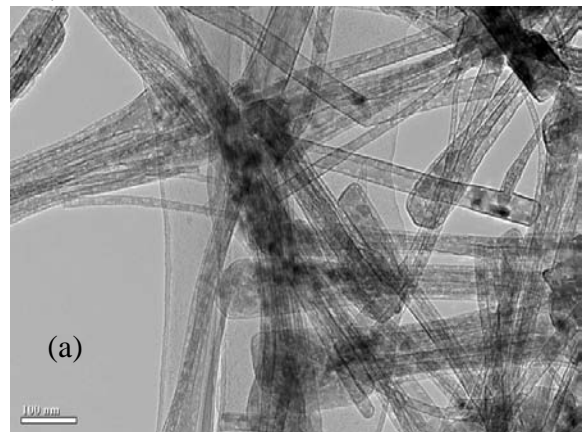


Fig.6 TEM images of samples (a) - MgH_2/C prepared through organo-magnesium decomposition at 220°C for 4h under 2 MPa hydrogen pressure and (b)- MgH_2/C prepared by ball-milling.

Conclusions

MgH_2/C composite can be synthesised through decomposition of an organo-magnesium precursor under hydrogen pressure. The sample synthesised at 250°C for 4 h under 2 MPa hydrogen pressure decomposed at lowest temperature in the TPD experiment and maximum temperature of hydrogen release was as low as 325°C . The MgH_2/C composite exhibits porous nanostructure with rod-like shape. Enhancement of the hydrogen storage properties was achieved by synthesising MgH_2/C composite by a simple method without using ball-milling technique or adding promoting noble catalysts. By using an organo-magnesium precursor the MgH_2 composite can be prepared as short as 4 hours. The same amount of MgH_2 would require 20 to 30 hours synthesis using ball-milling methods. Changes of morphology of MgH_2/C composite with synthesis parameters such as synthesis temperature, time and hydrogen gas pressures and effects of particle morphology on the hydrogen storage properties are under investigation.

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