

**MODIFICATION OF MAGNESIUM
HYDRIDE BY TRANSITION METAL
CARBIDES FOR HYDROGEN
STORAGE**

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A thesis submitted for the degree of
Master by Research in the Faculty of Science
at the University of East Anglia
September 2010

I, Mi Tian, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

ABSTRACT

Magnesium hydride is a promising compound for hydrogen storage but suffers from a high desorption temperature and slow desorption kinetics. This project focuses on improving these properties by modifying the particle size, structure and phases of the material using mechanical milling techniques and doping with transition metal carbides, e.g. TiC and Mo₂C. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were employed to characterize the morphologies and structures of the samples. The dehydrogenation/rehydrogenation properties were evaluated using an intelligent gravimetric analyzer (IGA).

Hydrogen absorption of dehydrogenated MgH₂ was enhanced by both cryogenic milling and ball-milling. The hydrogen content was increased greatly to 4 wt. % after 60 min absorption at 300 °C and 8 bar hydrogen pressure, compared to that of dehydrogenated as-received MgH₂ (< 0.5 wt. %), due to 8 h cryomilling and further 60 h ball-milling.

The hydrogen desorption temperature of MgH₂ catalyzed by 2 mol % TiC was significantly lower (190 °C) than that of the as-received MgH₂ (418 °C). The desorption improved further in terms of temperature and kinetics following the addition of 8 mol % TiC. TiC shows an effective catalytic influence upon the H₂ sorption of Mg/MgH₂, which is stable during H₂ uptake and release with no reaction with Mg or MgH₂. Whilst the reduction of nano particle and grain size by milling has a positive effect on the hydrogen storage properties of MgH₂. Molybdenum carbide Mo₂C does not seem to influence the hydrogen desorption temperature of MgH₂ and has a little effect on hydrogen absorption kinetics. With the addition of Ni in the milled (MgH₂ + TiC) mixture, there was no further reduction in desorption temperature. The work proves that nano-sized TiC particles are inserted into the grain boundary or inner

space of MgH_2 . TiC is an effective and stable catalyst that does improve the hydrogen sorption properties of MgH_2 .

In order to evaluate the possible effects of impurities on hydrogen sorption of Mg , a preliminary study was carried out using a gas mixture of (80 % H_2 + 20 % CO_2) to charge dehydrogenated MgH_2 with and without transition metal carbides at a pressure of 8 bar and a temperature of 300 °C in an IGA coupled with mass-spectrometer (MS). The reactions of Mg (from dehydrogenated MgH_2) with the (80% H_2 + 20% CO_2) gas mixture at 300 °C are rather complex. Magnesium preferentially reacts with H_2 due to the high content of H_2 in the gas mixture. This is followed by MgH_2 reacting with CO_2 to form other gases, such as CO and H_2O and solids such as MgO , which reacts easily with CO_2 to form MgCO_3 . The results prove CO_2 poisons the hydrogenation process of Mg , and provide useful information to further investigate materials for hydrogen storage or purification from the mixture gas streams of H_2/CO_2 or $\text{H}_2/\text{CO}_2/\text{CO}$.

ACKNOWLEDGEMENT

I would like to take this opportunity to thank a number of people for their contributions to this work, without which this thesis would not have been possible. Foremost, I would like to express my sincere gratitude to my supervisor, Dr. Congxiao Shang, for her continuous support during my Master by Research, for her patience, motivation, enthusiasm, immense knowledge, and guidance have helped me throughout my research and whilst writing up this thesis. I could not have imagined having a better supervisor and mentor for my master study. My sincere thanks also go to Dr. John Brindle for his technical help, and Mr. Chris Roberts and Dr. Lawson Baxter for proofreading my thesis.

Many thanks also to the academic and technical staff of the School of Environmental Science, within the University of East Anglia, for providing a friendly and worry-free environment. The friendship I have made during my time here have really helped me through lots of difficulties, and brightened up my life in the UK, particularly, Dr. Ping Jiang, Dr. Yu Liu, Qiao Li, Jianping Tian, Lien Huong Du and Dr. Matthew Bolton to mention just a few.

Last but not the least, I would like to thank my parents Lianzhang Tian and Chunmei Wang and my husband for their continuous support and endless love throughout my life.

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CHAPTER 1 INTRODUCTION

The increase in threats from global warming due to the consumption of fossil fuels requires our planet to adopt new strategies to harness the inexhaustible sources of energy^{1, 2}. CO₂ emission from burning fossil fuels has been clearly identified as the main culprit for global warming. Global CO₂ emission from fossil fuel combustion increases from 20.7 billion tones (Gross tonnage, Gt) in 1990 to 32.5 Gt in 2006 (9.9 Gt of carbon equivalent)³, currently growing 35% faster than expected because of high demand in fossil fuel use and the weakening of natural carbon sinks⁴. This has resulted in a sharp rise of atmospheric CO₂ from around 180–280 ppm in the last 400,000 years to >400 ppm in recent years (a quarter of the level that was once believed to cause extinction of all living species on land in the Triassic–Jurassic boundary, and it only takes less than 100 years to reach that level if no effective action is taken). Moreover, projected world energy demand will double by 2050, whereas available fossil fuels are likely to decline steeply after 20–30 years. There are quite a number of available alternative energy sources such as solar, wind, ocean, geothermal, hydrogen and others, but with a consideration regarding the application for transportation and environmental compatibility, hydrogen is concluded as one of the alternative fuels to fossil fuels⁵. Also hydrogen is an energy carrier which holds tremendous promise as a renewable and clean energy option². In fact, hydrogen can be produced from a variety of sources including fossil fuels, renewables and water (by means of nuclear, wind or solar energy). It is non-toxic and extremely environmentally benign since water is the only exhaust product when hydrogen is converted into energy.

Despite obvious benefits, an immediate incorporation of hydrogen into the world economy faces a number of challenges. Unlike oil and natural gas, hydrogen has no large-scale infrastructure supporting its transportation. Although it is routinely used by chemical and

refining industries, the cost of hydrogen storage and delivery is too high for practiced applications, thus impeding the introduction of the hydrogen economy in which energy is stored and transported using hydrogen as a major energy carrier. The hydrogen economy Infrastructure is comprised of five key elements—Production, Delivery, Storage, Conversion, and Applications, which are in different stages of technological advancement^{6,7,8}, described as following.

Production—Hydrogen can be produced using diverse, domestic resources including fossil fuels, such as natural gas and coal (with carbon sequestration); nuclear; biomass; and other renewable energy technologies, such as wind, solar, geothermal, and hydro-electric power.

Delivery—The existing infrastructure can be used to move the hydrogen from its point of production to an end-use device. Similar to natural gas distribution, pipelines are used to supply hydrogen to customers. Currently hydrogen pipelines have been used in a few areas of the United States⁹. Other options, such as blending with natural gas, a compressed gas or cryogenic liquid delivery as well as alternative hydrogen carriers (methanol, ethanol, and other organic liquids), are being considered.

Conversion—Hydrogen can be used both in engines and in fuel cells. Engines can combust hydrogen in the same manner as gasoline or natural gas, while fuel cells use the chemical energy of hydrogen to produce electricity and thermal energy. Since electrochemical reactions are more efficient than combustion at generating energy, fuel cells are more efficient than internal combustion engines.

Application—Hydrogen can be used in conventional power generation technologies, such as automobile engines and power plant turbines, or in fuel cells, which are relatively cleaner and more efficient than conventional technologies. Fuel cells have broad application

potential in both transportation and electrical power generation, including on-site generation for individual homes and office buildings.

Storage — Storage issues cut across the production, transport, delivery, and end-user applications of hydrogen as an energy carrier. Mobile applications are driving the development of safe, space-efficient, and cost-effective hydrogen storage systems, yet other applications will benefit substantially from all technological advances made for these on-board storage systems.

Hydrogen can be stored as a discrete gas or liquid or in a chemical compound. Currently available technologies permit the physical storage, transport, and delivery of gaseous or liquid hydrogen in tanks and pipeline systems. But none of the options in the market currently satisfy the needs of end users, which explains the growing interest and investment in hydrogen energy related research and development⁶. Compressed hydrogen storage is a mature technology, though improvements in cost, weight, and volume storage efficiency must continue to be made. Some automotive manufacturers are considering liquid hydrogen storage because of its good volumetric storage efficiency compared with compressed hydrogen; however the special handling requirements, long-term storage losses, and energy demands for liquefaction currently detract from its commercial viability. Metal hydrides offer the advantages of lower pressure storage, conformable shapes, and reasonable volumetric storage efficiency, but have weight penalties and thermal management issues. Although chemical hydrides present a potentially safer and more volumetrically efficient option, there are a number of challenges that must be addressed, including cost, recycling, overall energy efficiency, and infrastructure. Physical absorption materials with high surface areas are emerging, but the design of practical systems awaits a better understanding of the fundamental adsorption/desorption processes and development of mass production processes for the materials.

By translation vehicle performance requirements into storage system needs, U.S. Department of Energy (DOE) set a series of hydrogen storage targets for 2010 and 2015. A complete summary of DOE targets based on lower heating value of hydrogen and greater than 300-mile vehicle range is shown in Table 1-1. The targets are based on the U.S. weighted average corporate vehicle (WACV) that includes minivans, light trucks, economy cars, and SUV/crossover vehicles in proportion to their sales. Depending on progress in other areas related to hydrogen vehicle development, these targets have been altered in DOE 2009 Annual Progress Report¹⁰ and may have to be altered in the future.

Table 1-1 DOE technical targets: on-board hydrogen storage systems¹¹.

Storage Parameter	Units	2010	2015
Gravimetric Capacity	kWh/kg	2.0	3.0
	wt. % hydrogen	6	9
Volumetric Capacity	kWh/L	1.5	2.7
	g/L	45	81
Storage System Cost	\$/kWh	4	2
	\$/kg H ₂	133	67
Operating ambient Temperature	°C	-30/50 (sun) *	-46/60(sun) *
Min/Max delivery temperature	°C	-30/85	-40/85
Cycle life (1/4 tank to full)	Cycles	1 000	1 500
System Fill Time for 5 kg H ₂	min	3	2.5
Loss of usable H ₂	(g/h)kg H ₂ stored	0.1	0.05

* The notation (sun) indicates that the upper temperature is a hot soak condition in full direct sun, including radiant heat from the pavement.

Currently, research is focused on achieving the targets of volumetric and gravimetric capacity, while also meeting the energy and temperature requirements for hydrogen release and the kinetics of hydrogen charging and discharging. The current status of hydrogen storage system for vehicle is shown in Figure 1-1¹⁰, in comparison to the gravimetric and volumetric targets. An ideal hydrogen storage material should meet the targets at a high hydrogen capacity, low desorption temperature, moderate dissociation pressure, low heat dissipation during the exothermic hydride formation, good reversibility, fast kinetics, and low sensitivity to O₂ and moisture for long cycle life¹⁰.

On-board hydrogen storage approaches presently include compressed hydrogen gas, liquid hydrogen, high surface area adsorbents, and chemical hydrogen storage media, as already stated previously. Compressed and cryogenic hydrogen, adsorbents and some metal hydrides are categorized as “reversible” storage system which can be refilled with hydrogen completely, similar to gasoline refueling today. In contrast, some complex chemical hydrogen storage materials, such as LiBH_4 , NaAlH_4 etc.. known as complex hydride, generally require a chemical reaction pathway to be regenerated to the original form, so the storage system cannot be directly refueled with hydrogen on-board the vehicle. Such systems are referred to as “off-board regenerable”, requiring the spent media to be removed from the vehicle and then regenerated with hydrogen either at the fueling station or at a centralized processing facility. Complex chemical storage materials may also serve as a hydrogen delivery carrier by providing an alternative to transporting hydrogen as a gas or cryogenic liquid.

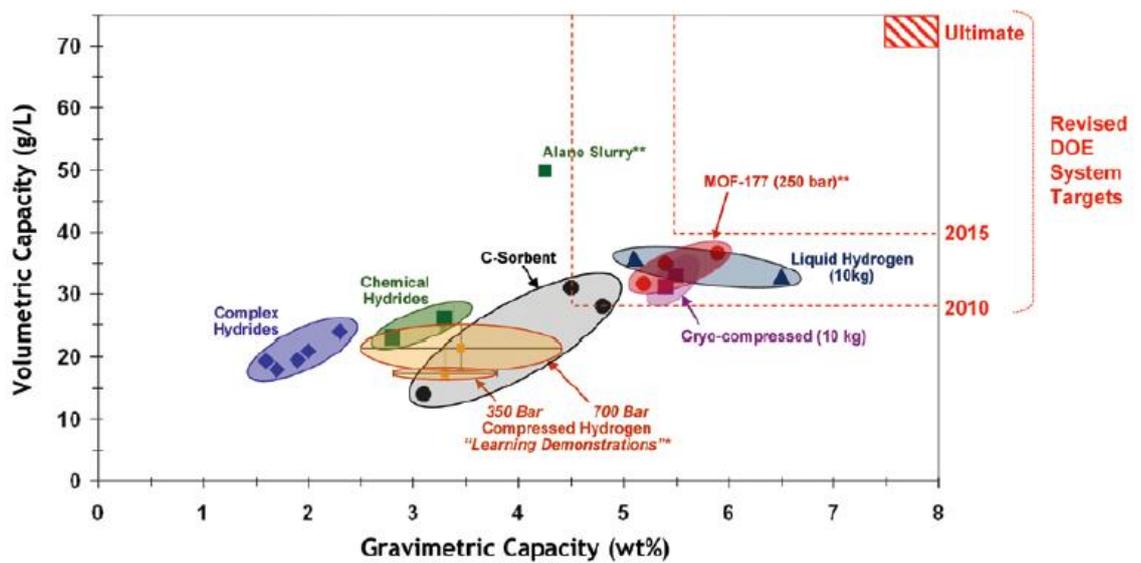


Figure 1-1 Status of hydrogen storage systems¹⁰.

For compressed gas and cryogenic tanks, volume and cost are the primary concerns. Cost and thermal management are issues for all material approaches. For complex chemical

storage materials, the cost and energy efficiency for off-board regeneration are key issues. Research is also needed on improving hydrogen discharge kinetics and simplifying the reactor required for discharging hydrogen on-board the vehicle (e.g. the volume, weight, and operation). For metal hydrides, weight, system volume and refueling time are the primary issues. Volumetric capacity, operating temperature and pressure are drawbacks for physical adsorbents that are inherently low density materials and have low hydrogen binding energies thus requiring cryogenic temperature. Finally, for all chemical materials approaches, transient performance and its control for hydrogen discharge is relatively unexplored from a “full” tank to the “nearly depleted” tank⁶.

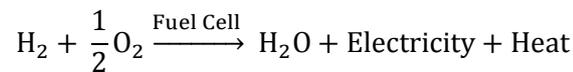
Magnesium hydride is considered as one of promising hydrogen storage materials due to its high capacity of 7.6 wt %, relatively low cost and light weight^{1, 12}. However its slow kinetics and high desorption temperature of >300 °C limits its practical applications¹³⁻¹⁶. Many methods such as doping with catalyst, reducing crystallite and particle size have been developed to improve the hydrogen sorption properties. It is reported that the sorption kinetics of MgH₂ can be dramatically increased by ball milling with some transition metals, oxides and fluorides^{16, 17}. Particularly, transition-metal compounds have attracted considerable interest as effective catalysts, due to high affinity of transition-metal cation toward hydrogen^{17, 18}. For example, the small addition of Nb₂O₅ significantly improves both the absorption and desorption kinetics of MgH₂^{19, 20}. Comparative studies based on various transition-metal oxides emphasize that the appropriate chemical interaction between catalyst and host hydride is essential for realizing high catalytic activity, suggesting the functionality of contact anion in tailoring the activity of transition-metal cation¹¹. Titanium-based compounds have been successfully used to improve sorption kinetics in several hydrogen storage systems, exhibiting a high affinity of Ti cation toward hydrogen even at moderate temperatures. For example, titanium halides are exceptionally effective in reducing the

kinetic barrier of dehydrogenation of alkaline alanates ^{17, 21, 22}. In addition, TiN is found to be very active in accelerating the amide/imide conversion as a promising catalyst for the Li-N-H system ¹⁷. It has been also found that the temperature for hydrogen release from MgH₂ can be greatly reduced by doping it with Ti-containing agents e.g. TiF₃ and TiC ^{16, 23}. The interactions between the hydrides and the Ti-containing agents weaken the Mg-H bonds and thus facilitate the recombination of hydrogen atoms to the hydrogen molecules.

Following this brief introduction, Chapter 2 provides a thorough literature review on metal hydrides storage systems, and the hydrogen sorption properties of Mg-based storage materials, addressing the thermodynamic properties, kinetic limitations, and various modifications to the system. Chapter 3 describes the experimental facilities and the process of sample preparation. The results are studied in Chapter 4. Chapter 5 covers a general discussion of all the experimental findings. The conclusions are drawn in Chapter 6 with a future plan. References cited in each chapter are listed at the end of the thesis.

CHAPTER 2 LITERATURE REVIEW

Hydrogen is the ideal fuel for the future since it significantly reduces the greenhouse gas emissions, reduces the global dependence on fossil fuels, for both internal combustion engines and proton exchange membrane fuel cells¹². Hydrogen used in the fuel cell directly converts the chemical energy of hydrogen into water, electricity, and heat²⁴ as represented by



2.1 Hydrogen Storage Methods

Hydrogen molecule H_2 can be found in various forms depending on the temperature and the pressure which are shown in the phase diagram Figure 2-1²⁵. At low temperature, hydrogen is a solid with a density of 70.6 kg/m^3 at $-262 \text{ }^\circ\text{C}$ and hydrogen is a gas at higher temperatures with a density of 0.09 kg/m^3 at $0 \text{ }^\circ\text{C}$ within a pressure of 1 bar. A small zone starting at the triple point and ending at the critical point exhibits the liquid hydrogen with a density of 70.8 kg/m^3 at $-253 \text{ }^\circ\text{C}$. At ambient temperature ($25 \text{ }^\circ\text{C}$) hydrogen is a gas and can be described by a Van der Waals equation:

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2}$$

Where p is the gas pressure, V the volume, T the absolute temperature, n the number of mols, R the gas constant $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, a is the dipole interaction or repulsion constant $2.476 \times 10^{-2} \text{ m}^6 \text{ Pa mol}^{-2}$ and b is the volume occupied by the hydrogen molecules itself $2.661 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ²⁶. The first criterion of hydrogen storage implies basically the reduction of the enormous volume of the hydrogen gas. One kilogram of hydrogen at ambient temperature and atmospheric pressure takes a volume of 11 m^3 . In order to increase the hydrogen density in a storage system either work can be applied to compress hydrogen or the temperature has

to be decreased below the critical temperature or finally the repulsion has to be reduced by the interaction of hydrogen with an other material.

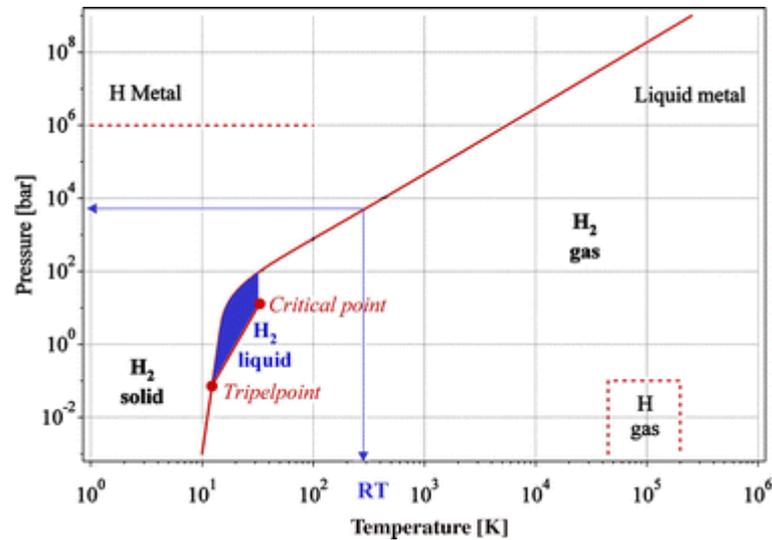


Figure 2-1 Primitive phase diagram for hydrogen. Liquid hydrogen only exists between the solidus line and the line from the triple point at 21.2K and the critical point at 32K

The second criterion for a hydrogen storage system is the reversibility of charging and discharging. Based on the two criteria, six methods of reversible hydrogen storage with a high volumetric and gravimetric density are known today, listed in Table 2-1^{2, 27, 28}. Each of these options possesses attractive attributes for hydrogen storage. Available technologies permit directly to store hydrogen by modifying its physical state in gaseous or liquid form in pressurized or in cryogenic tanks. The traditional hydrogen-storage facilities are complicated because of its low boiling point $-253\text{ }^{\circ}\text{C}$ and low density in the gaseous state 0.08988 g/L at 1 atm^2 . Liquid hydrogen requires the addition of a refrigeration unit to maintain a cryogenic state, thus adding weight and energy costs, and a resultant 40 % loss in energy content². High-pressure storage of hydrogen gas is limited by the weight of the storage canisters and the potential for developing leaks. Moreover, storage of hydrogen in liquid or gaseous form poses important safety problems for on-board transport applications. Designs involving the use of methane as a hydrogen source require the addition of a steam reformer to extract

hydrogen from the carbon which adds weight, additional space requirements, and the need for a device to sequester CO₂²⁹.

Table 2-1 the six basic hydrogen storage methods and phenomena. The gravimetric density ρ_m , the volumetric density ρ_v , the working temperature T, and pressure p are listed. RT stands for room temperature (25 °C)^{2, 27, 28}

Storage method	ρ_m mass %	ρ_v kg H ₂ /m ³	T °C	P bar	Phenomena and remarks
High pressure gas cylinders	13	<40	RT	80 0	Compressed gas in light weight composite cylinders (tensile strength of the material is 2000 MPa)
Liquid hydrogen in cryogenic tanks	Size dependent	70.8	-252	1	Liquid hydrogen, continuous loss of a few % per day of hydrogen at RT.
Physical adsorbents	~ 2	20	-80	10 0	Physisorption on materials, e.g. carbon with a very large specific surface area, fully reversible.
Adsorbed on interstitial sites in a host metal	~ 2	150	RT	1	Hydrogen (atomic H) intercalation in host metals, metallic hydrides working at r tater fully reversible
Complex chemical compounds	< 18	150	>10 0	1	Complex compounds ([AlH ₄] ⁻ or [BH ₄] ⁻), desorption at elevated temperature, adsorption at high pressures
Metals and complexes together with water	< 40	> 150	RT	1	Chemical oxidation of metals with water and liberation of hydrogen, not directly reversible.

The U.S. Department of Energy (DOE)¹⁰ published a long-term vision for hydrogen-storage applications considering economic and environmental parameters. The predicted minimum hydrogen-storage capacity of 2010 target should be 6.5 wt% and 65 g/L hydrogen available, at the decomposition temperature between 60 and 120 °C for commercial viability ideally. It was also required low temperature of hydrogen desorption and low pressure of hydrogen absorption (a plateau pressure of the order of a few bars at room temperature) and nonthermal transformation between substrates and products of decomposition, as reported by Schulz³⁰. Furthermore, the cost of a storage medium and its toxicity properties need to be carefully considered for the realization of the set goals.

Storage by absorption in chemical compounds or by adsorption on porous materials has definite advantages from the safety perspective such that some form of conversion or energy input is required to release the hydrogen for use. A great deal of effort has been made on solid forms of hydrogen storage systems, including metal hydrides, chemical complex hydrides, carbon nano structures and metallic alloy.

2.1.1 Physical adsorbents

Carbon materials such as high surface area activated carbons (AC), carbon nanotubes (SWNTs), carbon nanofibers and metal–organic frameworks (MOFs) have been proposed as storage media for hydrogen. The research on hydrogen storage in carbon materials was dominated by announcements of high storage capacities in carbon nanostructures. However, the experimental results on hydrogen storage in carbon nanomaterials scatter over several orders of magnitude. The hydrogen storage capacity for carbon materials is reported between 0.2 and 10 wt%^{31, 32}. Considering the experimental results for metal hydrides, the storage capacities of which have been reported to vary only within a few percent due to stable structures and good reversibility. Why it is so difficult to determine the hydrogen storage capacity of carbon nanostructures? The reasons may be the limited quantity and purity of carbon nanotubes and different experimental conditions. A reliable characterization of carbon nanostructures and the determination of their purity are extremely difficult.

Recently, metal–organic frameworks have attracted great attention for hydrogen storage because they are amenable to being designed³³⁻³⁵, have extraordinary permanent porosity^{35, 36}, and a large pore volume^{37, 38}. A series of MOF-n materials with various structures were reported in 2000 by Yaghi and co-workers³⁹. One member of the MOF-n family, MOF-5, has a zeolite-like framework in which inorganic $[\text{Zn}_4\text{O}]^{6+}$ groups are joined to an octahedral array of $[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]_2$ (1,4-benzendicarboxylate, BDC) groups to form a robust and highly porous cubic framework of space group (Fm-3m) with $a = 25.6690(3) \text{ \AA}$ and $V =$

16,1913.2 (3) Å³. In their first paper, they reported that MOF-5 showed high hydrogen capacities, 4.5 wt% at 77K and 0.8 bar, and 1 wt% at room temperature and pressure of 20 bar⁴⁰. In later research, this group observed that maximum uptakes hydrogen of MOF-5 can reach 1.32 wt% at 1 bar and 77K⁴¹. However Panella and Hirscher reported a hydrogen storage value of 1.6 wt% for MOF-5 at 77 K and pressures above 10 bar⁴². Nevertheless, the adsorption capacity of MOF-5 is very low at room temperature: less than 0.2 wt% at pressures up to 67 bar⁴². More recently, Panella et al. showed that the hydrogen uptake of MOF-5 can reach a saturation value of 5.1 wt% at 77 K and over 80 bar due to the synthesis of single-crystal MOF-5⁴³. The results show that there are considerable differences in the hydrogen storage capacities of MOF-5 synthesized by different approaches and even by the same approach (Table 2-2)².

Table 2-2 Adsorption Data for Metal–Organic Frameworks

Material	Wt % Hydrogen	Absorption condition	Raw materials	Surface Area (m ² /g)	Reference
MOF-5	2.96	77 K, 1.45 MPa	Zn(NO ₃) ₂ · 6H ₂ O H ₂ BDC Dimethylformamide(DMF) Triethylamine(TEA) H ₂ O ₂	611, BET	⁴⁴
MOF-5	4.5 1	77 K, 0.8 bar 298K, 20 bar	Zinc (II) nitrate H ₂ BDC DMF N,N'- H ₂ O ₂	2 900, Langmuir	⁴⁰
IRMOF	1.32	77 K, 1 bar	zinc oxide clusters benzene-1,4-dicarboxylate, naphthalene-2,6-dicarboxylate, 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate, 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate	3362, Langmuir	⁴¹
MOF-5	1.6	77 K, 10 bar	Zn(NO ₃) ₂ · γH ₂ O BDC TEA DMF	1014, Langmuir	⁴²

2.1.2 Metal hydrides

Hydrogen forms compounds with metals like Li, Na, Mg, Ti (Table 2-3), which are generally known as metal hydride. Many of these compounds, (MH_n), show large deviations from ideal stoichiometry ($n = 1, 2, 3$) and can exist as multiphases systems. The lattice structure is that of a typical metal with hydrogen atoms on the interstitial sites; and for this reason they are also called interstitial hydrides. This type of structure is limited to the compositions MH , MH_2 , and MH_3 , with the hydrogen atoms fitting into octahedral or tetrahedral holes in the metal lattice, or a combination of the two. Especially interesting are the metallic hydrides of intermetallic compounds, in the simplest case the ternary system $ABxH_n$, because the variation of the elements allows the properties of these hydrides to be tailored. Element A is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. Element B is often a transition metal and forms only unstable hydrides. Some well defined ratios of B: A, where $x = 1.5, 1, 2, 5$, have been found to form hydrides with a hydrogen to metal ratio of up to two⁴⁵.

Table 2-3 Volumetric and gravimetric hydrogen content in various materials ⁴⁵

Material	H-atoms per cm^3 ($\times 10^{22}$)	Wt % Hydrogen
H_2 gas, 200 bar (2850 psi)	0.99	100
H_2 liquid, 20 K (-253 °C)	4.2	100
H_2 solid, 2.4 K (-269 °C)	5.3	100
MgH_2	6.5	7.6
Mg_2NiH_4	5.9	3.6
$FeTiH_{1.95}$	6.0	1.89
$LaNi_5H_{6.7}$	5.5	1.37
$ZrMn_2H_{3.6}$	6.0	1.75
VH_2	11.4	2.10

The reaction of hydrogen gas with a metal is called the absorption process and the hydrogen atoms contribute their electron to the band structure of the metal. At a small hydrogen to metal ratio ($H/M < 0.1$), the hydrogen is exothermically dissolved in the metal (solid-solution, α -phase). The metal lattice expands proportional to the hydrogen concentration by

approximately 2-3 Å³ per hydrogen atom⁵. At greater hydrogen concentrations in the host metal (H/M >0.1), a strong hydrogen-hydrogen interaction becomes important because of the lattice expansion, and the hydride phase (β-phase) nucleates and grows. The hydrogen concentration in the hydride phase is often found to be H/M = 1. The volume expansion between the co-existing α- and β-phase corresponds, in many cases, to 10-20% of the metal lattice. At the phase boundary, therefore, a large stress builds up and often leads to a decrepitation of brittle host metals such as intermetallic compounds. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure-composition-isotherms (P-C-I), shown in Figure 2-2. When solid solution and hydride phases coexist, there is a plateau in the isotherms, the length of which determines the amount of hydrogen stored. In the pure β-phase, the hydrogen pressure rises steeply with the concentration. The two phases region ends in a critical point, T_c, above which the transition from the α- to β-phase is continuous. The equilibrium pressure, p_{eq}, is related to the changes ΔH and ΔS in enthalpy and entropy, respectively, as a function of temperature by the Van't Hoff equation:

$$\ln \left(\frac{p_{\text{eq}}}{p_{\text{eq}}^0} \right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R}$$

p_{eq}⁰ is the equilibrium constant at absolute temperature T, and R is the universal gas constant (8.314 J/ mol/K).

As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissolved solid hydrogen, it is approximately the standard entropy of hydrogen S₀ = 130 J K⁻¹ mol⁻¹ and is, therefore, ΔS_f ≈ -130 J K⁻¹ mol⁻¹ H₂ for all metal-hydrogen systems. The enthalpy term characterizes the stability of the metal hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K, ΔH should amount to 39.2 kJ mol⁻¹ H₂. The entropy of formation term for metal hydrides leads to a significant heat evolution ΔQ = T·ΔS (exothermal reaction) during hydrogen absorption. The same heat has to be provided to the

metal hydride to desorb the hydrogen (endothermal reaction). If the hydrogen desorbs below RT, the necessary heat has to be delivered from an external source, such as the combustion of hydrogen. For a stable hydride like MgH_2 , the heat necessary for the desorption of hydrogen at 300 °C and 1 bar is about 25 % of the higher heating value of hydrogen.

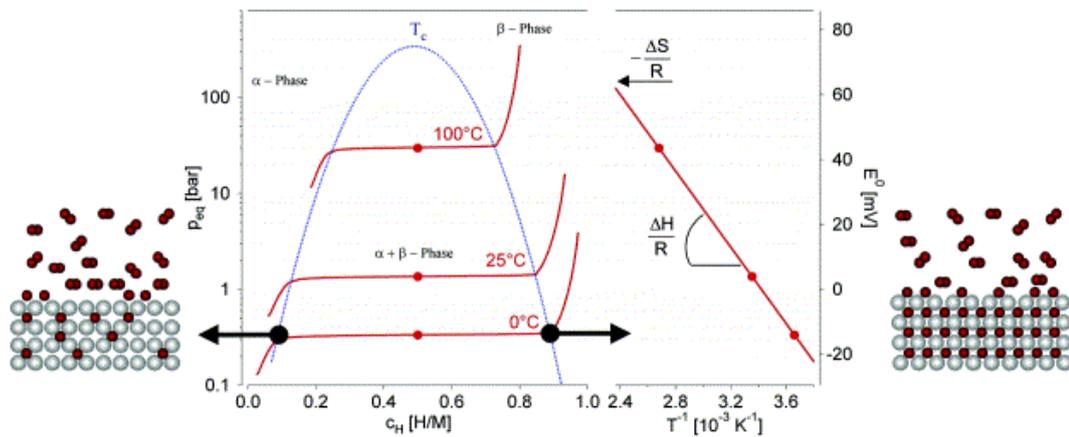


Figure 2-2 Pressure composition isotherms for hydrogen absorption in a typical intermetallic compound on the left hand side. The solid solution (α -phase), the hydride phase (β -phase) and the region of the coexistence of the two phases are shown. The coexistence region is characterized by the flat plateau and ends at the critical temperature T_c . The construction of the Van't Hoff plot is shown on the right hand side. The slope of the line is equal to the enthalpy of formation divided by the gas constant and the intercept is equal to the entropy of formation divided by the gas constant.⁴⁶

Metal hydrides, can absorb large amounts of hydrogen at a constant pressure, because of this phase transition, i.e. the pressure does not increase with the amount of hydrogen adsorbed. The characteristics of hydrogen absorption and desorption can be tailored by partial substitution of the constituent elements in the host lattice. Some metal hydrides adsorb and desorb hydrogen at ambient temperature and close to atmospheric pressure. Several families of intermetallic compounds listed in Table 2-4 are interesting for hydrogen storage²⁸. They all consist of an element with a high affinity to hydrogen, element A, and a low affinity one, element B. The latter is often at least partially Ni, since it is an excellent catalyst for hydrogen dissociation.

Table 2-4 the most important families of hydride-forming intermetallic compounds.

Intermetallic compound	Prototype	Structure
AB₅	LaNi ₅	Haucke phase, hexagonal
AB₂	ZrV ₂ , ZrMn ₂ , TiMn ₂	Laves phase, hexagonal or cubic
AB₃	CeNi ₃ , YFe ₃	Hexagonal
A₂B₇	Y ₂ Ni ₇ , Th ₂ Fe ₇	Hexagonal
A₆B₂₃	Y ₆ Fe ₂₃	Cubic
AB	TiFe, ZrNi	Cubic
A₂B	Mg ₂ Ni, Ti ₂ Ni	Cubic

One of the most interesting features of metallic hydrides is the extremely high volumetric density of hydrogen atoms present in the host lattice. The highest volumetric hydrogen density reported to date is 150 kg m⁻³ in Mg₂FeH₆ and Al(BH₄)₃. Both hydrides belong to the complex hydride family. However, all hydrides with hydrogen to metal ration of more than two are ionic or covalent compounds and belong to the complex hydrides group.

Metal hydrides are very effective in storing large amounts of hydrogen in a safe and compact way. All the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 mass%. It remains a challenge to explore the properties of the lightweight metal hydrides.

2.1.3 Complex hydrides

Group I and II salts of [AlH₄]⁻, [NH₂]⁻, and [BH₄]⁻ (alanates, amide, and borohydride) have recently received considerable attention as potential hydrogen storage materials. All of these materials are currently referred to as “complex hydrides”, although only the alanates contain anionic metal complexes. These materials have high hydrogen gravimetric densities (Table 2-5) and are, in some cases, commercially available. Thus, a priori, they would seem to be viable candidates for application as practical, on-board hydrogen storage materials. Many of these “complex hydrides” have, in fact, been utilized in “one-pass” hydrogen storage systems in which hydrogen is evolved from the hydride upon contact with water. However,

the hydrolysis reactions are highly irreversible and could not serve as the basis for rechargeable hydrogen storage systems. All of these materials are also plagued by high kinetics barriers to dehydrogenation and/or rehydrogenation in the solid state. Traditionally, it was thought that it would be impossible to reduce the barrier heights to an extent that would give reaction rates that even approached those that would be required for vehicular applications. Thus, until recently, complex hydrides were not considered as candidates for application as rechargeable hydrogen carriers. This situation was changed by Bogdanović and Schwickardi. Their pioneering studies demonstrated that, upon doping with selected titanium compounds, the dehydrogenation of anionic aluminum hydrides could be kinetically enhanced and rendered reversible under moderate conditions in the solid state⁴⁷. This breakthrough has led to a worldwide effort to develop doped alanates as practical hydrogen storage materials that was quickly expanded to include amides and borohydride.

Over the past decade, tremendous progress has been made toward the development of complex hydrides for potential use as an onboard hydrogen carrier. This approach to hydrogen storage, which was once thought to be “impossible”, has been brought to the threshold of commercial viability. Alanates are attractive because of the rapid kinetics of their dehydrogenation and rehydrogenation. Borohydrides have extremely high available hydrogen mass percents that meet the current, highly stringent U.S. DOE targets. Amides have reaction kinetics and hydrogen mass percents which both approach practical viability. However, all of the complex hydrides currently have practical limitations that must be overcome. Alanates have insufficient reversible capacity; Borohydrides suffer from unacceptably slow kinetics and also from undesirable evolution of diborane; and amides are plagued by capacity and kinetic limitations as well as undesirable evolution of ammonia. Additionally, the problem of thermal management on recharging is common to all complex hydrides. In view of the great progress that has been made, it can be anticipated that further

advances will be made toward the development of group I and II complex hydrides. Recently, the frontier of research in this area has been extended to the combinations of transition metal salts of these compounds. This new area of research may lead to the identification of materials which are free from the above-mentioned problems.

Table 2-5 Material Properties of Complex Hydrides⁴⁸

Material	Density (g/mol)	Density (g/cm ³)	Hydrogen (wt %)	Hydrogen (kg/m ³)	T_m^a (°C)	ΔH_f° (kJ/mol)
LiAlH ₄	37.95	0.917	10.54		190 ^d	-119
NaAlH ₄	54.00	1.28	7.41		178	-113
KAlH ₄	70.11		5.71	53.2		
Mg(AlH ₄) ₂	86.33		9.27	72.3		
Ca(AlH ₄) ₂	102.10		7.84	70.4	>230 ^d	
LiNH ₂	22.96	1.18	8.78	103.6	372–400	-179.6
NaNH ₂	39.01	1.39	5.15	71.9	210	-123.8
KNH ₂	55.12	1.62	3.66	59.3	338	-128.9
Mg(NH ₂) ₂	56.37	1.39	7.15	99.4	360	
Ca(NH ₂) ₂	72.13	1.74	5.59	97.3		-383.4
LiBH ₄	21.78	0.66	18.36	122.5	268	-194
NaBH ₄	37.83	1.07	10.57	113.1	505	-191
KBH ₄	53.94	1.17	7.42	87.1	585	-229
Mg(BH ₄) ₂	53.99	0.989	14.82	146.5	320 ^d	
Ca(BH ₄) ₂	69.76		11.47		260 ^d	
Al(BH ₄) ₃	71.51	0.7866	16.78	132	-64.5 ^d 44.5 ^b	

d and b represent decomposition and boiling temperatures, respectively.

2.1.4 Storage via chemical reactions

Hydrogen can be generated by reacting metals and chemical compounds with water. The common experiment, seen in many chemistry classes, where a piece of Na floating on water produces hydrogen, demonstrates the process.

The Na transforms to NaOH in this reaction. The reaction is not directly reversible, but NaOH can be removed and reduced in a solar furnace back to metallic Na. Two Na atoms react with two H₂O molecules and produce one hydrogen molecule. The hydrogen molecule produces a H₂O molecule in combustion, which can be recycled to generate more hydrogen gas. However, the second H₂O molecule necessary for the oxidation of the two Na atoms has to be added. Therefore, Na has a gravimetric hydrogen density of 3 mass%. The same

process carried out with Li leads to a gravimetric hydrogen density of 6.3 mass%. The major challenge of this storage method is reversibility and control of the thermal reduction process in order to produce the metal in a solar furnace. The process has been successfully demonstrated with Zn⁴⁹.

The six different hydrogen storage methods (in Table 2-1) have been described here. Alongside well-established, high-pressure cylinders for laboratory applications and liquid hydrogen storage methods for air and space applications, metal hydrides, complex hydrides and some physical adsorbents offer a safe and efficient way to store hydrogen. Further research and technical development will lead to higher volumetric and gravimetric hydrogen density. The best materials known today show a volumetric storage density of 150 kg m⁻³, which can still be improved by approximately 50 % according to theoretical estimations.

2.2 Parameters for Hydrogen Storage in Hydrides

In 2009, the on-board hydrogen storage system targets were revised to reflect knowledge gained in hydrogen fueled vehicles since original release of the targets by the US Department of Energy (DOE). In order to achieve system-level capacities of 1.8 kWh/kg system (5.5 wt.% hydrogen) and 1.3 kWh/L (0.040 kg hydrogen /L) and the ultimate targets of 2.5 kWh/kg system (7.5 wt.% hydrogen) and 2.3 kWh/L (0.070 kg hydrogen /L) in 2015, the gravimetric and volumetric capacities of the material respectively must clearly be higher than the system-level targets. In addition to high storage capacity, researcher must optimize other parameters like sorption temperature, hydrogen absorption/desorption kinetics, activation procedure, cycle-life, and so on in the materials development.

2.2.1 Mechanism of hydrogen absorption

The absorption of hydrogen to form a metal hydride consists of several steps which may be described using the long-range attractive/short-range repulsive Lennard-Jones potential. As

the molecular hydrogen approaches the metallic surface, it encounters successive minima in the potential curve corresponding to molecular adsorption, atomic adsorption, and bulk absorption, as shown in Figure 2-3. Molecular hydrogen is first physisorbed on the surface of the metal. Physisorption is a process whereby a molecule adheres to a surface without the formation of a chemical bond, usually by van der Waals forces or electrostatic attraction with energy levels approximating those of condensation. Physisorption is a reversible process strongly dependent on both pressure and temperature.

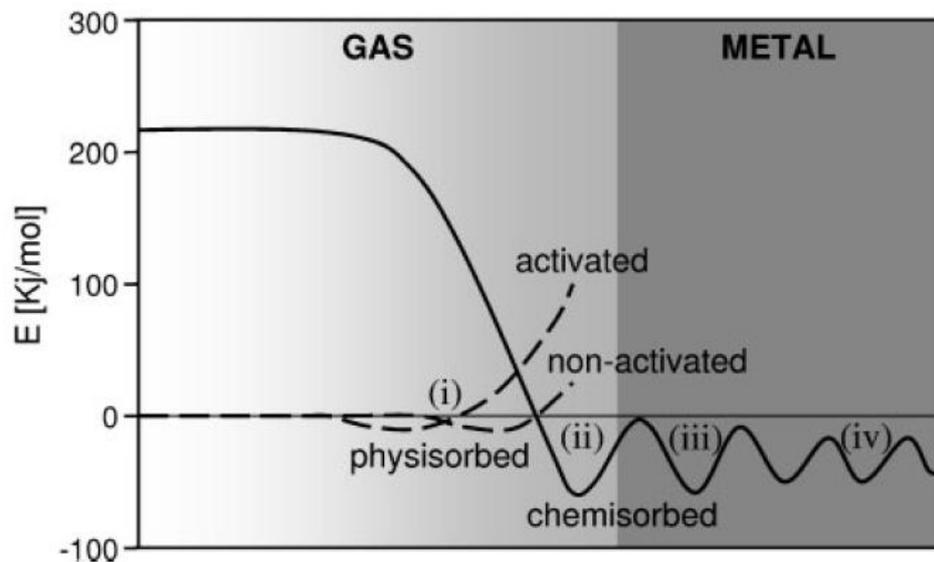


Figure 2-3 Potential energy curve for the Lennard-Jones potential for hydrogen binding to a metal indicating: (1) physisorption for both activated and non-activated processes; (2) dissociation and surface chemisorptions; (3) surface penetration and chemisorptions on subsurface sites; and (4) diffusion⁴⁶.

The weak bonding usually prevents significant absorption at room temperature, which is why hydrogen storage on high surface area materials like carbon nanotubes or metal organic frameworks is achieved only at cryogenic temperatures⁵⁰. Other models like the BET model are capable of describing multilayer adsorption⁵¹. The multiple layers are the result of the gas interacting with its condensate so that the binding energy approaches the condensation energy.

If the pressure and temperature are high enough, the adsorbed hydrogen is then dissociated at the surface and becomes chemisorbed. Chemisorptions are the chemical combination of hydrogen with the metal to form a new compound, which characteristically has a binding energy well above 50 kJ/mol. Both the host and adsorbate are chemically changed in the process and the initial compound is usually trapped irreversibly on the surface or within the bulk of the solid media. This involves an electron transfer between the metal and the hydrogen and may require thermal or catalytic activation due to the dissociation energy barrier.

After surface chemisorptions, the hydrogen atoms move to subsurface sites and rapidly diffuse through the material. This solution of H in the metal is referred to as the α phase. As the hydrogen concentration in the α phase increases, H-H interactions become important and a more stable phase nucleates (β phase), shown in Figure 2-4. Figure 2-4 (a) shows a few hydrogen atoms have dissociated and diffused into the low density α phase. Then as the hydrogen concentration increases in the α phase, Figure 2-4 (b), the interaction between hydrogen atoms through lattice deformations make nucleation of the high hydrogen density β phase energetically favorable. The β phase is characterized by a higher hydrogen density and often a different crystalline structure.⁵² This phase transition is usually characterized by a crystalline structure change, a volume expansion, and a nucleation energy barrier associated with volume expansion and interface energy between the phases.

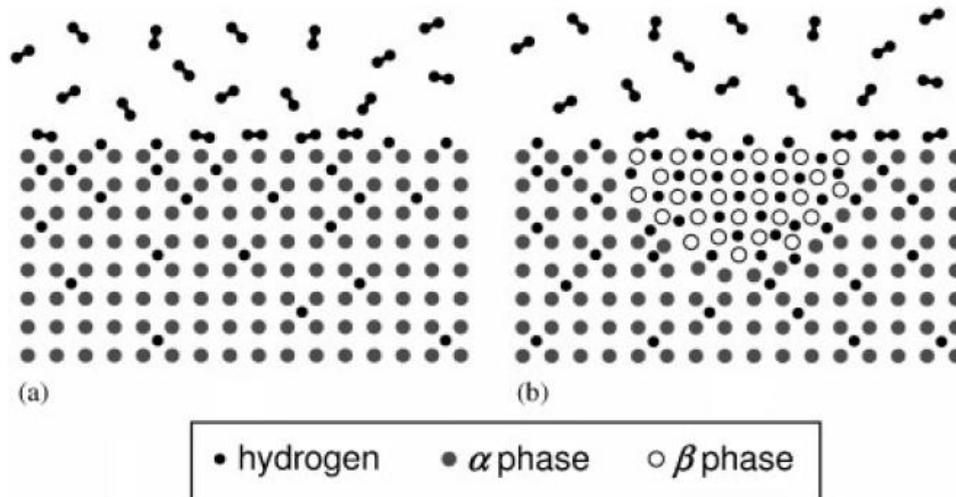


Figure 2-4 Simple representation of phase transition between the α phase and the β phase⁵².

2.2.2 Capacity

There are two capacities commonly used in discussion of hydrogen storage. One is the volumetric capacities and the other is the gravimetric capacity. The volumetric capacity is defined as the amount of hydrogen adsorbed either in mass or in volume divided by the total volume occupied by the adsorbents and hydrogen, i.e. kg/m^3 , H atm/m^3 or H atm/f.u that indicates the number of adsorbed H atoms per unit metal or alloy formula. The volumetric capacity is the more important in situations where space is limited, such as in a family car. Similarly, the gravimetric capacities are often defined as the weight percentage of the adsorbed gas to the total weight of the system, including the weight of the gas. Usually the gravimetric capacity is described as kg/m^3 or wt. %.

The theoretical hydrogen storage capacity for the hydrides with known hydride formula can be calculated from the atomic weight percentage of hydrogen in one unit formula. In practice, hydrogen storage capacity can be give determined from the thermogravimetry (TG), which will be given more details in Section 3.3.

2.2.3 Hydrogen sorption kinetics and sorption temperature

Kinetic properties of a hydrogen storage material determine its application in the industrial world. Fast hydrogenation kinetics directly leads to the short refilling time for a hydrogen-powered car and fast dehydrogenation kinetics is essential for adequate performance⁵². Song⁵³ reviewed the kinetic studies of the hydriding and the dehydriding reactions of Mg. Numerous works are in disagreement regarding the rate-controlling steps for the hydriding or dehydriding of magnesium. However, there is no contradiction surrounding the points that the hydriding and dehydriding reactions of Mg are nucleation-controlled under certain conditions and progress by the mechanism of nucleation and growth, and that the hydriding rates of Mg are controlled by the diffusion of hydrogen through a growing Mg hydride layer. The hydriding and dehydriding kinetics of magnesium can be improved, therefore, by a treatment such as mechanical alloying^{13, 54-56} which can facilitate nucleation by creating many defects on the surface and/or in the interior of Mg, or by the additive acting as active sites for nucleation, and shorten diffusion distances by reducing the effective particle size of Mg. Bobet et al.⁵⁷ reported that mechanical alloying in H₂ (reactive mechanical grinding) for a short amount of time, 2h, is an effective way to improve the hydrogen storage kinetics of both magnesium and Mg + 10% Co, Ni or Fe mixtures significantly. Huot⁵⁸ increased the hydrogenation rate of magnesium by milling under hydrogen with the addition of graphite. Imamura⁵⁹ improved the hydrogen sorption kinetics of magnesium by the mechanical milling of graphite and magnesium with organic additives. Oelerich⁶⁰, Dehouche⁶¹, and Barkhordarian¹⁹ increased the hydriding and dehydriding rates of magnesium via the planetary ball milling of magnesium hydride and a metal, a compound, or an oxide. Yavari⁶² improved the hydrogen sorption kinetics of MgH₂ powders through the use of Fe nanoparticles generated by a reactive FeF₃ addition.

An example has been given in Figure 2-5. Even if the hydriding reaction is thermodynamically favorable due to a negative Gibbs free energy ΔG , the reaction cannot take place at low pressure and temperature because of the energy barrier for adsorption E_{bar}^{ads} that must be overcome. The energy barrier E_{bar}^{des} is even larger for the desorption process, which explains the high release temperature for metal hydrides. The heat released is directly related to the difference in internal energy ΔE between the initial and the hydride states. Destabilizing the hydrides will speed up the desorption kinetics and reduce the heat released, while the use of a catalyst can help both the hydrogenation and dehydrogenation kinetics⁵².

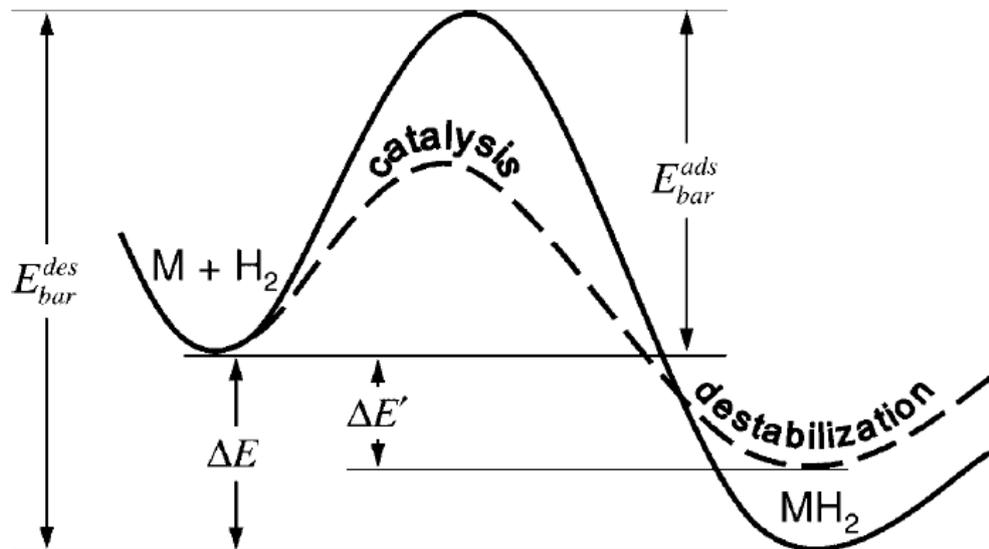


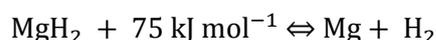
Figure 2-5 An example of an energy barrier for hydrogenation and dehydrogenation⁵².

Another important fact which has an effect on the hydrogenation/dehydrogenation kinetics is the metal surface. All hydrides except palladium have great affinity for oxygen than for hydrogen and they are normally coated with an oxidizing film that forbids the attack by the gaseous reactants at some points. Therefore, the oxide surface has to be removed or disrupted before the hydride formation. Heat treatment or cycling are mainly used on most metals to remove the oxide film⁶³.

There are several methods for calculating kinetic parameters which depend not only on the experimental conditions but also on the mathematical treatment of the data. In this work, TG and differential thermogravimetry (DTG) measurements are used for the kinetics of hydrogen sorption of the materials, using Friedman techniques which allow us to calculate every point in a TG curve and a DTG curve, and the variations with temperature are discussed⁶⁴. The dehydrogenation kinetics from TG-DTG has been described in Section 3.3. Kinetic curves also measure the content of adsorbed/desorbed hydrogen versus time at one or various constant pressures and temperatures. This curve also illustrates temperature dependence of both the hydrogenation and dehydrogenation reactions.

2.2.4 Cycle-life and stability

An ideal hydrogen storage system should have a good cyclability, meaning that the system should maintain its physical and chemical properties through multiple absorption/desorption cycles. In the case of MgH₂-Mg system, the desired reversible reaction is:



However, some loss in the hydrogen storage capacity of MgH₂/Mg could happen during cycling due to low kinetics or impurities. Dehouche⁶⁵ reported the presence of magnesium oxide is responsible for the degradation of the hydriding and dehydriding properties of the MgH₂/Mg after 1000 cycles. The MgO forms a barrier at the hydrogen diffusion stage, preventing the hydrogen from penetrating into the nanoparticle interior. Fan et al.⁶⁶ investigated the MgH₂+10 wt.% TiC composite has good cycle stability, its hydrogen capacity only decreases 3.3% of hydrogen of the 1st run after 10 de/hydrogenation cycles.

2.3 Mg for Hydrogen Storage

Mg has shown promise for on-board hydrogen storage especially for vehicular application due its high hydrogen content 7.6 wt % and volumetric density about twice to that of liquid

hydrogen. Metallic magnesium is fairly accessible and a low cost material. Besides, the Mg based hydrides possess good quality functional properties, such as heat resistance, vibration adsorbing, reversibility and recyclability². Magnesium hydride has the highest energy density (9 MJ / kg Mg) of all reversible hydrides applicable for hydrogen storage. Magnesium hydride differs from other metal hydrides according to the type of M-H bonds and crystal structure and properties and is similar to ionic hydrides of alkali and alkaline earth metals. MgH₂ is a stoichiometric compound with H/Mg atomic ration of 0.99 ± 0.01 ⁶⁷. The equilibrium modification of MgH₂ under normal conditions, α -MgH₂ has a tetragonal crystal structure of the rutile type⁶⁸⁻⁷⁰. Under high pressure α -MgH₂ undergoes polymorphic transformations to form two modifications: γ – MgH₂ and β – MgH₂, with an orthorhombic structure and a hexagonal structure, respectively⁷¹⁻⁷³.

2.3.1 Properties of Mg/MgH₂

Mg is the most practical option for hydrogen storage. Mg as a storage material meets two important storage criteria:

- 1) It can store large quantities of hydrogen, more than any other metal hydrides system.
- 2) It is relatively inexpensive. So it offers potential for storage of hydrogen for automobile or on-board applications.^{2, 74-76}

2.3.2 Limitation of MgH₂ for practical application

Although Mg fulfills many commandments required for practical applications but still it cannot be used onboard. The main reason is that the reaction for hydrogenation/dehydrogenation is very slow and occurs only at very high temperatures. In practice, both absorption and desorption of hydrogen require a temperature of at least 350–400 °C and even then only occur over a time scale of hours⁷⁷. The pressure of hydrogen gas in equilibrium with magnesium hydride is low (1bar at about 280 °C) and therefore

thermodynamically the hydride should form readily at room temperature. However, this never occurs in practice because of kinetic limitations. There are several factors that significantly reduce the rate of hydrogenation. One of them is the oxidation of magnesium surface and/or formation of magnesium hydroxide. Magnesium oxide forms easily on Mg surface exposed to air. Usually oxide layers on the metal surface are not transparent to hydrogen molecules so that MgO layer prevents hydrogen molecules from penetrating into the material⁷⁸. Hence to initiate hydrogen absorption, the oxide layer should be broken down by activation process. The activation may consist in the cyclic heating and cooling in a vacuum or hydrogen atmosphere. But even after such an activation process, magnesium could form hydride completely after several hours at 400 °C⁷⁸.

Another reason for the slow hydrogenation rate of magnesium (even after activation) is low dissociation rate of hydrogen molecules on the metal surface. A clean surface of pure magnesium needs a very high energy for dissociation⁷⁷. In addition the diffusion of dissociated hydrogen atoms within metal hydride is very difficult. The growth rate of MgH₂ phase depends on the hydrogen pressure since, as the pressure increases, the thermodynamic driving force for the reaction increases. However, if the initial hydrogenation process is sufficiently rapid, a surface magnesium hydride layer that blocks the hydrogen penetration is formed⁷⁹, the surface diffusion becomes an important and significant factor for hydrogenation. For pressures higher than about 30 bars, the absorption rate is again reduced⁸⁰. This effect occurs when initial hydrogenation is relatively fast and leads to the formation of a “surface shell” of magnesium hydride which blocks further hydrogen uptake. At this point, hydrogenation is limited by the growth of the hydride. Although in general, growth has been found to be faster than nucleation⁸⁰, growth limitations are usually responsible for reducing the final hydrogen capacity. Studies on hydrogenation kinetics showed that growth is controlled by diffusion of hydrogen atoms, which is very slow

throughout magnesium hydride⁸¹. Further experiments indicated that the growth is controlled by a slow migration of the interface between the hydride and magnesium⁸², in particular by hydrogen diffusion along the hydride–metal interface and not throughout the hydride layer⁸⁰. In any case, hydrogenation of magnesium is normally almost impossible to complete, even at very high temperatures and pressures. It has also been observed that hydrogen uptake declines when the hydride nuclei start to coalesce on the magnesium surface to form a compact hydride layer⁸³ and that the hydrogenation reaction diminishes completely when the hydride layer exceeds 30–50 μm . For kinetic reasons, the remaining magnesium cannot be further hydrogenated⁸⁰.

2.3.3 Approaches to improve sorption properties of Magnesium Hydride

Mg based systems can be modified to improve the sorption characteristics. Many efforts have been made to reduce desorption temperatures and to fasten the re/dehydrogenation reactions. The main approaches are listed as following:

- 1) Improving surface and kinetic properties by ball milling
- 2) Alloying with other transition metal and their oxides
- 3) Catalysis
- 4) Formation of thin film and nano-structured materials

Hydrogen absorption/desorption parameters for various Mg based Materials are summarized in Table 2-6.

Table 2-6 Hydrogen sorption properties of Mg based hydrides

Material	Method of preparation	Temperature (°C)	Pressure Conditions(bar)	Kinetics (min)	Max. Hydrogen (wt %)	Ref.
Mg- 20 wt%Ni–Y	Reactive Ball milling	T _{abs} :200 T _{des} :300	P _{abs} :30 P _{des} :1	t _{abs} :5 t _{des} :15	5.59	84
Mg-Ti _{0.28} Cr _{0.50} V _{0.22}	Reactive Ball milling	T _{abs} :275	P _{abs} :30	t _{abs} :10	4.0	85
Sn / MgH ₂	Ball milling	T _{des} :300			3.4	86
Mg ₂ NiH ₄	Hydriding combustion synthesis	T _{abs} :330C	P _{abs} :18	t _{abs} :<8 (for 90%)	3.4	87
MgH ₂ -17%Nb ₂ O ₅	Ball milling	T _{abs} :274 T _{des} :274	P _{abs} :10 P _{des} :0.001	t _{abs} :2 t _{des} :3	7.0	88
Mg-10%Ni	Melting, Casting, Ball milling	T _{abs} :300 T _{des} :350			4.6	89, 90
Mg ₂ Ni _{0.9} Co _{0.1}	Hydrogen Plasma Metal reaction & ultrasonic homogenizer	T _{abs} :300 T _{des} :300	P _{abs} :40 P _{des} :0.001	t _{abs} :2 t _{des} :4	2.66	90
MgH ₂ / C (graphite, CNT, carbon black)	Reactive Ball milling	T _{abs} :300 T _{des} :300	P _{abs} :12	t _{abs} :20	6.2	91
Mg–Mm–Ni alloy	Equal channel angular pressing	T _{abs} :300 T _{des} :300	P _{abs} :15 P _{des} :1		5.4	92

Continued Table 2-6

MgH ₂ -4 mol% TiF ₃	Reactive ball milling	T _{abs} :300 T _{des} :300	P _{abs} :20 P _{des} :0.1	t _{abs} :<1 t _{des} :10	5.0	93
Mg-10 wt%Ni-5 wt%Fe-5 wt%Ti	Reactive ball milling	T _{abs} :300 T _{des} :300	P _{abs} :12 P _{des} :1	t _{abs} :10 t _{des} :60	6.72	94
Mg-10 wt% Cr ₂ O ₃	Ball milling	T _{abs} :300 T _{des} :300	P _{abs} :10 P _{des} :1	t _{abs} :3 t _{des} :5	6.0	95
Mg-20 wt% CNM	Ball milling	T _{abs} :180	P _{abs} :20	t _{abs} :80	5.0	96
Mg-2 mol% NbF ₅	Reactive ball milling	T _{abs} :300 T _{des} :300	P _{abs} :20 P _{des} :<10 Pa	t _{abs} :60 t _{des} :60	6.0	97
Mg-20 wt%Ni-1 wt%TiO ₂	Reactive ball milling	T _{abs} :180 T _{des} :370	P _{abs} :40 P _{des} :1	t _{abs} :3 t _{des} :5	5.32	98
MgH ₂ -1mol%La ₂ O ₃	Ball milling	T _{abs} :303 T _{des} :303			6.0	99
MgH ₂ -5 wt%LaNi ₅	Reactive ball milling	T _{abs} :285 T _{des} :285	P _{abs} :20	t _{abs} :2 t _{des} :100	6.0	100
MgH ₂ -35 wt%LaNi ₅	Reactive ball milling	T _{abs} :285 T _{des} :285	P _{abs} :20	t _{abs} :10 t _{des} :15	4.0	100
Mg-23.5 wt%Ni-10 wt%La	Gravity casting	T _{abs} :300 T _{des} :350	P _{abs} :11	t _{abs} :30 t _{des} :15	4.96	101
MgH ₂ + 10 wt%Zr-Ni alloy	Ball milling	T _{abs} :304, 324	P _{abs} :20 P _{des} :0.25	t _{abs} :100s t _{des} :300s	5.4	102
Mg + 30 wt% LaNi ₅	Hydriding combustion synthesis followed by mechanical milling	T _{des} :197	P _{abs} :0.003	t _{abs} :50s	3.8	103

Continued Table 2-6

MgH ₂ + 1 mol% Cr ₂ O ₃ + 0.2 mol% Nb ₂ O ₅	Mechanical milling	T _{abs} :300		t _{abs} :5 t _{des} :20	6.0	104
Mg + WO ₃ Mg + H _{0.23} WO ₃	Ball milling	T _{abs} :300 T _{des} :330	P _{abs} :0.01 P _{des} :0.0003			105
Mg _{1.9} Nd _{0.1} Ni	Vacuum induction melting	T _{abs} :300 T _{des} :300	P _{abs} :0.00135 P _{des} :0.0011		3.35	106
Mg + 5 wt%LaMg ₂ Ni	Ball milling	T _{abs} :180 T _{des} :300	P _{abs} :0.003 P _{des} :0.0001	t _{abs} :100 t _{des} :30	4.4	99
MgH ₂ + Cr ₂ O ₃	Ball Milling	T _{abs} :300 T _{des} :300	P _{abs} :0.003 P _{des} :0.0001	t _{abs} :20 t _{des} :30	6.3	95
Mg+ TiF ₃	Ball milling	T _{abs} :150 T _{des} :320	P _{abs} :10 P _{des} :1	t _{abs} :100 t _{des} :0.5	3.8	107
Mg + TiC	Ball milling	T _{abs} :300 T _{des} :199	P _{abs} :10	t _{abs} :20 t _{des} :30	6.2	16
MgH ₂ +5wt%SiC	Ball milling	T _{abs} :350 T _{des} :350	P _{abs} :30 P _{des} :0.1	t _{abs} :0.5 t _{des} :6.7	6.3	15
MgH ₂ + 0.1 TiH ₂	Ball milling	T _{abs} :300 T _{des} :240	P _{abs} :20 P _{des} :0.1	t _{abs} :240 t _{des} :20	4	108

2.4 Improvement of Kinetics by Milling

It has been found that the milling of MgH_2 instead of pure Mg produces a nanocrystalline powder with high surface area beneficial for the hydrogen sorption properties³⁰. The surface of pure Mg is important for hydrogen kinetics. Diffusion is not the limiting step initially, but after a partial formation of MgH_2 surface it becomes important as the diffusion coefficient in MgH_2 is much smaller than that in Mg^{81, 109, 110}. It has been reported that after the formation of certain amount of MgH_2 the hydrogenation rate decreases with increase of hydride layer thickness and finally become zero after a critical thickness¹¹¹.

There are different types of high-energy ball mills which are used for the engineering of MgH_2 in its nanocrystalline form in combination with different additives. These mills differ in their milling energies, milling modes and uniformity of milling which have strong influence on end milling product, shown in Figure 2-6. Marek⁹⁵ have found that the high-energy (ball) milling greatly improves the hydrogen sorption kinetics of MgH_2 . There is no significant difference in the hydriding/dehydriding properties between MgH_2 powders milled in different commonly used mills.

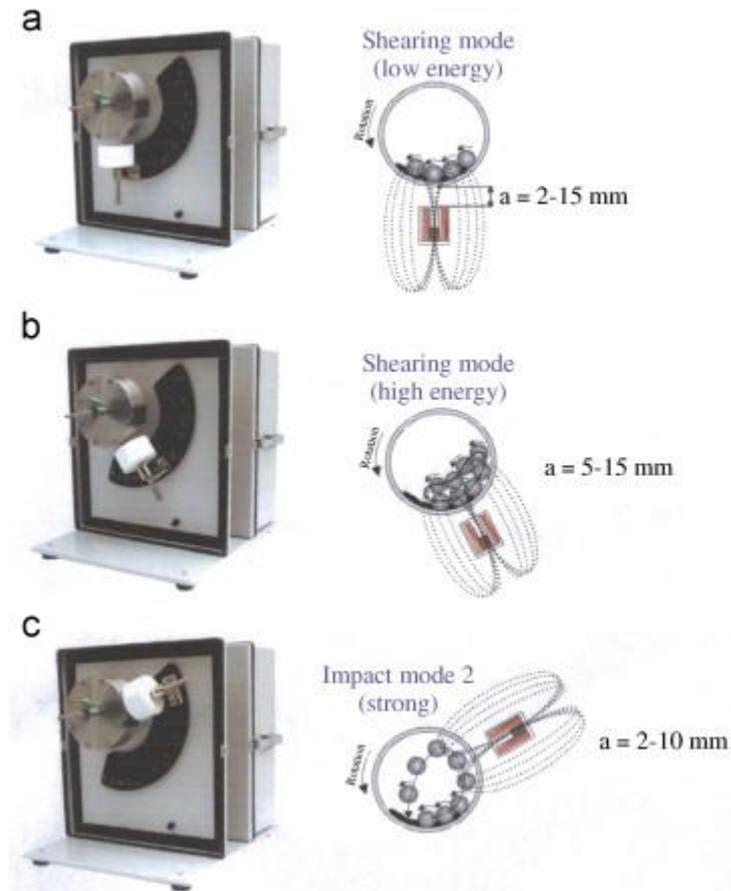


Figure 2-6 Different controlled milling modes available in the Uni-ball: (a) low-energy shearing, (b) high-energy shearing and (c) impact.

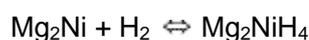
The mechanical/ball milling has shown a path to overcome this problem which relies on mechanical impact and friction to refine and alloy powder materials. Mechanical alloying can lead to several changes by the introduction of structural defects, phase change, and/or crystallinity¹¹². Depending on the ball milling conditions, the onset temperature of MgH_2 desorption can be decreased as large as 100 °C¹¹³. It has been found that with the decrease in crystal grain size, the desorption energy decreases drastically, reducing the desorption temperature up to 200 °C¹¹⁴. Another approach has been adopted in the form of milling under hydrogen atmosphere which provides an easy way to diffuse hydrogen into the material¹¹⁵. The results indicated that the pulverization and deformation processes occurring during high energy ball milling play a major role in the hydriding reaction. So it is

concluded that nano-structured materials can provide much better results for storing high a content of hydrogen with fast kinetics¹¹⁶. However, the preparation of such small particles by ball milling at large scale is a major challenge⁵. The method is based on infiltration of nanoporous carbon with molten magnesium. The size of thus prepared Mg crystallites has been reported from 2-5 nm to less than 2 nm. Another alternative for ball milling to modify the microstructure of the material is equal-channel angular pressing technique¹¹⁷. The microstructure refinement and increase in the density of the crystal lattice defects caused by equal channel angular pressing increase hydrogen desorption pressure, change the slope of the pressure plateau in pressure-composition isotherms, decrease the pressure hysteresis, and accelerate the hydrogen desorption kinetics¹¹⁸. Even though on the basis of present knowledge it is doubtful that such a procedure could be applied to a scale greater than laboratory.

2.5 Alloying with other Elements and Catalyst

2.5.1 Alloying with other elements

This method has also shown a way to reduce the desorption temperature and to remove other thermodynamic constraints. Mg₂Ni is the very first and most popular alloy prepared in this category¹¹⁹. Since then Mg₂Ni and its multiphase alloys have been studied intensively¹¹⁹⁻¹²¹. Mg₂Ni reacts with hydrogen as per the following reaction at 470 – 500 K¹¹⁹:



The standard enthalpy of this reaction was found to be 65 kJmol⁻¹H₂ which is less than that of pure MgH₂ (78 kJmol⁻¹H₂)¹²². Amorphous and nano-crystalline MgNiRe based alloys were also prepared for the improvement in hydrogen storage properties¹²³⁻¹²⁵. Recently Ren¹²⁵ has reported the improvement in the hydrogenation and electrochemical performance of Mg₂Ni type alloy by introducing a fraction of La in place of Mg. It is found that the

hydrogen absorption and desorption capacities and kinetics of the as-cast alloys clearly rise with increasing La content. For La content $x = 2$, the as-quenched alloy displays an optimal hydrogen desorption kinetics at 200 °C. Actually this alloying could be done on the basis of nature of heat of mixing⁷⁶. First route is to use the elements which exhibit negative heat of mixing with Mg and thus forms stable Mg compounds; Mg₂Ni is a strong example of this case, and Mg₂Si, Mg₂Ca are other good examples. Mg₂Si is important for having -79 kJmol^{-1} enthalpy of formation but having densely packed crystal structure interaction is not possible at moderate conditions and hence attempts were made to modify the crystal structure by doping it with other elements such as Li, C, Al, Ca, Co, Ni & Cu. The second category involved the systems having positive heat of mixing e.g. Mg₂FeH₆ materials which has highest volumetric capacity of hydrogen i.e. 150 Kg/m³,^{27, 126} but as Mg and Fe do not form any intermetallic compound, the hydride phase is more difficult to synthesize. However, hydrogen can act as binding component to form Mg₂FeH₆¹²⁷. Another example of this family is Mg–Ti alloy which was synthesized by using a high pressure anvil cell by the reaction of MgH₂ and TiH_{1.9} at 8GPa and 873 K^{27, 128}. Recently, an Mg–Al alloy has attracted worldwide attention as an alternative for hydrogen storage applications¹²⁹. Aluminum is considered to destabilize MgH₂ and forms Mg/Al alloys after dehydrogenation¹²⁹⁻¹³¹. Recently, Grivello had studied a series of this kind of alloy Mg_xAl_{100-x}^{130, 131}. It was found that for the two process $x = 70$ compound, the reversible hydrogenation is accomplished in three transformation steps. At first, only Mg reacts and forms MgH₂ then the γ -Mg₁₇Al₁₂ phase is decomposed into the Mg-poor β -Mg₂Al₃ phase. Finally, the Mg hydride phase is fully completed for the resulting Mg₂Al₃. These reactions are reversible.

2.5.2 Catalysis

The use of catalysts has been proved an important pathway to enhance surface kinetics. Firstly several catalysts were used such as transition metals^{20, 132-134}, metal oxides,

intermetallic compounds that adsorb hydrogen in milder conditions^{19, 135} and carbon materials¹³⁶⁻¹³⁸. It has been investigated the catalytic effects of five 3d elements Ti, V, Mn, Fe & Ni on the reaction kinetics of Mg hydride by the rapid desorption at low temperature for MgH₂-V followed by MgH₂-Ti, MgH₂-Fe, MgH₂-Ni & MgH₂-Mn^{18, 139}. Among the different oxides i.e. Nb₂O₅, TiO₂, V₂O₅, Cr₂O₃, Mn₂O₃, Fe₃O₄, CuO, SiC; Nb₂O₅ found to have better improved kinetics in comparison to the other oxides^{88, 135, 140}. Bhat et al.¹⁴¹ reported that high specific surface area nanocrystalline Nb₂O₅ induces fastest kinetics than does commonly used Nb₂O₅. A further improvement in the sorption properties of Nb₂O₅ doped MgH₂ was found when a small amount of Cr₂O₃ was added by Patah et al¹⁰⁴. They reported drastic reduction in the activation energy of Cr₂O₃ and Nb₂O₅ doped MgH₂ upto 136 kJmol⁻¹ in comparison to 197 kJmol⁻¹ and 206 kJmol⁻¹ for 1 mol% doped MgH₂ and pure MgH₂, respectively. Recently, the use of a new catalyst SiC has been reported to improve the hydrogenation properties of MgH₂ by Ranjbar et al^{15, 142}. They found improved hydrogen absorption/desorption kinetics by adding SiC and capacity of MgH₂ is also found to be increased by increasing the surface area and defect concentration. An additional improvement was achieved by adding Ni to the MgH₂/SiC composite because of catalytic effects of Ni. Although the explanation for the action of these catalyst is still not clear but it is suggested that these catalysts are responsible for modification of Mg surface on mechano-chemical treatment destruction of MgO layer, formation of active nucleation centers and partial reduction of the oxides to form metal cluster⁷⁴.

The second route to lower reaction enthalpy of MgH₂ is the formation of composite with other hydrogen sorbing alloys such as LaNi₅, FeTi, ZrCr₂ based IMCs^{100, 102, 143-145}. LaNi₅ has a significant effect on reducing the working temperature and to increase the reaction kinetics. It was found that Mg- LaNi₅ based composites can desorb significant amounts of hydrogen at 245 °C with reasonable reaction rate¹⁰⁰. Deposition processes could occur even at a low

temperature of 185 °C with an extremely slow desorption rate. Another processing material for making compounds with Mg is Zr based alloys. ZrNi is one of the promising materials to prepare composite with MgH₂. MgH₂+10 wt %¹⁰² composite could adsorb about 5 wt% in less than 3 mins and desorb the same amount in 7 mins at 300 °C. FeTi has also been reported as an exciting material to improve the kinetics of MgH₂. The maximum capacity was found to be 5.8 wt% at 300 °C and 5.12 wt% at 290 °C for Mg-5 wt% FeTi¹⁴⁴. The surface modification of MgH₂ with nanosized Ti_{0.4}Cr_{0.15}Mn_{0.15}V_{0.3} alloy could also enhance the kinetics of MgH₂. It desorbed 5.7 wt% hydrogen in 3 mins at 290 °C and adsorbed more than 90% of its capacity within 100 min even below 100 °C¹⁴⁵.

The third route is the combination of MgH₂ with other light hydrides^{126,146}. This category termed as reactive hydride composite as the composite compounds taking path in reaction with each other upon desorption e.g. of this category is MgH₂+ LiBH₄, MgH₂+NaBH₄, MgH₂+Ca(BH₄)₂ which form MgB₂ during desorption and can be reversibly hydrogenated.

The most recent effort is to make the composite of MgH₂ with a carbon based material^{91, 96, 136, 147-149}. Due to their high specific surface area and unique adsorbing properties, nano structured carbon has been shown to have a high catalytic activity¹⁵⁰. Imamura^{59, 136} in a series of publications confirmed that the magnesium/graphite (Mg/C) composite formed by mechanical milling with the organic additives not only show improved hydriding-dehydriding properties of magnesium but also additional hydrogen uptake other than that due to the magnesium component. Several reasons have been given by them for this prominent effect¹⁵¹: (1) Segregation of carbon at grain boundary thus resulting the increment in hydrogen diffusion along the boundaries. (2) The dispersive feature of carbon assists to obtain Mg particles that shorten the diffusion path.

2.6 Aims and Objectives

MgH₂ is an ideal hydrogen carrier due to its high theoretical storage capacity, 7.6 wt%, low cost, light weight and good reversibility. However, widespread industrial application are inhibited by its stable thermodynamic properties (high desorption temperature 300 °C-400 °C, and low plateau pressure of 10 Pa at ambient condition) and slow hydrogenation/dehydrogenation kinetics. Many experimental efforts have been focused on improving the reaction kinetics of MgH₂, increasing the plateau pressure and reducing the thermodynamic stability. However, none of them has made Mg-based hydrogen storage materials meet all the requirements for on-board applications successfully. Therefore, the main aims of this work are to improve the hydrogen sorption kinetics of MgH₂ by ball milling and by the catalysts.

In order to improve further the properties of Mg-based hydrogen storage materials, the investigation will focus on the following specific objectives:

- To identify the effects of different milling modes on the hydrogen sorption properties of MgH₂ in order to facilitate the dehydrogenation/hydrogenation kinetics and thermodynamic destabilization;
- To analyze role of particle size and grain size on hydrogen sorption and kinetics of MgH₂;
- To investigate the influence of transition metal carbides on surface modification and on dehydrogenation/hydrogenation properties of MgH₂;
- To identify the catalytic mechanism of the selected catalysts on hydrogen sorption properties of MgH₂.

CHAPTER 3 EXPERIMENTAL METHODS

3.1 Materials and Sample Preparation

3.1.1 Materials

MgH₂ powder was the main material for the study that was purchased from Th. Gold Schmidt AG, with a composition of 95 wt. % MgH₂ and a mean particle size of 50 μm. Other chemicals used for modification of MgH₂ are detailed in Table 3-1.

Table 3-1 Details of chemicals were used in the study at UEA.

Materials	Suppliers	Purity (wt. %)	Particle size
MgH ₂	Th. Gold Schmidt AG	95	50 μm
TiC	Sigma-Aldrich	95	< 200 nm
Mo ₂ C	Sigma-Aldrich	99.5	-325 mesh
Ni	Sigma-Aldrich	99.9	< 100 nm

3.1.2 Sample preparation

The powder mixtures were cryogenically milled for 8 h using liquid nitrogen to freeze the sealed milling vial in a SPEX SamplePrep 6750 Freezer/Mill, then were further mechanically milled for 16 h and 60 h at ambient temperature using a high energy ball mill, SPEX 8000D, under Argon atmosphere. Stainless steel vial and balls were used for milling. The initial ball-to-powder weight ratio was 10:1. The weight of (MgH₂ + TiC) mixture was 1.92 g MgH₂ and 0.08 g TiC; the weight of (MgH₂+Mo₂C) mixture was 1.74 g MgH₂ and 0.26 g Mo₂C. After milling, the resulting powder was removed from the vial inside the glove box under high purity argon. Some 60h ball-milled (MgH₂ + TiC)/ (MgH₂+Mo₂C) was mixed with nickel in the high energy ball mill, SPEX 8000D for 15 min, equal-weight-ration of Ni to MgH₂ is 5wt.%. The framework of the experiment is listed in Figure 3-1. All the powder handling was performed in a dry glove box under high purity argon.

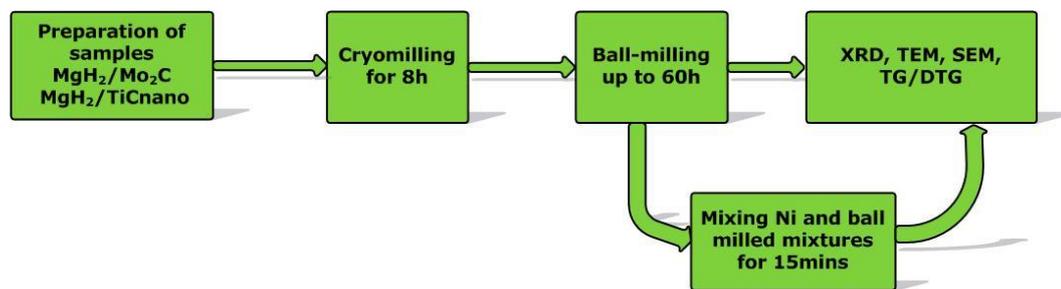


Figure 3-1 The experimental framework

3.1.3 Glove box

A glove box was used during sample preparation, as shown in Figure 3-2. The moisture and oxygen levels were maintained below 5 ppm by the function of recirculation of the glove box. A SPEX mill was encased within the glove box to prevent sample oxidation during milling. All steps of sample transfer and preparation for characterization were performed inside the glove box under argon.

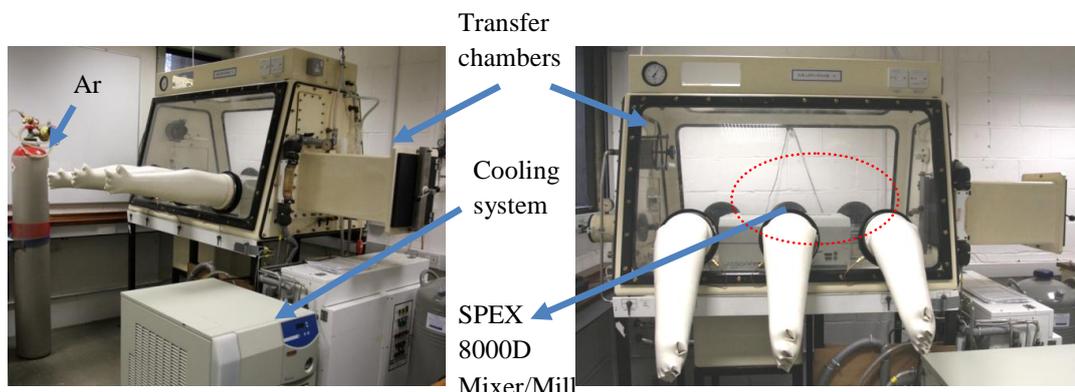


Figure 3-2 Synthesis in a glove box

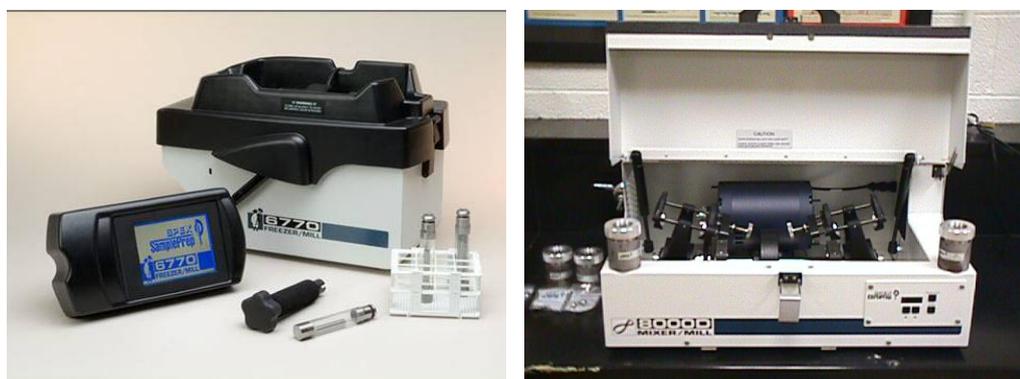


Figure 3-3 SPEX SamplePrep 6750 Freezer/Mill (left) and SPEX 8000D Mixer/Mill (right)

3.1.4 Cryogenic milling

SPEX SamplePrep Freezer/Mill 6750 (Figure 3-3 left) is a cryogenic laboratory mill which chills samples in liquid nitrogen and pulverizes them with a magnetically driven impactor. Each sample is placed in a separate grinding vial which is immersed in a liquid nitrogen bath inside the mill. This maintains the low temperature of the sample during grinding. Chilling materials in liquid nitrogen (at temperatures approaching $-190\text{ }^{\circ}\text{C}$) has two important consequences for sample preparation; it embrittles flexible samples so they can be pulverized by impact milling, and it preserves structural and compositional aspects usually damaged or lost during room temperature pulverizing. A Freezer/Mill incorporates an insulated tub into which liquid nitrogen is poured. The grinding mechanism is a magnetic coil assembly suspended in the nitrogen bath. Each sample was placed in a closed grinding vial along with a steel impactor. The magnetic coil shuttles the impactor rapidly back and forth pulverizing the sample against the end plugs of the vial (Figure 3-4). The cryomilling cycles used in this study were 10 min grinding with 1 min rest in-between each grind. The total grinding time was 8 h.

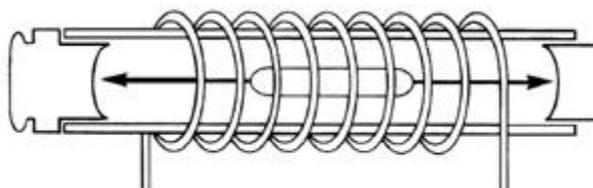


Figure 3-4 Vial and impactor in the SPEX SamplePrep Freezer/Mill 6750¹⁵²

3.1.5 Ball milling

Mechanical milling is an effective technique for the preparation of fine metallic and ceramic powders and can also be used to drive a wide range of chemical reactions. Functionally described high-energy ball mill or shaken mill, the SPEX SamplePrep 8000D (shown in Figure 3-3 right), shakes two clamps back and forth several thousand times a minute. In each

clamp, a vial containing sample and balls, is shaken in a complex motion which combines back-and-forth swings with short lateral movements, shown in Figure 3-5. With each swing the balls impact against one end of the vial, simultaneously milling the sample and blending it. Because of the amplitude and velocity of the clamp's swing, each ball develops fairly high grinding-forces.

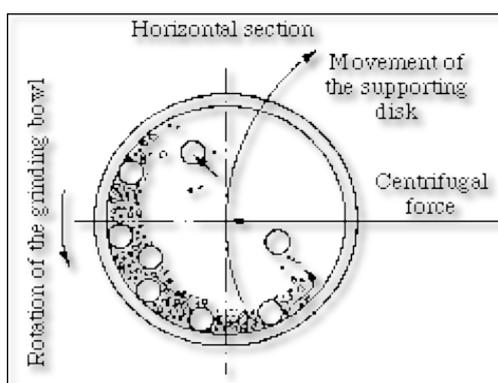


Figure 3-5 Diagram of ball milling¹⁵³.

3.2 Analysis of Sample Morphology and Structure

3.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of the materials. XRD used in this study was mainly for detecting the phase transformation of the materials during mechanical milling, dehydrogenation, and for the analysis of crystallite size. A XTra diffractometer (Thermo ARL, the United States) was used for powder X-ray diffraction. The source was Cu K_{α} ($\lambda=1.554056\text{\AA}$) radiation from a conventional water-cooled X-ray tube. The scan range was from $2\theta = 10^{\circ}$ to 80° and the scan rate was $1.2^{\circ}/\text{min}$ with a step size of 0.02° . In order to avoid exposure to air, the XRD samples were prepared in the glove box and a sample holder covered with an airtight plastic dome which had a negligible effect on diffraction patterns was used. The nanograin (crystallite) size of phases residing in the

milled powders was calculated from the broadening of their respective XRD peaks. Since the Bragg peak broadening in an XRD pattern is due to a combination of grain refinement (nanograin/crystallite) and lattice strains, it is customary to use computing techniques by means of which one can separate these two contributions. The crystallite size was obtained from Scherrer formula:

$$D = K\lambda/(B\cos\theta) \quad \text{Equation 3-1}$$

Where D is the averaged dimension of crystallites; K is the Scherrer constant, a somewhat arbitrary value that falls in the range 0.87-1.0 (it is usually assumed to be 1); λ is the wavelength of X-ray; and B is the integral breadth of a reflection (in radians 2θ) located at 2θ . B is often calculated relative to a reference solid (with crystallite size >500 nm) added to the sample: $B^2 = B_s^2 - B_r^2$. The program JADE 5.0 was used to evaluate the diffraction patterns.

3.2.2 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample. All the samples were coated with an ultrathin coating of gold by vacuum sputter coating. The coating of gold increases signal and surface resolution, especially with samples of low atomic number. The improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

Backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam, which are reflected, or back-scattered, out of the specimen interaction volume by

elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), they appear brighter in the image. BSE were used to detect contrast between areas with different chemical compositions in this study. A JEOL (Japan) thermionic SEM was used for the image analyses.

Transmission Electron Microscopy (TEM) was employed to further examine the particle size and particle distribution of samples. It exploits the very small wavelengths of high-energy electrons to probe solids at the atomic scale. A Jeol JEM 2100 TEM in the 200kV class analysis has been developed to achieve the highest image quality and analytical performance with a probe size under 0.2 nm. For TEM observation, a dilute suspension of sample powder was dropped onto a TEM grid, and dried.

The particle sizes of the powder mixtures were calculated from the SEM and TEM images as the equivalent circle diameter, $ECD = \frac{1}{2} \left(\frac{4A}{\pi} \right)^{1/2}$, where A represents the projected particle area, using the *Image Tool v.3.00 software*.

3.3 Analysis of Hydrogen Sorption Properties: Intelligent Gravimetric Analyzer -Mass Spectrometry (IGA-MS)

Thermogravimetry (TG) measurements for dehydrogenation and gas sorption were carried out using the IGA-003 supplied by Hidden Analytical Ltd, Figure 3-6. The IGA apparatus is an ultrahigh vacuum system which allows the adsorption-desorption isotherms and the corresponding kinetics of gas and vapor sorption on materials. The system consists of a fully computerized microbalance which constantly measures the mass of specimen as the test proceed, Results are displayed as a mass loss or gain as a function of temperature and time. By analysis of IGA results, the hydrogen sorption kinetics and storage capacities of the materials at different temperatures can be obtained. The method of differential

thermogravimetry (DTG) analysis, which was calculated from TG data, was used for thermal investigations of analytical precipitates. The peak of DTG curve means that the maximum rate of weight loss recorded by TG. There is good agreement of the onset temperature and the peak temperature of the materials between the DTG and MS curves.



Figure 3-6 Intelligent Gravimetric Analyzer (IGA-003) combined with Mass Spectrometer.

Desorption was performed from 20 to 500 °C under 1 bar Helium pressure at a heating rate of 10 °C/min and He flow rate of 150 ml/min. Hydrogen absorption was measured at hydrogen pressure of 8 bar with H₂ flow rate of 150 ml/min and isothermal temperature of 300 °C for 120 min with heating rate of 10 °C/min. Impurity gas absorption was measured using 80 % H₂ and 20 % CO₂ gas mixture at 8 bar and 300 °C for 120 min. The gas sorption procedure for all the sample (shown in Figure 3-7) was to start from the desorption because MgH₂, as the basic synthetic material, need to be dehydrogenated, and then was gas adsorption process. After a circle of sorption, some materials run the second circle for further analyses. The system need to be purged by He 3 times when every new sample is loaded into the IGA instrument. The IGA provided a highly sensitive measurement with precise temperature and pressure control for automated measurements of adsorption and

desorption isotherms. With a typical sample size of 20~50 mg, the error in the hydrogen absorption and desorption processes due to instrumental limitations is (0.02 wt % absolute).

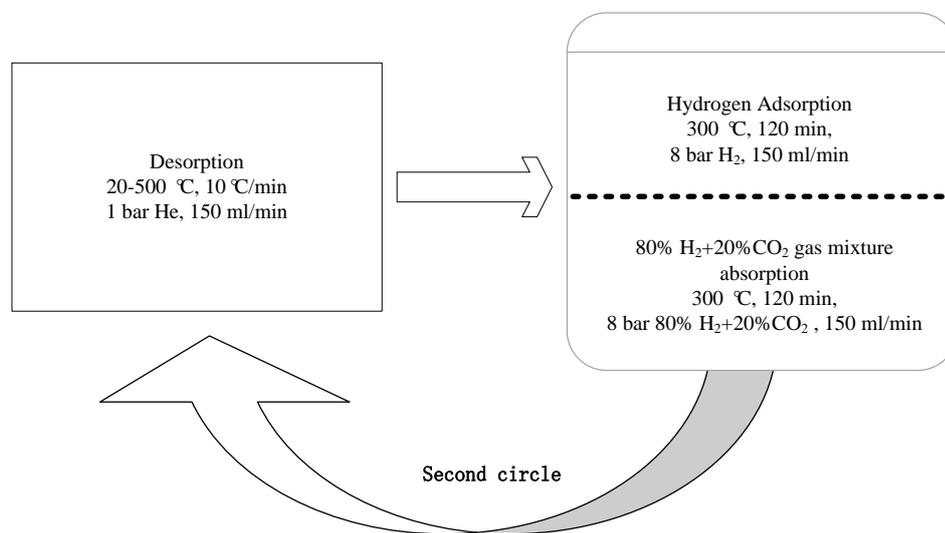


Figure 3-7 Gas sorption procedure in IGA-MS

MS (Mass Spectrometry) is an analytical technique for the determination of the elemental composition of a sample or molecule. The technique has both qualitative and quantitative uses. These include identifying unknown compounds, determining the isotopic composition of elements in a molecule, and determining the structure of a compound by observing its fragmentation. The technique employs chemical fragmentation of a sample into ions and measurements of two properties, charge and mass, of the resulting chemical compounds. The ratio of charge-to-mass of the chemicals or molecules is calculated by passing them through electric and magnetic fields in a mass spectrometry.

MS instruments consist of three modules: an ion source, which can convert gas phase sample molecules into ions (or in the case of electrospray ionization, move ions that exist in solution into the gas phase); a mass analyzer, which sorts the ions by their masses to charge ration

within a varying electromagnetic field; and a detector, which measures the quantity of each indicator providing data for calculating the abundances of each ion present.

The sample gas, liberated from the IGA reactor during thermal desorption, is introduced into the mass spectrometer via a pipe connecting the IGA to the MS (Figure 3-6). The MS analysis software includes two kinds of scan: BAR scan, is used to detect the unknown compounds during the scanning, these mass values need to be matched to the library database to determine the product. MID scan, is designed to detect the already supposed compounds by setting up the mass of possible molecules before running the experiment along with their mass spectrum and their mass evolution during the experiment as a function of time. In this study, MID method was used to investigate the gaseous species released from IGA reactor during sorption process.

There are several methods (proposed by Chan and Balke¹⁵⁴, Friedmam¹⁵⁵, Freeman and Carroll¹⁵⁶, and Chang¹⁵⁷) for calculating kinetic parameters which depend not only on the experimental conditions but also on the mathematical treatment of the data⁶⁴. In this study, The Chan and Balke¹⁵⁴ method is used to evaluate the **activation energy E** based on the DTG analysis. For many kinetic processes, a rate of reaction may be expressed as a product of a temperature-dependent function, $k(T)$, and a composition- or conversion-dependent term, $f(x)$:

$$r = \frac{dX}{dt} = k(T)f(x) \quad \text{Equation 3-2}$$

Where T is absolute temperature (in K); X is conversion and r is the rate of change of conversion or composition per unit time (t). The temperature-dependent term in Equation 3-2 is the reaction rate constant, which is assumed to obey the usual Arrhenius relationship:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad \text{Equation 3-3}$$

Where E is the activation energy of the kinetic process, A is the pre-exponential factor, and R is the universal gas constant (8.314 J/ mol/K). The conversion-dependent function, $f(x)$, is generally very complicated. A particular term is usually valid only for a limited range of experimental conditions. However, if it is assumed that a simple n th-order kinetic relationship holds for the conversion-dependent term such that

$$f(X) = (1 - X)^n \quad \text{Equation 3-4}$$

and that the quantity (1-X) can be replaced by W, the weight fraction remaining in a TG run, then:

$$r = -\frac{dW}{dt} = AW^n \exp\left(-\frac{E}{RT}\right) \quad \text{Equation 3-5}$$

Or

$$\ln r = \ln\left(-\frac{dW}{dt}\right) = \ln A + n \ln W - \frac{E}{RT} \quad \text{Equation 3-6}$$

Published methods of deriving kinetic parameters from TG data centre around Equation 3-6. They involve either a single thermogram or multiple thermograms with different constant heating rates. The constant heating rate method for determining the rate equation parameters is used in this study.

In the work, the order of reactions n , including dehydrogenation and hydrogenation, is 1 (a first-order reaction), then Equation 3-6 becomes:

$$\ln r = \ln \left(-\frac{dW}{dt} \right) = \ln A + \ln W - \frac{E}{RT} \quad \text{Equation 3-7}$$

$$\ln \left(-\frac{dW}{dt} \right) - \ln W = E \left(-\frac{1}{RT} \right) + \ln A$$

$$\ln \left(\frac{-\frac{dW}{dt}}{W} \right) = E \left(-\frac{1}{RT} \right) + \ln A \quad \text{Equation 3-8}$$

If we assume that the activation energy E is constant over a specific temperature range, then the slope over this range of a plot of $\ln \left(\frac{-\frac{dW}{dt}}{W} \right)$ versus $\left(-\frac{1}{RT} \right)$ should be equal to the activation energy E .

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Particle Size and Grain Size Effects on Sorption Properties of MgH₂

The development of nanograins occurs during hydride powder processing by mechanical (ball) milling, which is the principal process used to induce a nanostructure⁴⁶. Particle size reduction by mechanical milling improves MgH₂ dehydrogenation properties due to a shortened hydrogen diffusion path. It is reported that the desorption temperature of MgH₂ decreases rapidly with decreasing mean particle size to nanometric value ~338 nm, resulting in the reduction of the onset and peak desorption temperatures by as much as 70 and 40 °C, respectively¹⁵⁸. The objective of this section is to explore the effect of cryogenic milling and ball milling on particle & grain size, and understand in more depth the role of particle size and grain size on the reduction of desorption temperature.

4.1.1 Structural characterizations of MgH₂ powder produced by cryogenic milling and ball milling

The XRD pattern of the as-received MgH₂ shows the only major peaks of β-MgH₂. Cryogenic milling for 8 h and longer durations of ball-milling resulted in the appearance of XRD peaks arising from the γ- MgH₂ phase, as shown in Figure 4-1. The metastable γ- MgH₂ is a high pressure polymorphic form of β-MgH₂ and is commonly observed to appear after ball milling of MgH₂. The high pressure required to transform β-MgH₂ into γ- MgH₂ is provided during milling through the localized on-contact impacting action of the impactor and steel balls on the MgH₂ powder particles in the vial (Figure 3-3 and Figure 3-4). It is suggested that the formation of γ-MgH₂, as a metastable high-pressure phase, has a positive effect on hydrogen desorption as a result of a rearrangement in the cation and anion substructures, which destabilises β-MgH₂ reducing the desorption temperature^{71, 159}. The XRD peaks of MgH₂ broadened with milling time, indicating a decrease of crystallite size,

compared with the as-received powders. Table 4-1 shows the estimates of nanograin size of the β -MgH₂ phase according to Equation 3-1. The grain size of the as-received MgH₂ is of the order of 65 ± 5 nm, which correlates very well with the grain size reported by Kojima *et al*¹⁶⁰ and Varin *et al*¹⁶¹. After cryogenic milling for 8 h, a decrease of β -MgH₂ grain size of $\sim 25 \pm 3$ nm occurred. It has been suggested that the presence of liquid nitrogen during cryomilling has several advantages, such as decreased oxygen contamination²¹ and enhanced deformation during milling¹⁶². Cryogenic milling in particular offers an effective solution for achieving fine powders by enhancing the brittleness and reducing the tensile strength of the materials¹⁶². At the same time broadened and less intense XRD peaks of γ -MgH₂ did not allow us to make any meaningful estimate of γ -MgH₂ grain size. However, based on the extent of the γ -MgH₂ peak broadening, it can be concluded with reasonable certainty that the grain size of the γ -MgH₂ phase is not larger than that of β -MgH₂ counterpart. With a further 60 h ball milling, the grain size of MgH₂ is only reduced slightly to 20 ± 3 nm with the appearance of MgO due to the presence of oxygen in the glove box and the high reactivity of magnesium. The γ -MgH₂ peak is enhanced, which indicates more β -MgH₂ phase is transformed to γ -MgH₂ with increased milling time.

The morphology and microstructure of the as-received MgH₂, 8 h cryomilled MgH₂, and 60 h ball-milled MgH₂ after 8 h cryomilling were further investigated by scanning electron microscope (SEM), shown in Figure 4-2. The average particle sizes and the range of particle sizes were calculated according to the SEM images. The average particle size of MgH₂ is reduced to about $\sim 190 \pm 20$ nm after 8 h of cryomilling (Figure 4-2b). Some of the particles become smaller and others are aggregated to relatively bigger particles after further ball milling for 60 h milling, shown in Figure 4-2c. SEM images and the mean particle sizes figure illustrate the slight increase of the mean particle sizes of MgH₂ after a further 60 h. Compared with the cryomilled powder, due to the agglomeration of fine particles and

perhaps cold weld of some particles during 60 h milling, it is also noticed that the range of particle sizes is broadened because of the formation of smaller particles and the aggregation of fine particles, Figure 4-2 d. A smaller particle size or grain size enhances hydrogen absorption/desorption, because it shortens the diffusion path of hydrogen through the bulk area, and enlarges the grain boundaries and active surface area¹⁵.

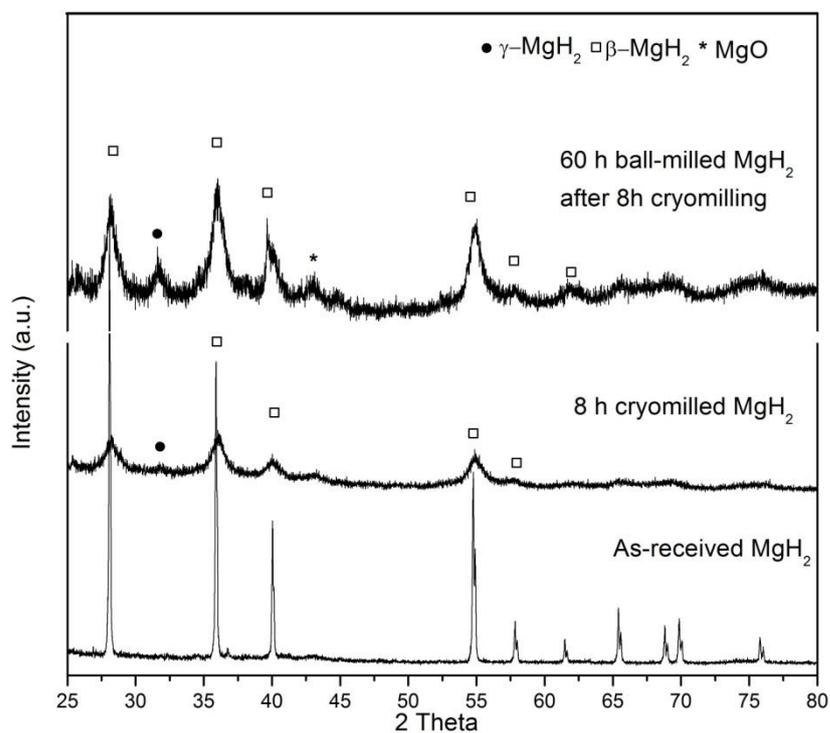


Figure 4-1 X-ray diffraction patterns of the as-received MgH₂, 8 h cryomilled MgH₂ and 60 h ball-milled MgH₂ after 8 h cryomilling.

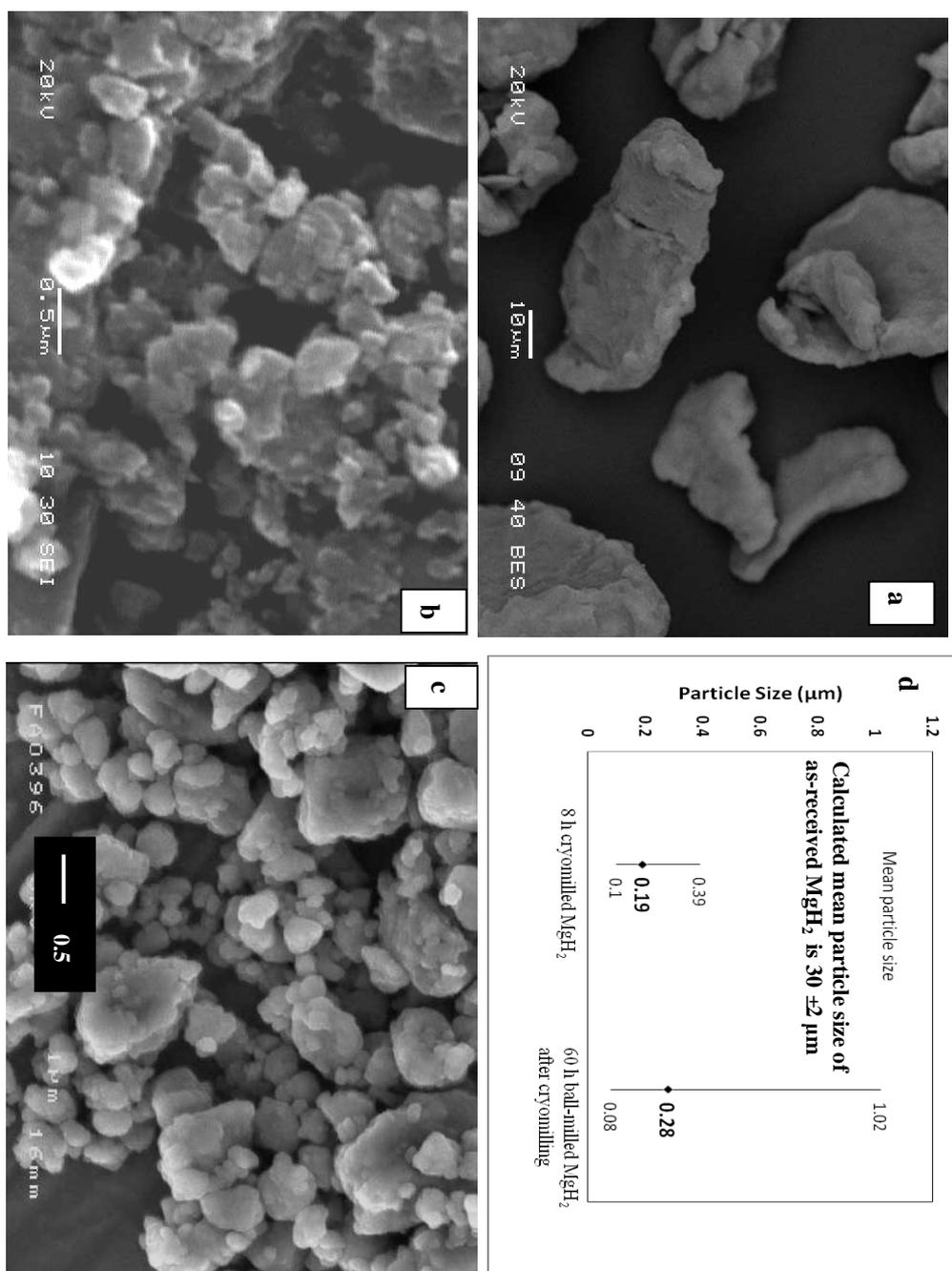


Figure 4-2 SEM images of (a) as-received MgH₂, (b) 8 h cryomilled MgH₂, (c) 60 h ball-milled MgH₂ after cryomilling; and (d) particle sizes of them.

4.1.2 Dehydrogenation of MgH_2 by cryogenic milling and ball milling

Figure 4-3 and Figure 4-4 show the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of hydrogen desorption of the cryomilled and cryomilled followed by ball-milled MgH_2 for different hours. The total relative weight loss of as-received MgH_2 and cryomilled MgH_2 for 8 h is about 7 ± 0.02 wt. % and 7.2 ± 0.02 wt. %, respectively. The extra 0.2 ± 0.02 wt. % is due to the more thorough desorption of nanosized MgH_2 particles. The weight loss of dehydrogenation of 60 h ball-milled MgH_2 is 6 ± 0.02 wt. % due to the formation of an insignificant amount of MgO during cryomilling detected from the XRD patterns, or small amount of hydrogen released during high energy milling at room temperature.

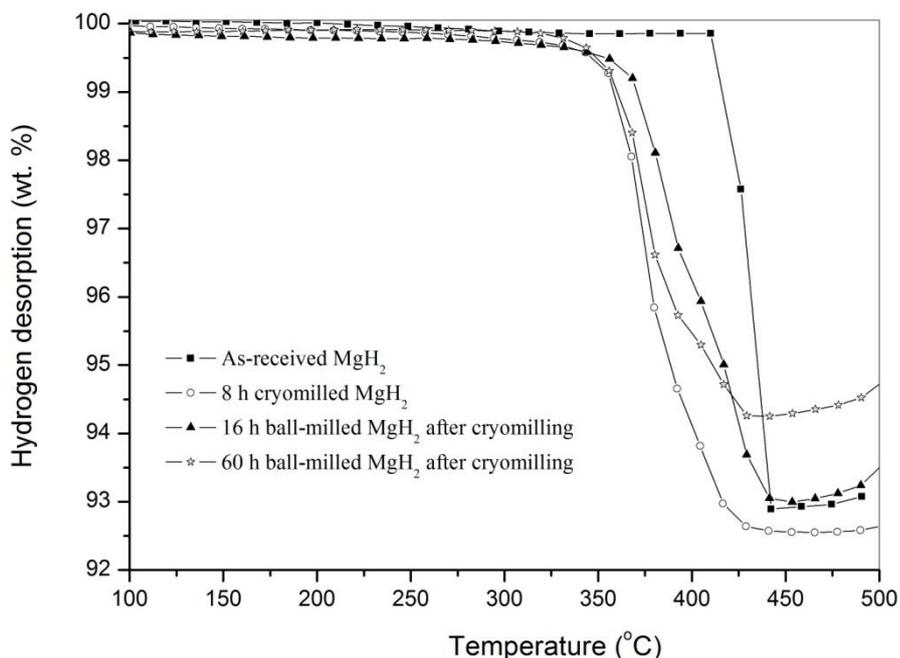


Figure 4-3 Thermogravimetry (TG) curves of cryomilled and ball-milled MgH_2 at the heating rate of 10 K/min and 1 bar helium pressure.

DTG curves of dehydrogenation for the milled mixtures are calculated to identify the onset and peak desorption temperatures, as previously explained in Chapter 3. A single

endothermic hydrogen desorption peak with the maximum at ~ 434 °C characterises hydrogen desorption from as-received MgH_2 (the calculated mean particle size is around $31 \mu\text{m}$, as shown in Table 4-1). The 8 h cryomilled MgH_2 starts to decompose at 320 °C and reaches the peak at temperature 362 °C (seen Table 4-1). It is also investigated a peak doublet/shoulder on the right hand side appears after cryomilling, which suggesting an overlap of low-temperature and high-temperature desorption peaks. Two research groups, Varin *et al* and Czujko *et al* reported that such a two-step hydrogen desorption may occur owing to the existence of two fractions of powder particles: small and large, which could desorb at lower and higher ranges of differential scanning calorimetry (DSC) temperatures, respectively¹⁶³. The existence of smaller and larger fractions of particle sizes is well supported by the SEM and particle sizes range from Figure 4-2, as discussed earlier in this chapter. However, an alternative explanation can be based on the findings of Schimmel *et al.*¹⁶⁴, who reported that in a ball-milled nanostructure of MgH_2 , there may exist a substoichiometric nanostructure, MgH_x phase (where $x < 2$). Such a hydrogen deficient phase is likely to exhibit much faster diffusion of hydrogen due to the large concentration of vacancies and could desorb at lower temperatures than the stoichiometric $\beta\text{-MgH}_2$, giving rise to a shoulder or even peak doublet (Figure 4-4). Furthermore, this could occur with dual-phase ($\beta\text{-MgH}_2$ and $\gamma\text{-MgH}_2$) powders. The low-temperature peak in a doublet could correspond to the desorption from the $\gamma\text{-MgH}_2$ hydride due to the lower desorption temperature for $\gamma\text{-MgH}_2$ and the high-temperature peak would correspond to the desorption from $\beta\text{-MgH}_2$, as reported by Gennari *et al*⁷³.

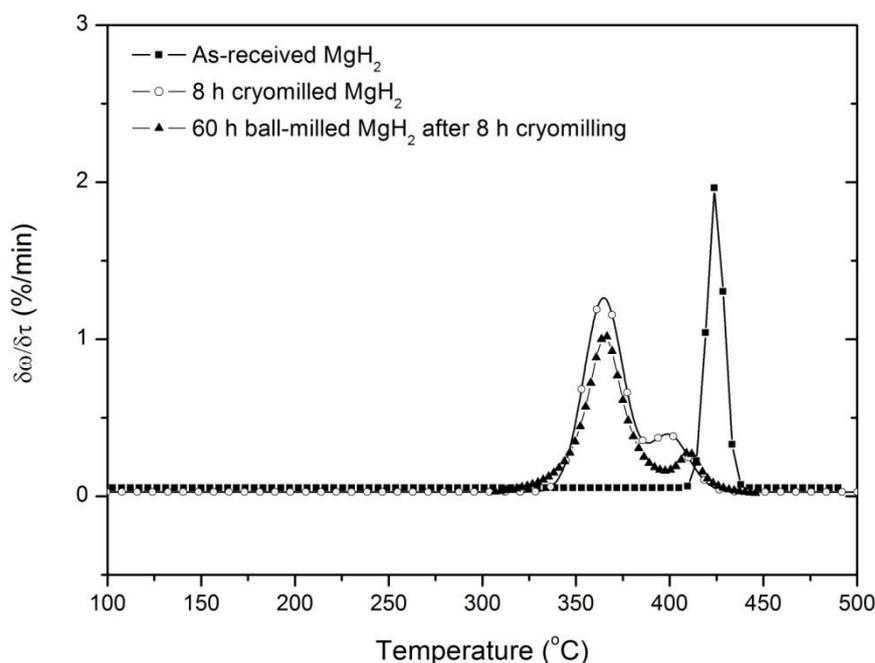


Figure 4-4 Derivative thermogravimetric (DTG) curves of cryomilled and further ball-milled MgH_2 , derived from Figure 4-3.

The starting desorption temperature of 8 h cryomilled MgH_2 is 320 °C much lower compared to that of the as-received MgH_2 ($T_{\text{onset}}=418$ °C, $T_{\text{peak}}=434$ °C), which is due to the effect of milling on particle and grain size reduction. After a further 60 h ball-milling of cryomilled MgH_2 , the onset temperature is only slightly reduced to 305 °C due to the smaller grain size of MgH_2 , although the formation of γ - MgH_2 is more prevailing in ball-milled MgH_2 than that in cryomilled sample. There is no difference in peak temperature between cryomilled MgH_2 and further 60 h ball-milled MgH_2 . This indicates that the factor of refined nano particle size and grain size within the particles are responsible for a substantial reduction of hydrogen desorption temperature of MgH_2 .

From the slope of the fitted line, the overall activation energy (E') of H_2 desorption of the samples is obtained, as shown in Figure 4-5. The activation energy of desorption is as high as 235 ± 10 kJ/mol for as-received MgH_2 . When as-received MgH_2 is cryogenically milled

for 8 hours, the value is decreased to 200 ± 9 kJ/mol. Further ball milling to 60 h after cryomilling doesn't reduce the activation energy further. The desorption kinetics can be improved greatly by cryogenic milling. The lower activation energy also facilitates the reduction of the desorption temperature.

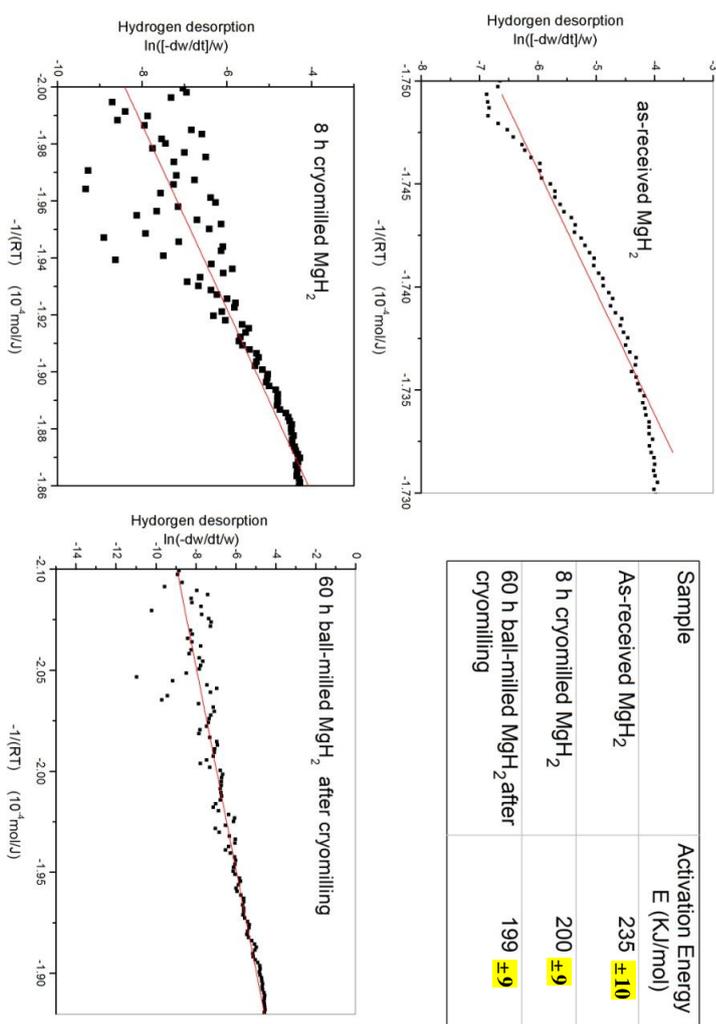


Figure 4-5 Kinetic plots and activation energy of the MgH₂ samples, based on Figure 4-4 and Equation 3-8

4.1.3 Hydrogenation of MgH₂ by cryogenic milling and subsequent ball milling

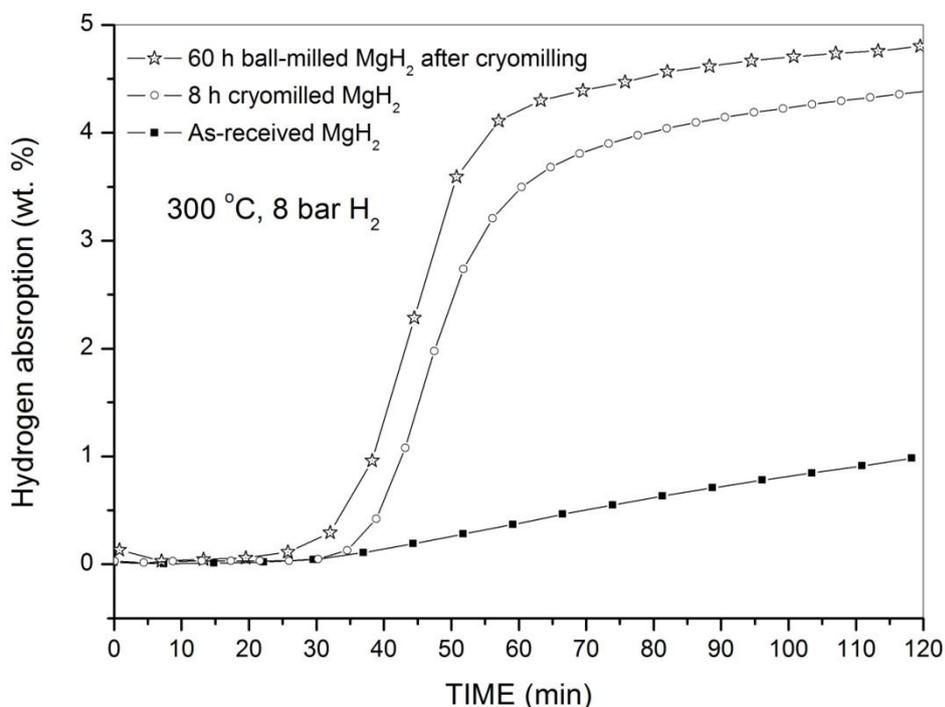


Figure 4-6 Hydrogen absorption curves of the cryomilled and ball-milled MgH₂, measured under 8 bar H₂ pressure at 300 °C.

The hydrogen absorption kinetics of the dehydrogenated MgH₂ samples were measured within 8 bars H₂ pressure at 300 °C, Figure 4-6. The hydrogen uptake is very slow for the as-received MgH₂ after dehydrogenation. However, about 4 wt. % of hydrogen is adsorbed in 60 min for dehydrogenated cryomilled-MgH₂. After cryomilling and ball-milling, H₂ absorption of the dehydrogenated sample is 5 ± 0.02 wt. % in 60 min, also the absorption rate is enhanced to 0.10 ± 0.0001 Δwt. %/min due to the ball milling process (Table 4-1). The relatively lower maximum weight percentage of H₂ uptake of dehydrogenated milled-MgH₂ is probably due to slow kinetics and slight oxidation of the samples during milling.

Table 4-1 Estimates of grain size (crystallite size), particle size of β -MgH₂ from XRD and SEM analysis, and TG-DTG desorption temperature (T_{Onset} is onset temperature of desorption, T_{Peak} is peak temperature of desorption.)

Sample	As-received MgH ₂	8 h cryomilled MgH ₂	60 h ball-milled MgH ₂ after cryomilling
Grain Size of β-MgH₂ (nm)	65 \pm 5	25 \pm 3	20 \pm 3
Mean particle size (μm)	30 \pm 2	0.19 \pm 0.02	0.28 \pm 0.02
T_{Onset} (°C)	418	320	305
T_{Peak} (°C)	434	362	360
E' (KJ/mol)*	235 \pm 10	200 \pm 9	199 \pm 9
Absorption Rate (wt. %/min)	0.008 \pm 0.00004	0.06 \pm 0.0001	0.10 \pm 0.0001

* Activation energy calculated from Equation 3-8.

4.1.4 Summary

Continuous refinement of the powder particle and nano-grain (crystallite) size of as-received MgH₂ was achieved by cryogenic milling and subsequent ball milling. The microstructure of MgH₂ powders after ball-milling showed obvious dual phases (β -MgH₂ + γ -MgH₂), where β -MgH₂ as the main peak of MgH₂ in XRD pattern has nanometric size grains (crystallites). Cryogenic milling is effective in reducing the grain sizes and particle sizes. The smallest mean powder particle size achieved in this work after 8 h cryogenic milling was 190 nm.

The onset and peak temperatures of H₂ desorption of the MgH₂ were substantially reduced by cryogenic milling for 8 h due to the smaller and more uniform nano particles achieved by cryomilling in the presence of liquid nitrogen.

The hydrogen absorption property of dehydrogenated MgH₂ was enhanced by cryogenic milling and ball-milling. The absorption of dehydrogenated MgH₂ after cryomilling and ball-milling increased greatly to 4 \pm 0.02 wt. % in 60 min compared to that of dehydrogenated as-received MgH₂ (< 0.5 wt. %) at 300 °C and 8 bar hydrogen pressure. Further ball-milling increased slightly the rate of hydrogen absorption of dehydrogenated MgH₂.

4.2 Effects of TiC Nanoparticles on Hydrogen Sorption of MgH₂

The hydrogen sorption properties of MgH₂ may be improved by transition metals, oxides and fluorides^{13, 16, 165}. Transition-metal compounds have attracted considerable interest as effective catalysts, due to the high affinity of transition-metal cation for hydrogen^{18, 107}. For example, the addition of small quantities of Nb₂O₅ significantly improves both the absorption and desorption kinetics of MgH₂^{19, 20}. Comparative studies based on various transition-metal oxides emphasise that the appropriate chemical interaction between catalyst and host hydride is essential for realising high catalytic activity, suggesting the functionality of the contact anion in tailoring the activity of the transition-metal cation²⁰. Titanium-based compounds have been successfully used to improve sorption kinetics in several hydrogen storage systems, exhibiting a high affinity of Ti cation for hydrogen even at moderate temperatures. For example, titanium halides are exceptionally effective in reducing the kinetic barrier to dehydrogenation of alkaline alanates^{21, 22, 107}. It has also been found that the temperature for hydrogen release from MgH₂ can be greatly reduced by doping it with Ti-containing agents (e.g. TiF₃ and TiC)^{16, 23}. The interactions between the hydrides and the Ti-containing agents weaken the Mg–H bonds and thus facilitate the recombination of hydrogen atoms to the hydrogen molecules. The aim of this part of the project is to gain further understanding of the influences of TiC with cryomilling and ball-milling on hydrogen sorption properties of MgH₂.

4.2.1 Structural characterizations of milled mixtures of MgH₂ and TiC

Figure 4-7 presents the XRD patterns of the (MgH₂ + 2 mol. % TiC) mixtures milled for different hours. After cryomilling and ball milling of MgH₂ with TiC nanoparticles, the main phases that appear are only the parent materials, MgH₂ and TiC. The Fe phase was detected in the ball-milled samples was from the collision of milling vial and balls. There is no new compound formed from the mixture. The metastable orthorhombic γ -MgH₂ is detected

simultaneously with β -MgH₂ from 16 h ball-milled (MgH₂+ 2% TiC) pre-cryomilled for 8 h. The formation of γ -MgH₂ during high energy ball milling of MgH₂ was investigated earlier in chapter 4.1. The XRD peaks of MgH₂ broaden with milling time, indicating the decrease of crystallite size, compared with the as-received powders. From the XRD patterns of the dehydrogenated (MgH₂ + 2%TiC) mixture cryomilled for 8 h and further ball-milled for 60 h, Figure 4-7, only Mg and TiC peaks are detected in the dehydrogenated mixture. There is no reaction between TiC and Mg/MgH₂. TiC retains its original form during milling and after dehydrogenation, TiC is known to be a very stable compound with a formation enthalpy of -190.4 ± 17.0 kJ/mol based on direct reaction from Ti and C powders²⁰.

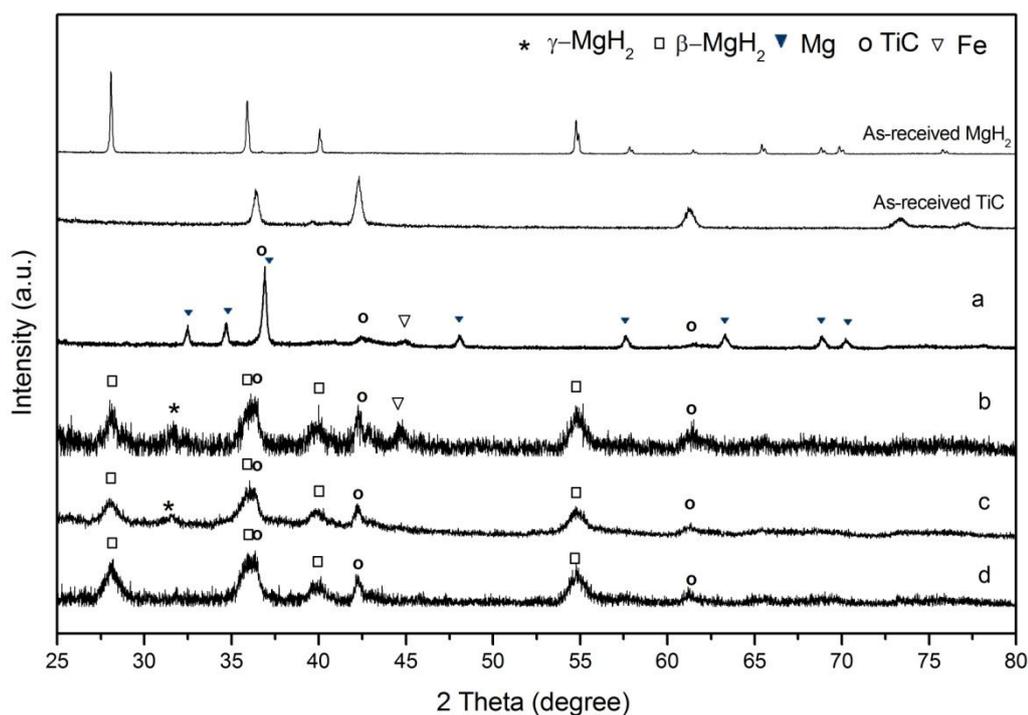


Figure 4-7 X-ray diffraction patterns of the as-received MgH₂, TiC and the milled (MgH₂+2mol.% TiC) mixtures. (a) Dehydrogenated (MgH₂+2%TiC) after cryomilling and 60 h ball milling, (b) (MgH₂+2%TiC) ball milled for 60 h after cryomilling, (c) (MgH₂+2%TiC) ball milled for 16 h after cryomilling, (d) (MgH₂+2%TiC) cryomilled for 8h.

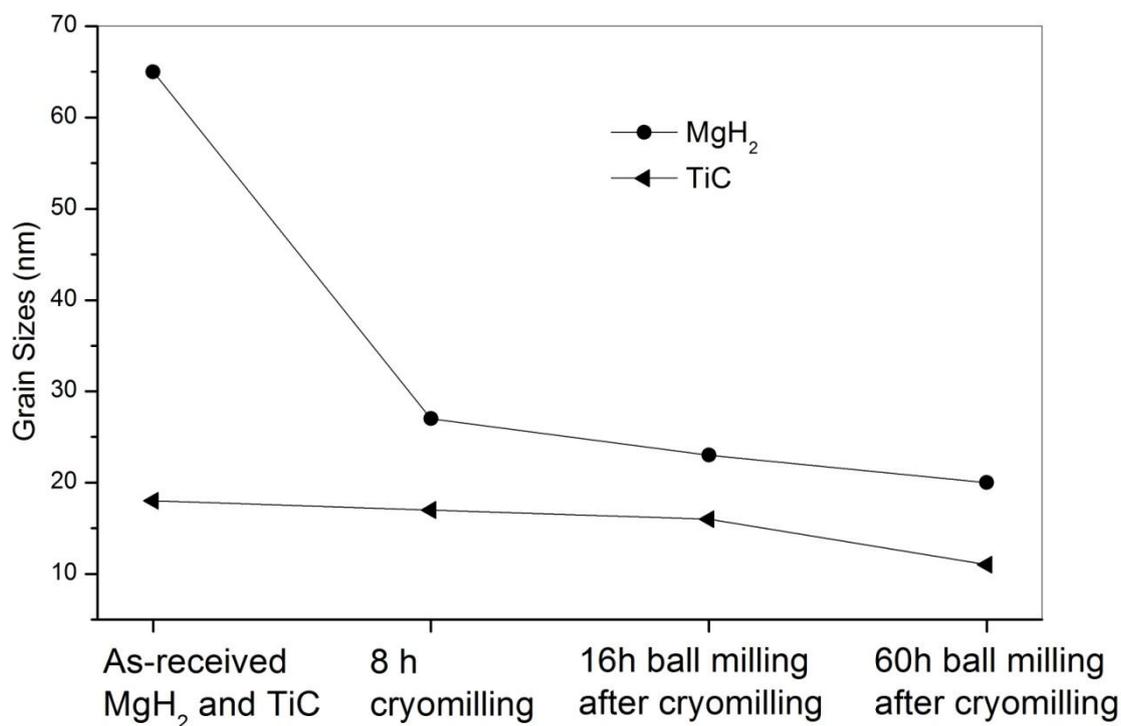


Figure 4-8 Grain sizes of MgH₂ and 2%TiC before and after milling, calculated from XRD patterns of the as-received MgH₂, TiC and the milled (MgH₂+2%TiC) mixtures.

Figure 4-8 shows the estimates of the nanograin size of the as-received MgH₂ calculated based on XRD pattern is of the order of 65 ± 5 nm. After 8 h cryogenic milling, the grain size of MgH₂ is decreased greatly to 25 ± 3 nm. It has been suggested that the presence of liquid nitrogen during cryomilling has several advantages, such as decreased oxygen contamination¹⁶⁶ and enhanced deformation during milling¹⁶². With a further 60 h ball milling, the grain size of MgH₂ is only reduced slightly to 20 ± 3 nm. Furthermore, the grain size of TiC is decreased to 10 ± 1 nm with a further 60 h ball-milling, compared with the initial size of 18 ± 3 nm. Therefore, the cryogenic milling process is very effective in reducing the crystallite size of MgH₂, and further high energy ball milling only reduces the grain size to some extent. Cryogenic milling provides significant improvements to surface residual stresses and the effectiveness of grinding forces mainly due to a substantial

temperature reduction in grinding zone and a decrease in magnitude of tensile residual stress for all the materials¹⁴⁸. However, the grain size of TiC does not decrease greatly after 8 h cryomilling (17 ± 3 nm) due to its very low content in the mixture (2 mol %) and original small grain size (18 ± 3 nm) which is more difficult to reduce further by cryogenic milling.

The morphology and microstructure of the mixtures were further investigated by scanning electron microscope (SEM), shown in Figure 4-9. The average particle sizes and the range of particle sizes were calculated according to the SEM images, in Figure 4-10. Figure 4-9b shows the particle morphology of the as-received TiC, indicating an agglomeration or cluster of nanometer-scaled TiC particles. The average particle size of the mixture is reduced to about ~ 200 nm after 8 h of cryomilling (Figure 4-9c and Figure 4-10). Some of the particles become smaller and others are aggregated to relatively bigger particles after ball milling to 16 h and 60 h, Figure 4-9d&e. Figure 4-10 also illustrates the slight increase of the mean particle sizes of ($\text{MgH}_2 + 2\% \text{TiC}$) mixture after further 16 h and 60 h ball-milling.

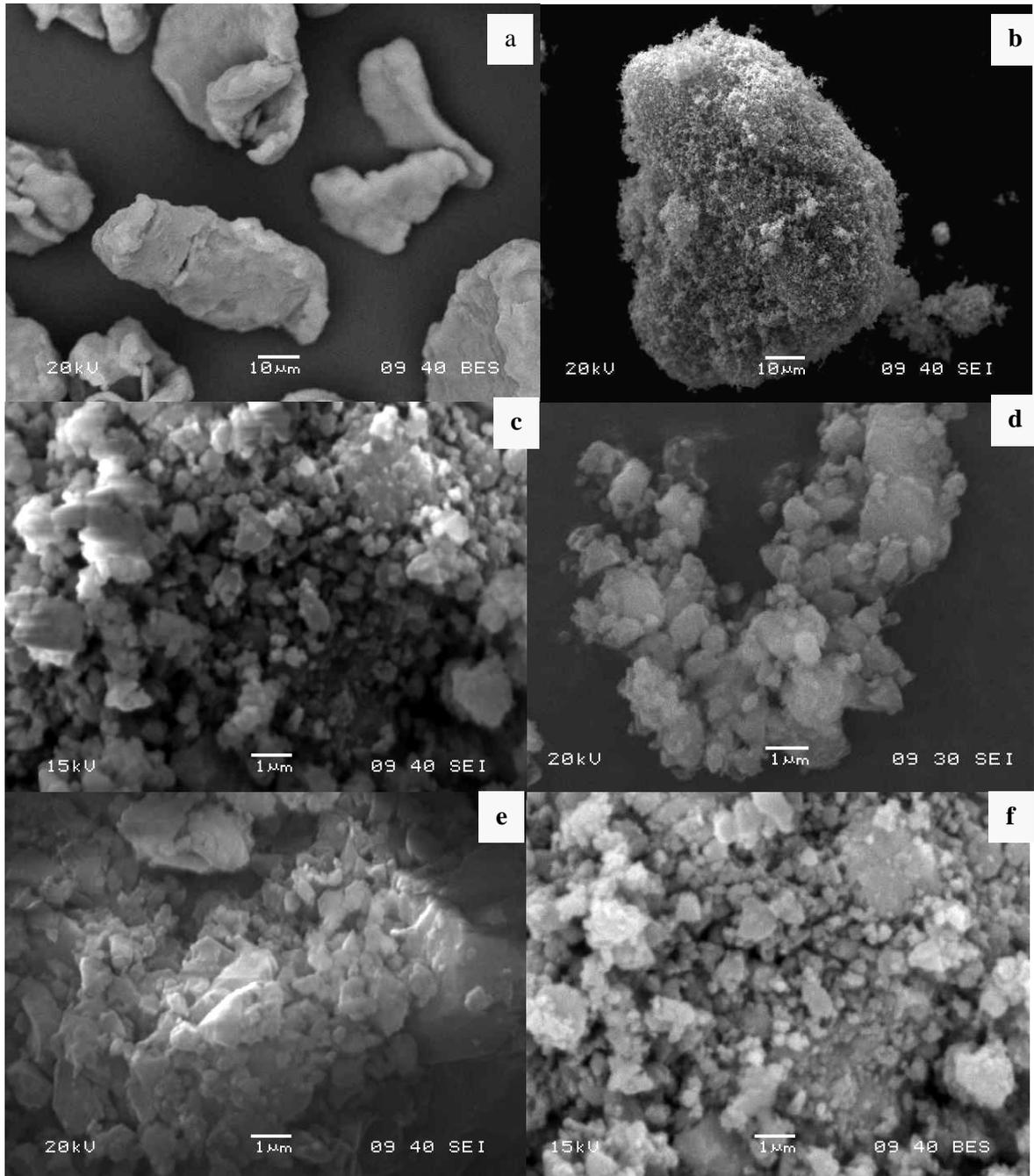


Figure 4-9 SEM micrograph of (a) as-received MgH₂, (b) as-received TiC, (c) (MgH₂+2%TiC) cryomilled for 8 h, (d) (MgH₂+2%TiC) ball milled for 16 h after cryomilling, (e) (MgH₂+2%TiC) ball milled for 60h after cryomilling and (f) Back Scattering Electron (BSE) image of (MgH₂+2%TiC) cryomilled for 8h.

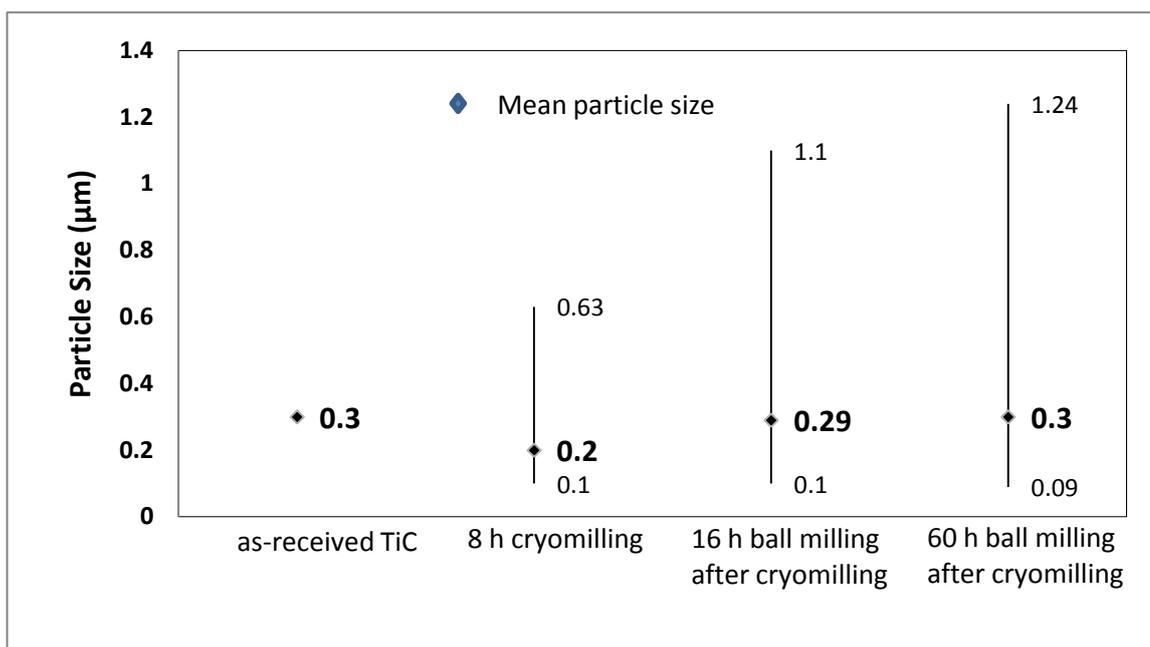


Figure 4-10 Mean particle sizes of the milled ($\text{MgH}_2+2\%\text{TiC}$) mixtures, calculated from SEM images Figure 4-9.

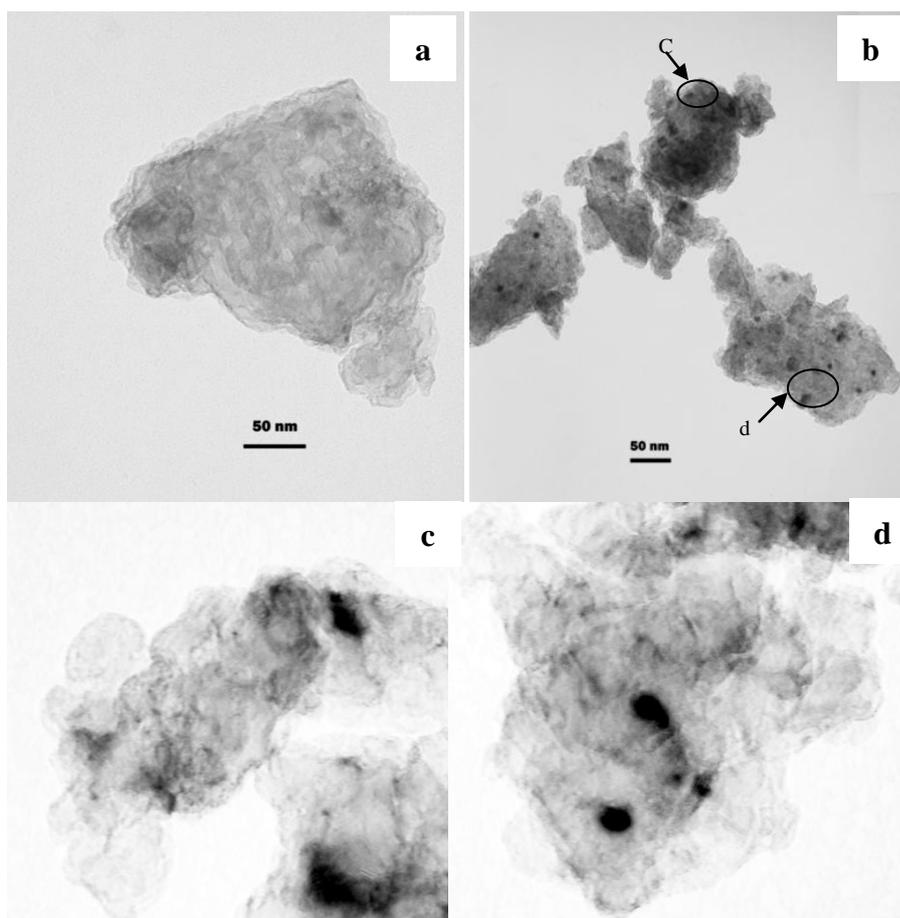


Figure 4-11 TEM images of the samples cryomilled for 8 h and further ball milled for 60 h: (a) MgH_2 and (b) (MgH_2+TiC) mixture (c)&(d) partial enlarged view from b.

From the back-scattered electron (BSE) image of the ($\text{MgH}_2+2\%\text{TiC}$) cryomilled for 8h, Figure 4-9f, the BSE signals for the heavier element or the compound containing heavier element should be observed as much brighter spots. However, the contrast between the elements is not recognized. Therefore, it is concluded that the distribution of nano-sized TiC particles in the mixture (<100nm) cannot be detected by the SEM-BSE analysis with a resolution in the micrometer scale.

TEM was performed to identify how the TiC particles are distributed on the surface of MgH_2 in a nanometer scale. Figure 4-11 shows the TEM images of the MgH_2 cryomilled for 8 h and the (MgH_2+TiC) mixture cryomilled for 8 h and further ball-milled for 60 h, where the average size of the large particles is estimated to be about 200-400 nm in diameter. There are many much darker small particles distributed on the large particles, from Figure 4-11 b. By comparing Figure 4-11 a and Figure 4-11 b, the large bright particles are identified as MgH_2 and the tiny dark particles as TiC. The particle size of TiC is estimated to be 10 ~ 20 nm. The Figure 4-11 c and d are partial enlarged images from Figure 4-11 b, which clearly reveal the grain boundaries and TiC particles. From the above observations, the nano-sized TiC particles are either distributed on the surface of MgH_2 particles or inserted between grains of MgH_2 , which enhances the interaction between MgH_2 and TiC which could act as an effective catalyst or nucleation sites for H_2 sorption, hence lead to fast kinetics.

4.2.2 Dehydrogenation of milled mixtures of MgH_2 and TiC

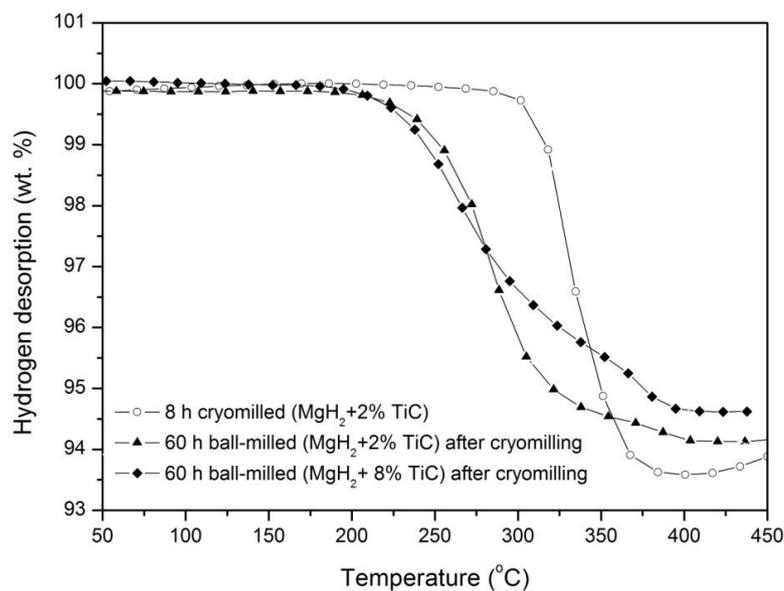


Figure 4-12 Thermogravimetric (TG) curves of the MgH_2 milled with TiC, measured at 1 bar He pressure with a heating rate of 10 K/min.

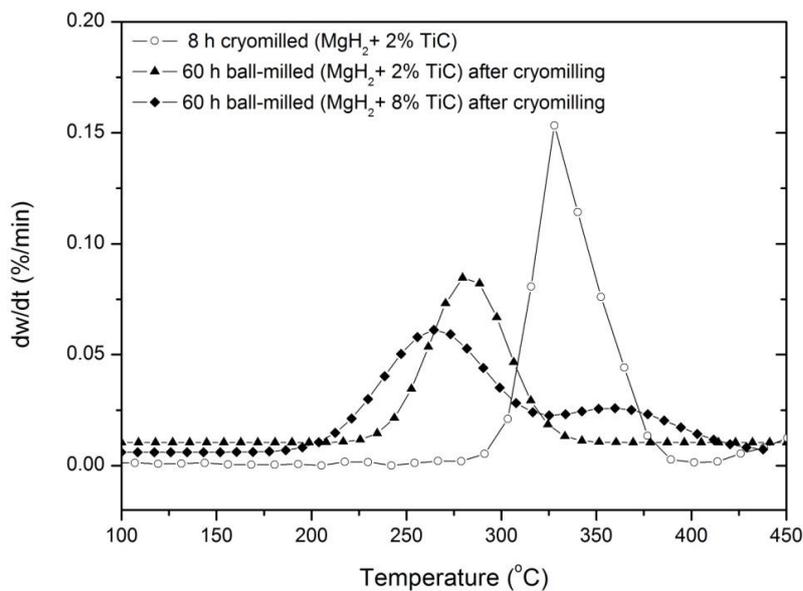


Figure 4-13 Derivative thermogravimetric (DTG) curves of the MgH_2 milled with TiC, derived from Figure 4-12.

Table 4-2 Onset & Peak desorption temperatures and absorption rates of the MgH₂ catalyzed by TiC.

Sample	As-received MgH ₂	cryomilled (MgH ₂ + 2%TiC)	60 h ball-milled (MgH ₂ + 2%TiC) after cryomilling	60 h ball-milled (MgH ₂ + 8%TiC) after cryomilling
Grain Size (nm) of MgH ₂	65 ± 5	27 ± 3	23 ± 3	20 ± 3
Mean Particle Size (µm)	30 ± 2	0.2 ± 0.02	0.29 ± 0.02	0.3 ± 0.02
T _{Onset} (°C)	418	280	190	175
T _{Peak} (°C)	434	332	275	264
E' (KJ/mol)*	235 ± 10	157	104	89
Absorption Rate (wt. %/min)	0.008 ± 0.00004	0.08 ± 0.0001	0.12 ± 0.0001	–

* Activation energy calculated from Equation 3-8.

Figure 4-12 and Figure 4-13 show the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of hydrogen desorption of the mixtures, respectively. The total relative weight loss of as-received MgH₂ and (MgH₂+2 % TiC) is about 7 ± 0.02 wt. % and 6.5 ± 0.02 wt. %, respectively. The 0.5 ± 0.02 wt. % loss is due to the addition of TiC since the theoretical capacity of H₂ storage is 7.3 ± 0.02 wt. % for (MgH₂+2 mol% TiC) and 7.6 ± 0.02 wt. % for pure MgH₂. 8 mol % TiC was mixed with MgH₂ following the same synthesized process of (MgH₂+2 mol% TiC) mixture. 5.5 ± 0.02 wt. % of hydrogen is released from 60 h ball-milled (MgH₂+ 8 mol% TiC) mixture after 8 h cryomilling owing to 6.4 ± 0.02 wt. % theoretical H₂ capacity. The difference between the observed value and the theoretical value of hydrogen releasing is due to the formation of MgO during the long time milling.

DTG curves of dehydrogenation for the milled mixtures are calculated to identify the onset and peak desorption temperatures. For 8 h cryomilled samples, (MgH₂+ 2 mol% TiC) mixture starts H₂ desorption at 280 °C (lower than onset temperature of cryomilled MgH₂, 320 °C), the peak temperature is decreased to 332 °C from 362 °C (the peak temperature of cryomilled MgH₂ without TiC). After a further 60 h ball-milling of cryomilled (MgH₂+2 mol% TiC), the onset temperature is reduced to 190 °C due to the smaller grain size and enhanced

interaction between TiC and MgH₂. For the 60 h ball-milled MgH₂ without TiC, the onset temperature was 305 °C, Figure 4-4. The 8 mol% TiC-doped MgH₂ shows a lower onset and peak temperature, 175 °C and 264 °C, respectively. Thus the hydrogen desorption temperature decreases with increasing TiC content. The catalytic effect of TiC is particularly important in reducing the decomposition temperature of MgH₂, being more marked in the starting desorption temperature.

The overall activation energy (E') of H₂ desorption of the samples is obtained according to Equation 3-8, as shown in Table 4-2. The activation energy of desorption is as high as 235 ± 10 kJ/mol for as-received MgH₂. When 2 mol % TiC nanoparticles are added, the value is decreased to 157 ± 9 kJ/mol after 8 h cryomilling. With further ball milling for 60 h after cryomilling, the activation energy falls as low as 104 ± 6 kJ/mol. Thus the desorption kinetics can be improved greatly by the catalytic action of TiC nanoparticles. Milled MgH₂ with a content of 8 mol % TiC requires less activation energy of 89 ± 5 kJ/mol to release hydrogen, shown in Figure 4-14 and Table 4-2. TiC is shown to be an effective catalyst for hydrogen desorption of MgH₂.

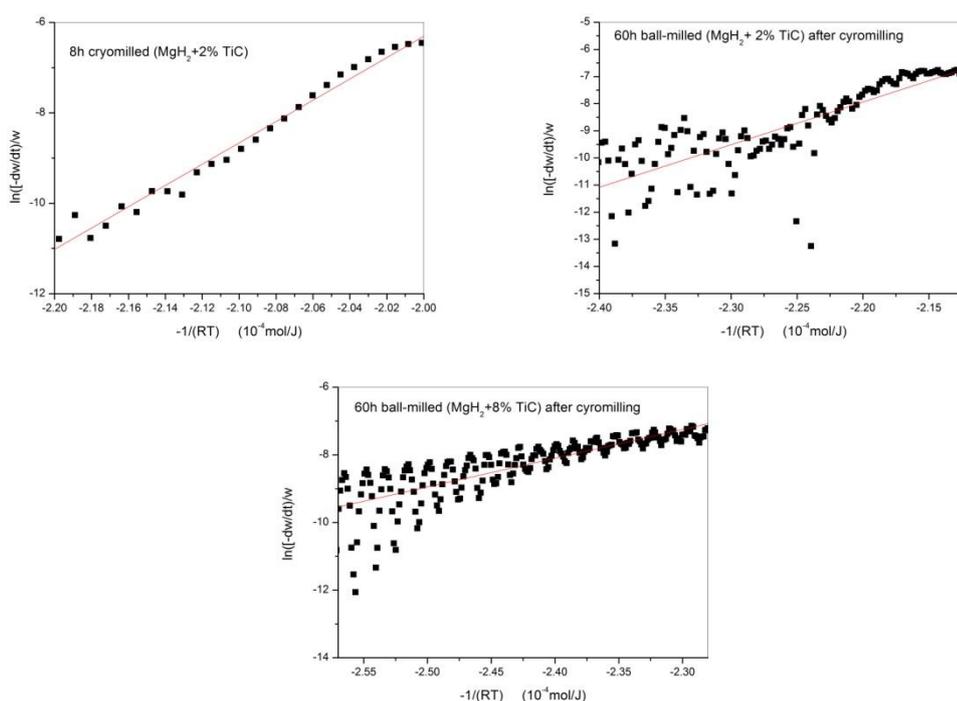


Figure 4-14 Kinetic plots and activation energy of cryomilled and ball-milled (MgH₂+ 2 %TiC) and ball-milled

4.2.3 Hydrogenation of milled mixtures of MgH_2 and TiC

The hydrogen absorption kinetics of the dehydrogenated MgH_2 and ($\text{MgH}_2 + 2 \text{ mol.} \% \text{ TiC}$) mixtures were measured under 8 bars H_2 pressure at 300 °C, Figure 4-15. The hydrogen uptake is very slow for the as-received MgH_2 after dehydrogenation. However, about 4 wt. % of hydrogen is absorbed in 60 min after cryomilling of MgH_2 . The mixture of ($\text{MgH}_2 + 2 \text{ mol} \% \text{ TiC}$) after cryomilling and ball-milling shows faster H_2 absorption with $5 \pm 0.02 \text{ wt.} \% \text{ H}_2$ uptake in 50 min. It was also found that the absorption rate increased to $0.12 \pm 0.0001 \text{ wt.} \%/\text{min}$ due to the milling process and the addition of the catalyst TiC (Table 4-2). The relatively lower maximum weight percentage of H_2 uptake of cryomilled MgH_2 and ($\text{MgH}_2 + 2 \text{ mol} \% \text{ TiC}$) is probably due to slow kinetics and slight oxidation of the samples during milling.

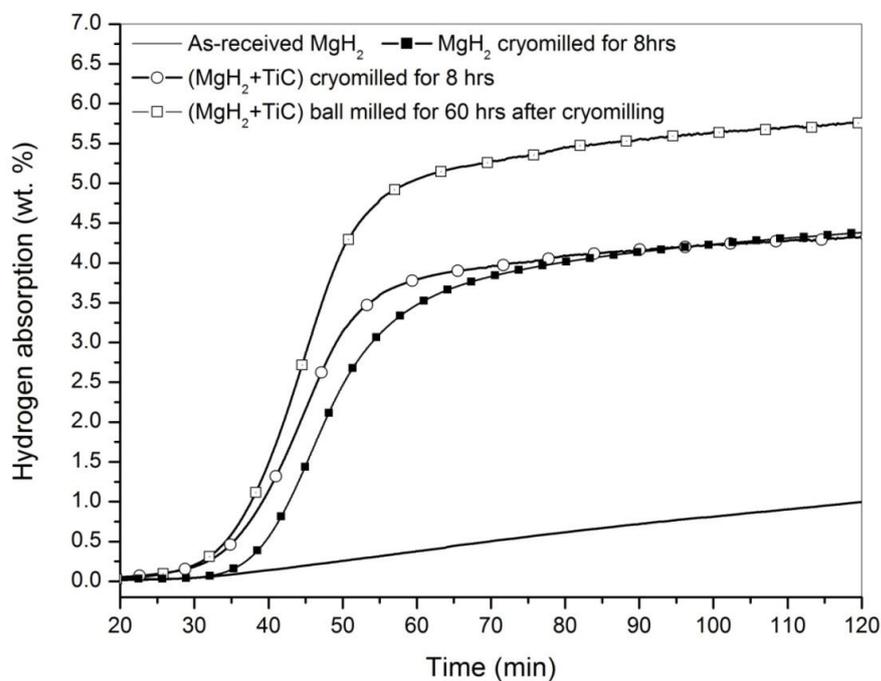


Figure 4-15 Hydrogen absorption curves of the MgH_2 catalyzed with and without TiC, measured under 8 bar H_2 pressure at 300 °C.

4.2.4 Summary

Hydrogen storage properties of MgH_2 catalysed with 2 mol % and 8 mol % TiC by cryomilling and ball-milling were investigated respectively. The crystallite sizes decreased with increasing milling time. TiC, which is a very stable compound at the testing temperature and pressure ($< 500\text{ }^\circ\text{C}$, 1 bar), retains its original form during milling and after dehydrogenation. From SEM-BSE and TEM observations, the nano-sized TiC particles were either distributed on the surface of MgH_2 particles or inserted between grains of MgH_2 , which enhanced the interaction between MgH_2 and TiC.

The desorption temperatures and activation energy of the milled MgH_2 were reduced by the addition of 2 mol% TiC. It was also found that a better desorption performance in terms of temperature and kinetics was recorded with the addition of 8 mol % TiC. TiC shows an effective catalytic property for H_2 sorption of Mg/MgH_2 , which is stable during H_2 uptake and release with no reaction with Mg or MgH_2 . Based on the microstructural observations and hydrogen sorption property analysis, it is concluded that the reduction of nano particle size has an positive effect on hydrogen storage properties of MgH_2 , but TiC as a catalyst is crucially important for the enhancement of hydrogen sorption of Mg/MgH_2 .

4.3 Effects of Mo_2C Nanoparticles on Hydrogen Sorption Properties of MgH_2

More recently, early transition metal carbides have attracted much attention for displaying catalytic properties similar to those of noble metals¹⁶⁷. It is reported that the increase of effect on hydrogen absorption property seems related to the increase of atomic number (Z) of the transition element¹⁶⁸. Since TiC shows promising catalytic effect on the hydrogen storage properties of MgH_2 , Mo_2C with high thermal stability and low cost is selected as another alternative catalyst for hydrogen storage of MgH_2 because of the atomic number of molybdenum in the periodic table is larger than titanium. The effect of Mo, W, Nb, etc. on

hydrogen storage properties of metal hydrides has been investigated by K. Iwase *et al.*¹⁶⁹. Their results indicated that Mo additive delayed the formation of AB₅-hydride, in accordance with increased hydrogen absorption capacity. The findings together with high thermal stability and low cost, make Mo₂C an interesting additive to modify the sorption properties of MgH₂.

The aim of the study is following this point to evaluate the influence of Mo₂C on hydrogen sorption of MgH₂, in comparison with the results of TiC in previous section 4.2.

4.3.1 Structural characterizations of milled mixtures of MgH₂ and Mo₂C

XRD patterns of the samples obtained by milling of MgH₂ with 2 mol % Mo₂C are shown in Figure 4-16. There were no addition of diffraction peaks detected which suggested new phases or products resulting from cryomilling and ball-milling of (MgH₂+ Mo₂C), shown in Figure 4-16b and c. The two main components of β-MgH₂ and Mo₂C were observed in the milled mixtures. The Fe phase was detected in the ball-milled samples was from the collision of milling vial and balls, which was also found in the MgH₂ and (MgH₂+ TiC) powders after 60 h ball milling. After a further 60 h ball-milling, γ-MgH₂ was formed, shown in Figure 4-16c. As discussed earlier in section 4.1, a 60 h ball-milling led to broadening of peaks of β-MgH₂, with the grain size becoming a few nanometers and further reduced with increasing milling. The XRD pattern of the dehydrided 60 h ball-milled (MgH₂+ Mo₂C) showed the Mg phase and Mo₂C phase. There was no reaction during dehydrogenation of (MgH₂+ Mo₂C).

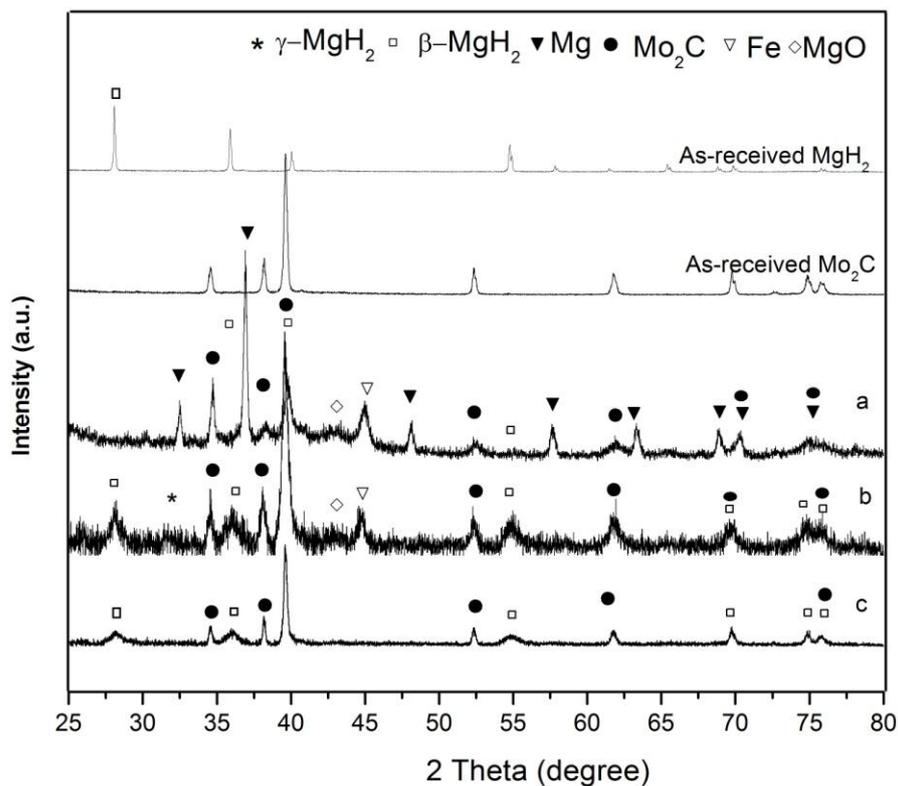


Figure 4-16 XRD patterns of the as-received MgH_2 , Mo_2C and milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) mixtures. (a) Dehydrogenated ($\text{MgH}_2 + \text{Mo}_2\text{C}$) after cryomilling and 60 h ball-milling, (b) ($\text{MgH}_2 + \text{Mo}_2\text{C}$) ball milled for 60 h after cryomilling, (c) ($\text{MgH}_2 + \text{Mo}_2\text{C}$) cryomilled for 8 h.

Figure 4-17 shows estimates of the nanograin size of as-received MgH_2 and Mo_2C calculated from XRD patterns to be of the order of 65 nm and 30 nm. After 8 h cryogenic milling, the grain size of MgH_2 has decreased greatly to 27 ± 3 nm. Following a further 60 h ball milling, the grain size of MgH_2 was only reduced slightly to 20 ± 3 nm. The grain size of Mo_2C was decreased from 31 ± 3 nm to 18 ± 3 nm during 60 h ball milling. It can be seen that the grain size of MgH_2 with or without Mo_2C is similar, which is only relevant to the duration time of cryomilling and ball-milling, comparing with the results from section 4.1 (Table 4-1).

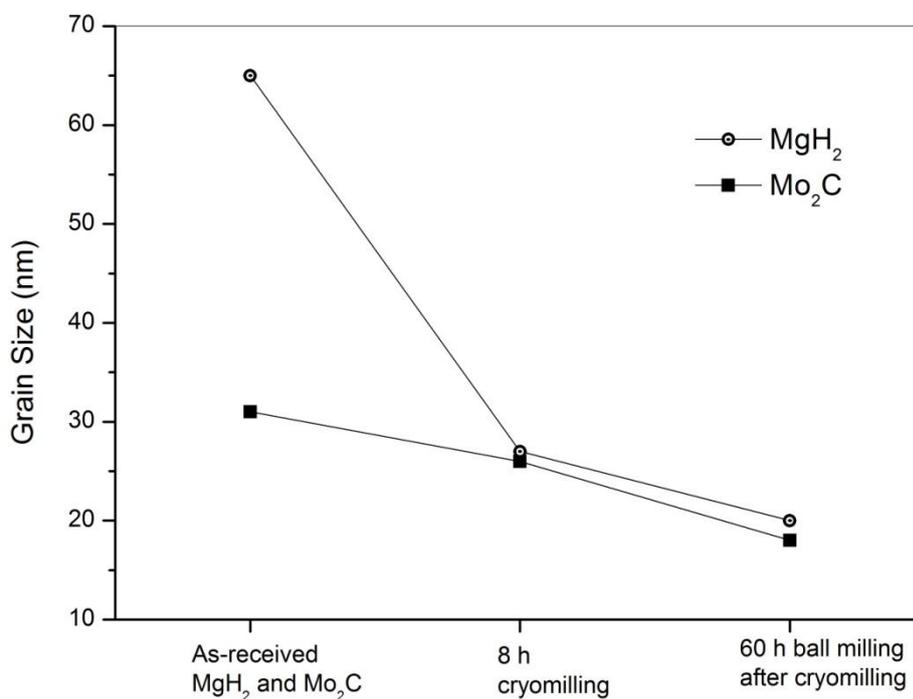


Figure 4-17 Grain sizes of MgH₂ and Mo₂C before and after milling, calculated from XRD patterns of the as-received MgH₂, Mo₂C and the milled (MgH₂+ Mo₂C) mixtures.

The as-received Mo₂C particles have a platelet-like shape with the mean size of ~1.3 μm in diameter, seen in Figure 4-18 and Figure 4-19. After 8 h cryomilling, the average particle size of the (MgH₂+Mo₂C) is reduced to about 440 nm with irregular morphology. As shown in Figure 4-19, the particle size distribution after 60 h ball-milling becomes broader compared with that of only 8 h cryomilling. The smaller particle size range could reach to 60 nm.

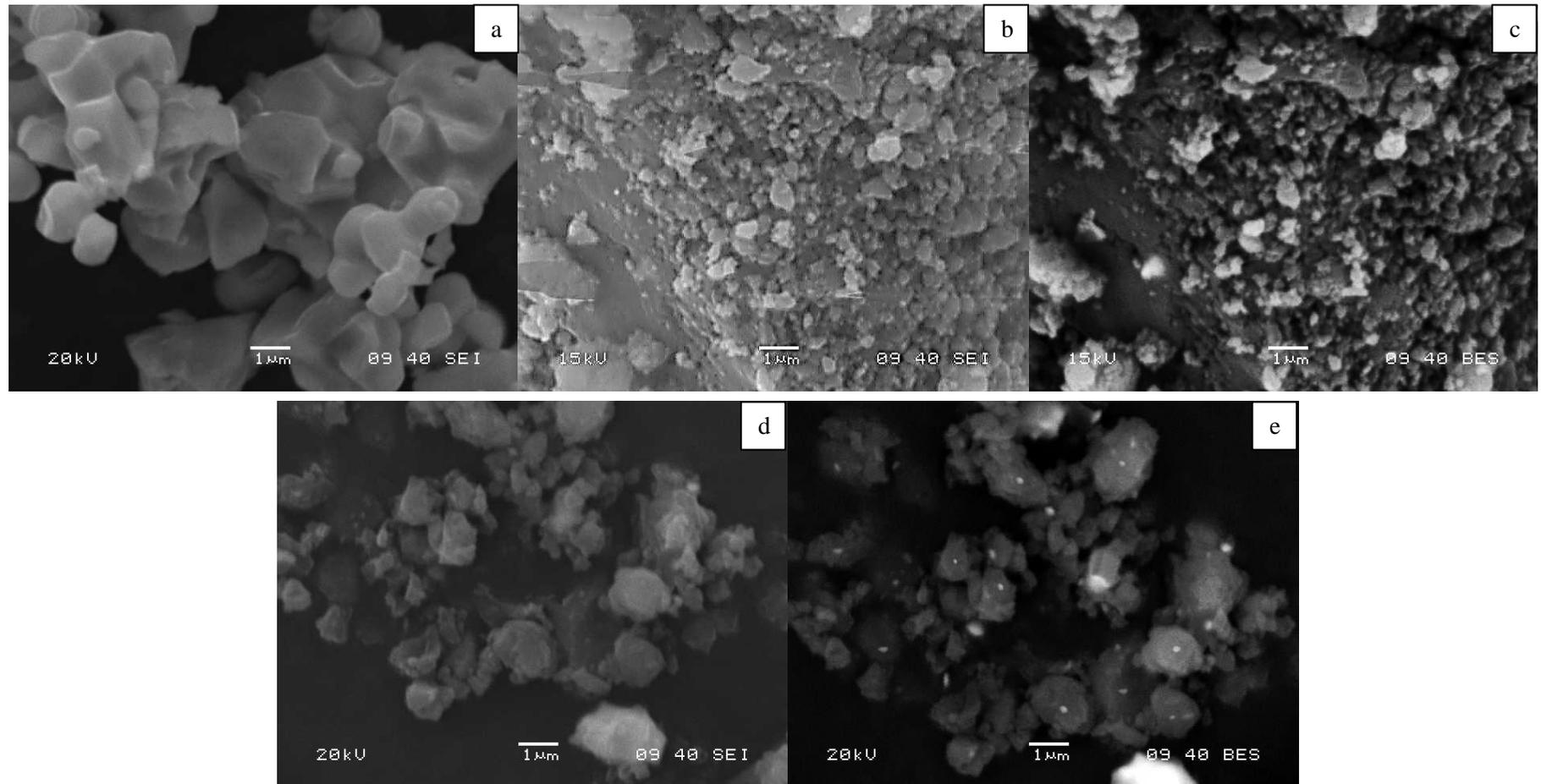


Figure 4-18 SEM micrographs of (a) as-received Mo_2C , (b) 8 h cryomilled ($\text{MgH}_2+2\text{mol}\%$ Mo_2C), (c) BSE of cryomilled ($\text{MgH}_2+2\text{mol}\%$ Mo_2C), (d) 60 h ball-milled ($\text{MgH}_2+2\text{mol}\%$ Mo_2C) after cryomilling, and (e) BSE of ball-milled ($\text{MgH}_2+2\text{mol}\%$ Mo_2C)

From a back-scattered electron (BSE) image of the ($\text{MgH}_2 + \text{Mo}_2\text{C}$) cryomilled for 8 h, in Figure 4-18 c, the bright small particles were distributed over the dark particles, which can also be observed in the BSE image of 60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) after 8 h cryomilling, Figure 4-18(g). The bright particles/area are the distribution of Mo_2C particles, because the BSE signals for heavier element or compound containing the heavier element should have brighter images. Mo has a much larger atomic number than Mg. The observation indicates that the Mo_2C particles homogeneously distribute in such a micrometer scale range on the surface of MgH_2 .

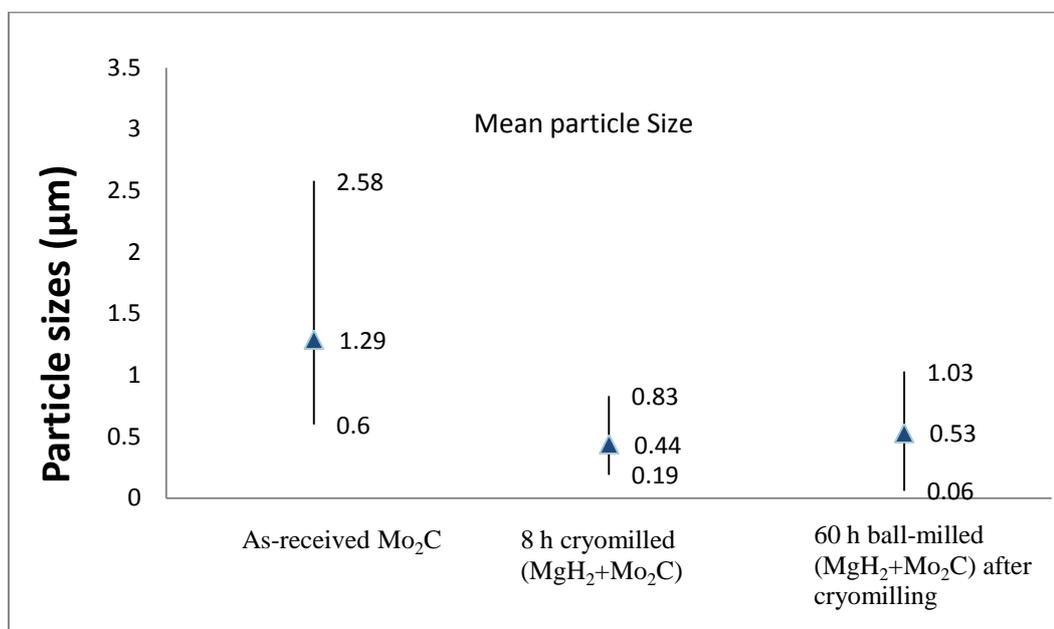


Figure 4-19 Mean particle sizes of the milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$), calculated from the SEM images Figure 4-18.

4.3.2 Dehydrogenation of milled mixtures of MgH_2 and Mo_2C

The TG and DTG curves show 6 ± 0.02 % weight loss of cryomilled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) and 60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$), with the starting desorption temperature of 320 °C and 300 °C respectively, as shown in Figure 4-20, Figure 4-21 and Table 4-3. Comparing with the onset temperatures of the cryomilled MgH_2 (320 °C) and 60 h ball-milled MgH_2 after cryomilling (305 °C), the desorption temperature of milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) mixture show almost no

reduction. Therefore Mo_2C didn't have an obvious effect on the dehydrogenation temperature of MgH_2 . From Table 4-3, it is indicated that the activation energy of ($\text{MgH}_2 + \text{Mo}_2\text{C}$) ball milled for 60 h after cryomilling is 167 ± 9 kJ/mol, lower than that of 60 h ball-milled MgH_2 (199 kJ/mol, Table 4-1) and higher than that of 60 h ball-milled ($\text{MgH}_2 + 2\% \text{TiC}$) (104 kJ/mol, Table 4-2). It is in accordance with desorption onset temperature of ($\text{MgH}_2 + \text{Mo}_2\text{C}$), MgH_2 and ($\text{MgH}_2 + 2\% \text{TiC}$), which are 300 °C, 305 °C and 190 °C respectively.

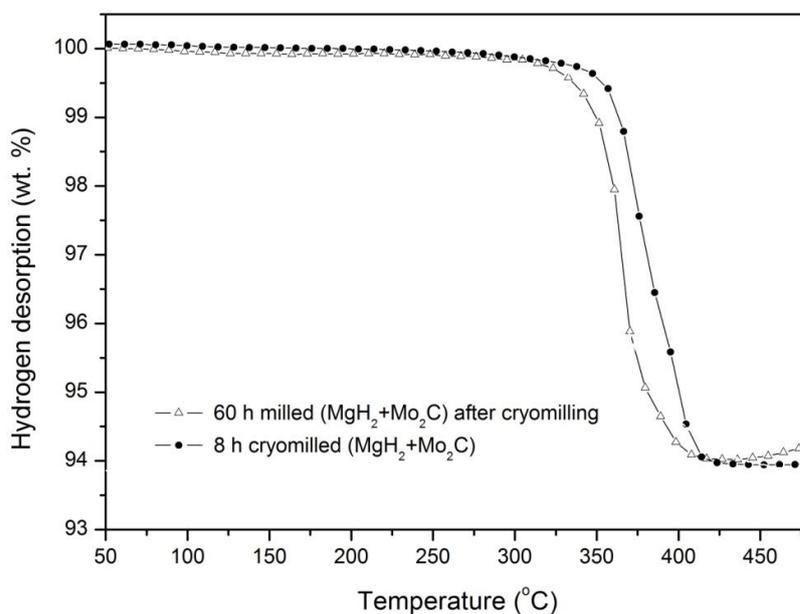


Figure 4-20 Thermogravimetric (TG) curves of MgH_2 milled with Mo_2C , measured at 1 bar He pressure with a heating rate of 10 K/min.

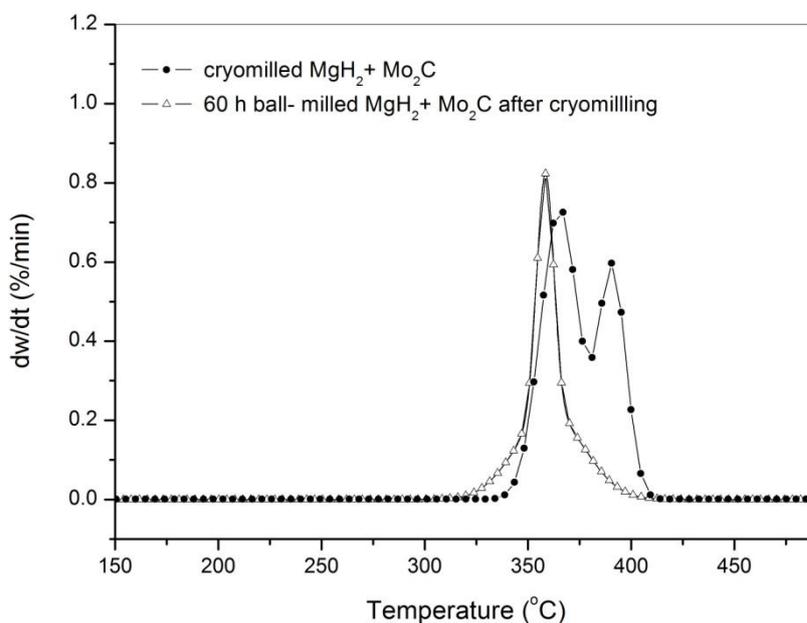


Figure 4-21 Derivative thermogravimetric (DTG) curves of the MgH_2 milled with Mo_2C , derived from Figure 4-20.

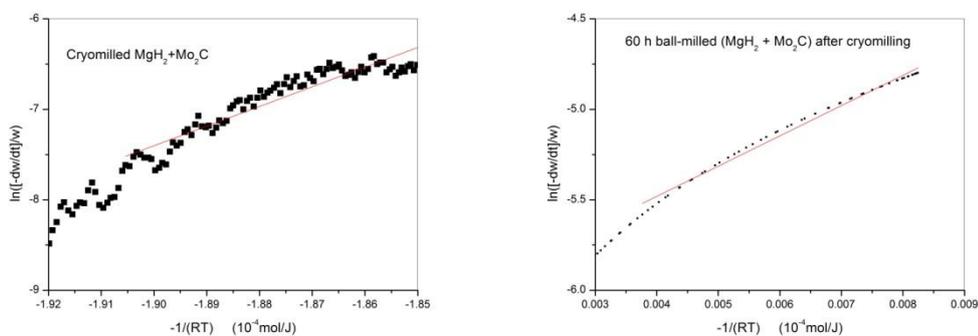


Figure 4-22 Kinetic plots and activation energy of cryomilled and ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$), based on Figure 4-21 and Equation 3-8.

Table 4-3 Onset & Peak desorption temperatures and absorption rates for the MgH_2 catalyzed with Mo_2C .

Sample	cryomilled ($\text{MgH}_2 + \text{Mo}_2\text{C}$)	60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) after cryomilling
T_{Onset} (°C)	320	300
T_{Peak} (°C)	360	358
E' (KJ/mol)	217 ± 10	167 ± 9

Absorption Rate	0.074 ± 0.0001 (40-60 min)	0.074 ± 0.0001 (40-60 min)
(Δ wt. %/min)	0.021 ± 0.0001 (60-180 min)	0.023 ± 0.0001 (60-180 min)

4.3.3 Hydrogen absorption of milled mixtures of MgH_2 and Mo_2C

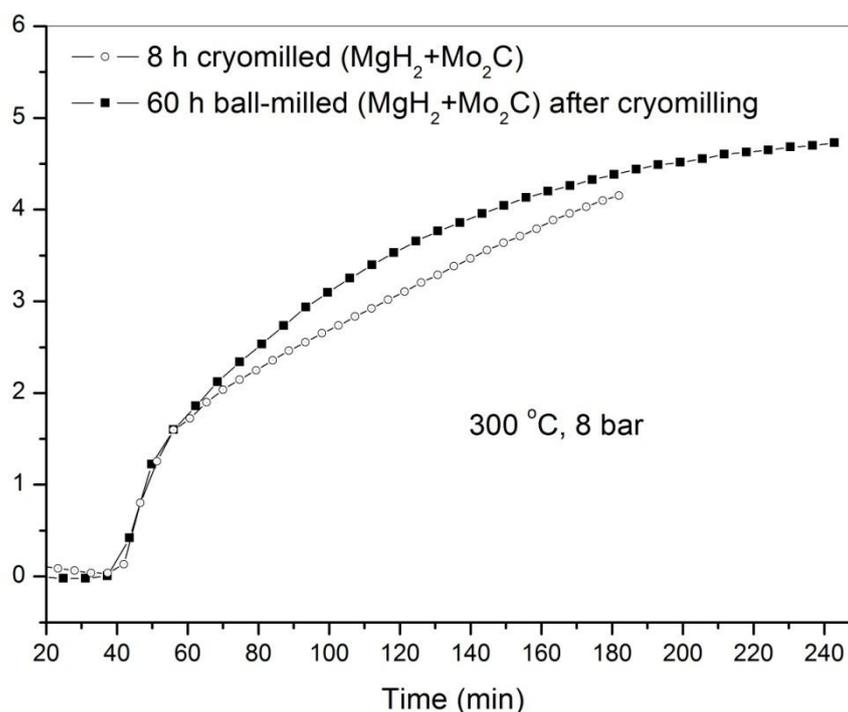


Figure 4-23 Hydrogen absorption of MgH_2 catalyzed by Mo_2C , measured under 8 bar H_2 pressure at 300 °C.

Figure 4-23 shows the hydrogen absorption of $(\text{MgH}_2+\text{Mo}_2\text{C})$ mixture. The dehydrided 8 h cryomilled $(\text{MgH}_2+\text{Mo}_2\text{C})$ can absorb 4.1 ± 0.02 wt. % hydrogen in 180 min at 300 °C at 8 bar H_2 pressure, which included two steps: hydriding with the speed of 0.074 ± 0.0001 wt.%/min from 40 min to 60 min, and then the decreased rate of 0.021 ± 0.0001 wt.%/min from 60 min to 180 min (in Table 4-3). The absorption curve was continuously increasing after 180 min, which indicates that the hydrogenation was incomplete in 180 min due to slow absorption kinetics. The absorption rate was slightly improved for dehydrided 60 h ball-milled $(\text{MgH}_2+\text{Mo}_2\text{C})$ after cryomilling. The adsorption reached a certain value of 4.5 ± 0.02 wt. % in 240 min. Mo_2C has little effect on improving the absorption kinetics of

Mg/MgH₂ under the present testing conditions. Furthermore, it can be observed the absorption rate of dehydrided ball-milled (MgH₂+Mo₂C) is lower than that of 60 h ball-milled MgH₂ ($0.1 \pm 0.0001 \Delta\text{wt. \%}/\text{min}$, Table 4-1) because the Mo₂C particles were dispersed on the surface of Mg/MgH₂ particles to block the interaction between Mg and H.

4.3.4 Summary

XRD results indicate that no reaction happened during milling and dehydrogenation of (MgH₂+Mo₂C). The grain sizes of MgH₂ and Mo₂C are decreased greatly after 8 h cryomilling.

SEM-BSE characterizations showed that some micro-scaled Mo₂C particles of less than 500 ± 20 nm were distributed onto MgH₂ particles.

Comparing the TG and DTG results of MgH₂ with Mo₂C, the onset and peak temperatures have not been reduced, which is coinciding with the results of the activation energy. The absorption kinetics of dehydrided MgH₂ doped with Mo₂C is even lower than that dehydrided MgH₂ without Mo₂C under the same milling process and conditions. Thus it is concluded that the Mo₂C shows no catalytic effect on hydrogen sorption of MgH₂.

4.4 Effects of Ni Nanoparticles on Hydrogen Desorption Properties of 60 h Ball-milled (MgH₂ +TiC or Mo₂C)

Nickel (Ni) is a very effective catalyst to improve hydrogen sorption kinetics of MgH₂^{18, 170-173}. Hanada et al. have suggested that nanoparticles transition-metal such as Fe, Co, Cu and Ni can enhance the kinetics dramatically¹⁷⁴. After milling with 2 mol% Ni nanoparticles for a short time of 15 min under a slow milling speed of 200 rpm, a large amount of hydrogen (6.5 ± 0.02 wt%) was desorbed in the temperature range 423 to 523 K at a heating rate of 5 K/min under He gas flow.

In this section, 60 h ball-milled ($\text{MgH}_2 + 2 \text{ mol.}\% \text{TiC/Mo}_2\text{C}$) after 8 h cryomilling was mixed with 2 mol.% Ni nanoparticles for 15 min to investigate the synergetic effect of the addition on hydrogen sorption of the mixture.

4.4.1 Structural characterizations of ($\text{MgH}_2 + \text{TiC/Mo}_2\text{C} + 2 \text{ mol.}\% \text{Ni}$) mixtures

Figure 4-24 presents the XRD patterns of prepared samples. After mixing, the 60 h ball-milled ($\text{MgH}_2 + \text{TiC/Mo}_2\text{C}$) with Ni nanoparticles, the main phases were not changed. There was no new compound, such as Mg_2NiH_4 , formed during the short milling time. The Ni peaks were well presented in the XRD patterns. Determined by the Sherrer equation, the crystallite sizes of MgH_2 , $\text{TiC/Mo}_2\text{C}$ and Ni nanoparticles in the mixtures are almost the same as those of the 60 h ball-milled samples without mixing with Ni due to the mild milling condition.

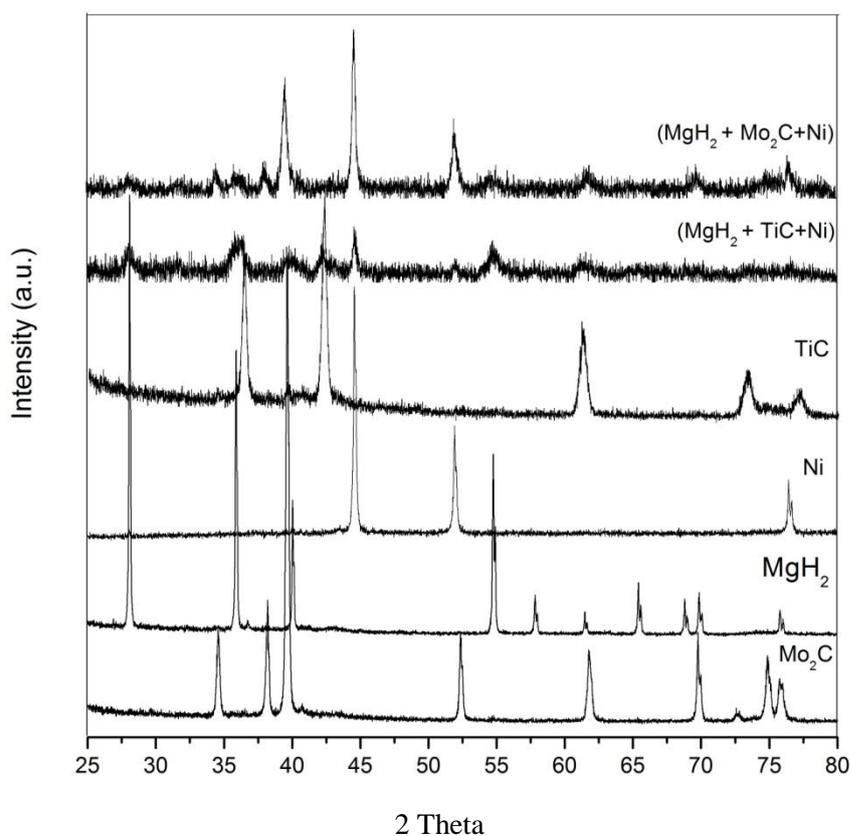


Figure 4-24 XRD patterns of the as-received MgH_2 , TiC , Mo_2C , Ni, $(\text{MgH}_2 + \text{Mo}_2\text{C} + \text{Ni})$ and $(\text{MgH}_2 + \text{TiC} + \text{Ni})$

Figure 4-25 shows that the particle size and morphology of the ($\text{MgH}_2+\text{Mo}_2\text{C}+\text{Ni}$) remained almost the same as the 60 h ball-milled ($\text{MgH}_2+\text{Mo}_2\text{C}$) after cryomilling, as discussed in section 4.3. From

Figure 4-26 and Figure 4-27, the mean particle size of the 60 h ball-milled ($\text{MgH}_2+\text{TiC}+\text{Ni}$) increased slightly. From the BSE image of the ($\text{MgH}_2+\text{TiC}+\text{Ni}$), the Ni could not be investigated due to the very small size of Ni nanoparticles.

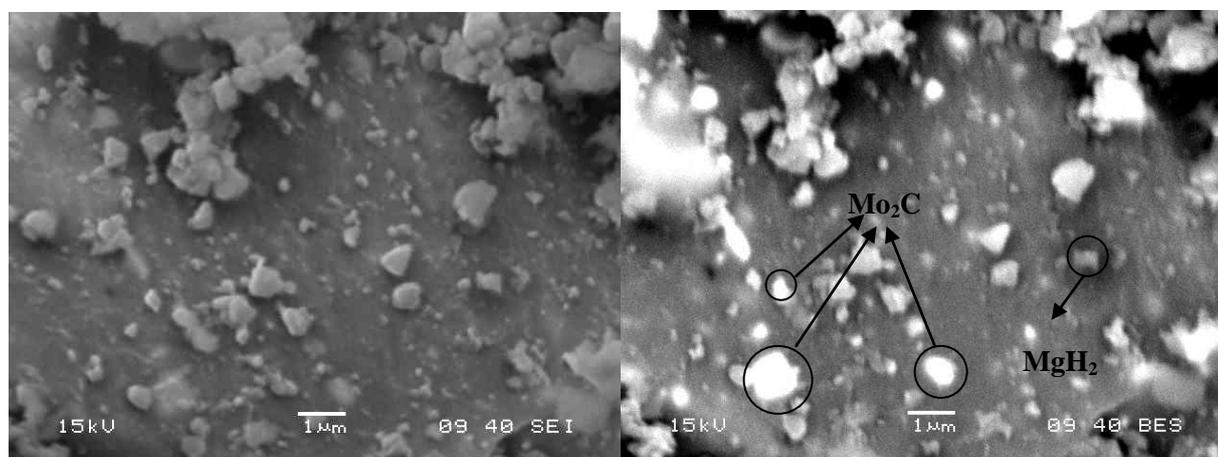


Figure 4-25 SEM-BSE images of ($\text{MgH}_2+\text{Mo}_2\text{C}+\text{Ni}$)

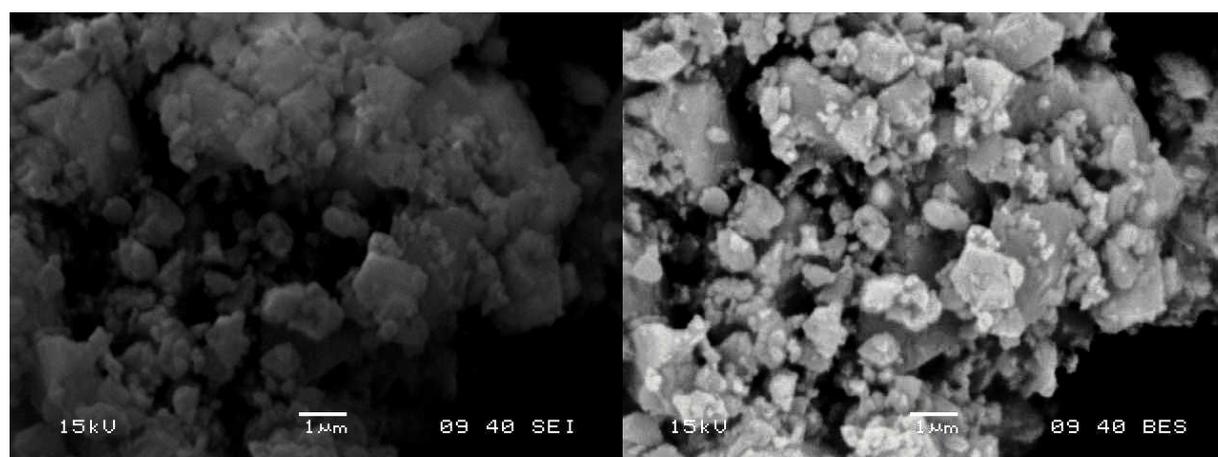


Figure 4-26 SEM-BSE images of ($\text{MgH}_2+\text{TiC}+\text{Ni}$)

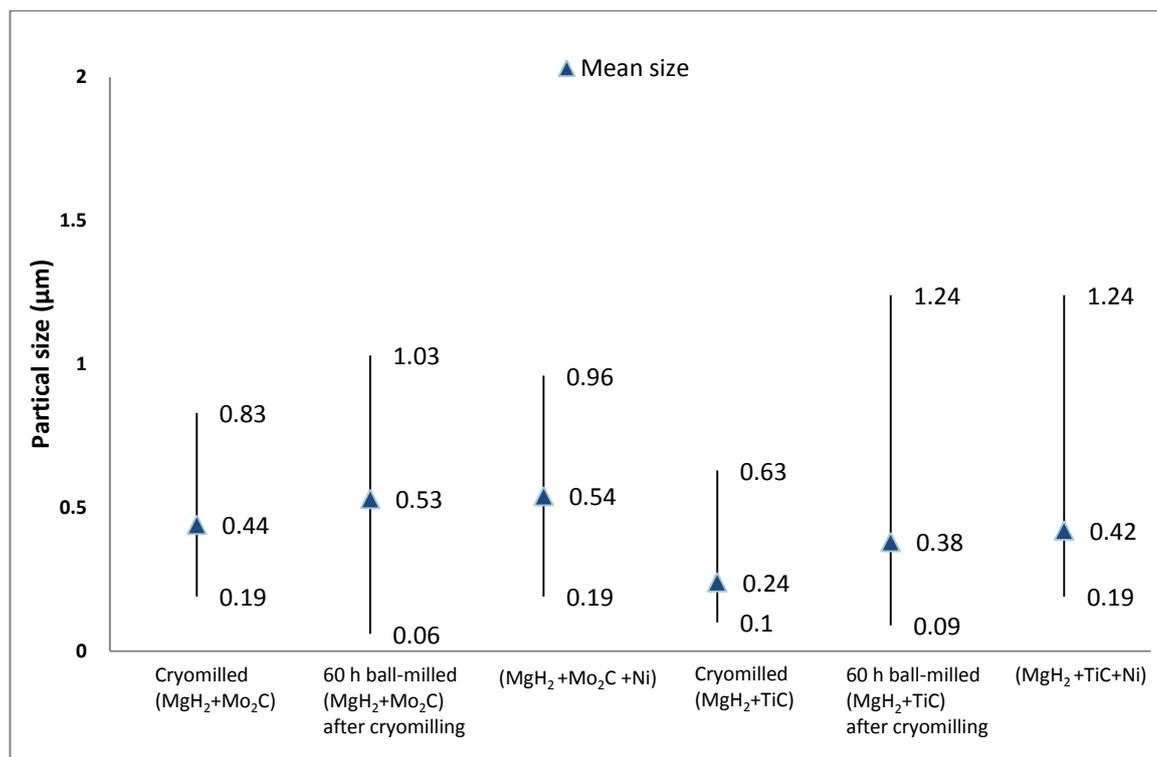


Figure 4-27 Comparison of mean particle size of the milled samples

4.4.2 Dehydrogenation of milled mixtures of MgH₂ and catalysts

The hydrogen desorption performance of the samples was investigated by thermal analysis at 10 k/min from room temperature to 500 °C under helium atmosphere, as seen in Figure 4-28. The temperatures corresponding to desorption peaks are presented in DTG curves of the mixtures, Figure 4-29. The starting desorption temperature of the 60 h ball-milled MgH₂ with Ni for 15 min without carbides is 195 °C, similar to that of (MgH₂+TiC+Ni), 190 °C, whereas the onset temperature of (MgH₂+Mo₂C+Ni) is higher, 240 °C. The peak temperatures of (MgH₂+TiC+Ni), (MgH₂+Ni) and (MgH₂+ Mo₂C+Ni) are 282 °C, 301 °C and 328 °C respectively. From Figure 4-12 and Figure 4-13, the onset and peak temperature of 60 h ball-milled (MgH₂+2% TiC) without Ni are 190 °C and 275 °C respectively, which are slightly lower than (MgH₂+ TiC+Ni). The possible reasons are: firstly, the mean particle size of (MgH₂+TiC+Ni) is 0.42 ± 0.02 µm, slightly bigger than that of (MgH₂+TiC), 0.38 ± 0.02 µm; in addition, it is suggested that the Ni nanoparticles were dispersed on the surface

of MgH_2 with the short milling process. The catalytic effect on the inner phase transformation and growth is limited. According to the discussion in section 4.2, some TiC nanoparticles are inserted into the inner space or grain boundary of MgH_2 particles. It proves that TiC is a very effective catalyst on improving the hydrogen desorption kinetics of MgH_2 , and possibly have better performance than Ni in terms of efficiency and stability.

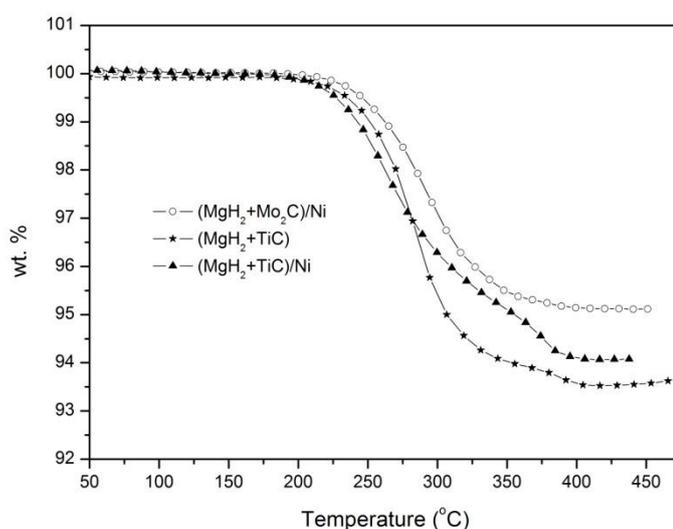


Figure 4-28 TG curves of the milled samples with Ni

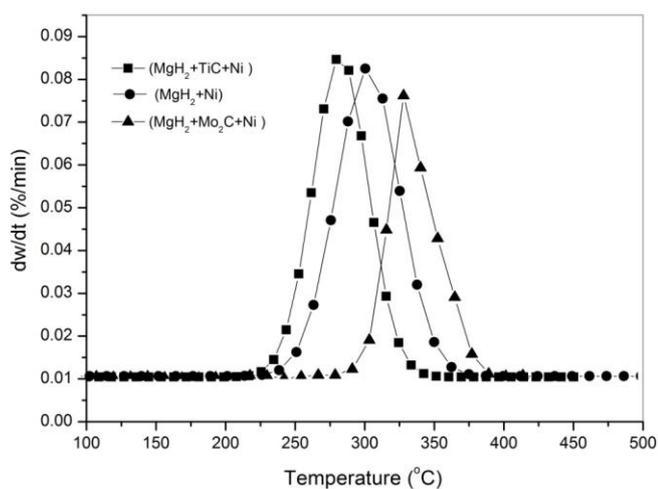


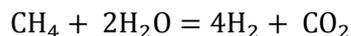
Figure 4-29 DTG curves of the milled samples with Ni, derived from Figure 4-28

4.4.3 Summary

Mixing of 60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) with Ni for 15 min reduces the hydrogen desorption temperature of MgH_2 . However, the 60 h ball-milled ($\text{MgH}_2 + \text{TiC}$) without Ni has more effective catalysis on hydrogen desorption of MgH_2 than ($\text{MgH}_2 + \text{TiC} + \text{Ni}$), because 60 h ball-milled ($\text{MgH}_2 + \text{TiC}$) get the finer nanoparticle size of catalysts and the TiC nanoparticles are inserted into the grain boundary or inner space of MgH_2 . Experimental results show that TiC has better performance in improving hydrogen desorption kinetics of MgH_2 .

4.5 Effects of Selected Gas Mixture of (H₂ + CO₂) on Hydrogen Sorption of MgH₂

One of the current common hydrogen production methods is steam re-forming of natural gas^{175, 176}, which can be represented by the following reaction



Hydrogen produced during this process is accompanied by about 20% CO₂ and some CO. To obtain pure hydrogen for fuel cell application, H₂ separation and purification are usually required steps. So far, both the storage and use of hydrogen involve pure hydrogen, which is generally produced via a very expensive separation/purification process. A low cost and high tolerant material is required for hydrogen storage or purification.

In order to evaluate possible effects of impurities on hydrogen sorption of Mg, a preliminary study was carried out using a gas mixture of (80 % H₂ + 20 % CO₂) to charge a dehydrogenated MgH₂ with and without transition metal carbides at a pressure of 8bar and temperature of 300 °C in IGA coupled with mass-spectrometry (MS). It is interesting to see how the transition metal carbides influence the selectivity and kinetics of the sorption process from the gas mixture.

The samples were prepared by cryomilled and ball-milled. 80 % H₂ + 20 % CO₂ gas mixture is considered as the model product of the steam reforming of natural gas¹⁷⁷. Before charging the samples with the standard gas mixture, MgH₂ or doped MgH₂ was dehydrogenated fully to Mg. Figure 4-30 shows TG-Mass spectrometry (MS) curves of H₂ + CO₂ absorption of the empty sample holder to compare with the sorption of samples. There was no weight change during the blank test. Whereas it was found that the mass spectrometry curves of three gases, H₂O, CH₄ and CO were increasing with time, which means there are impurities gases H₂O, CH₄ and CO existing in the original H₂ + CO₂ gas mixture.

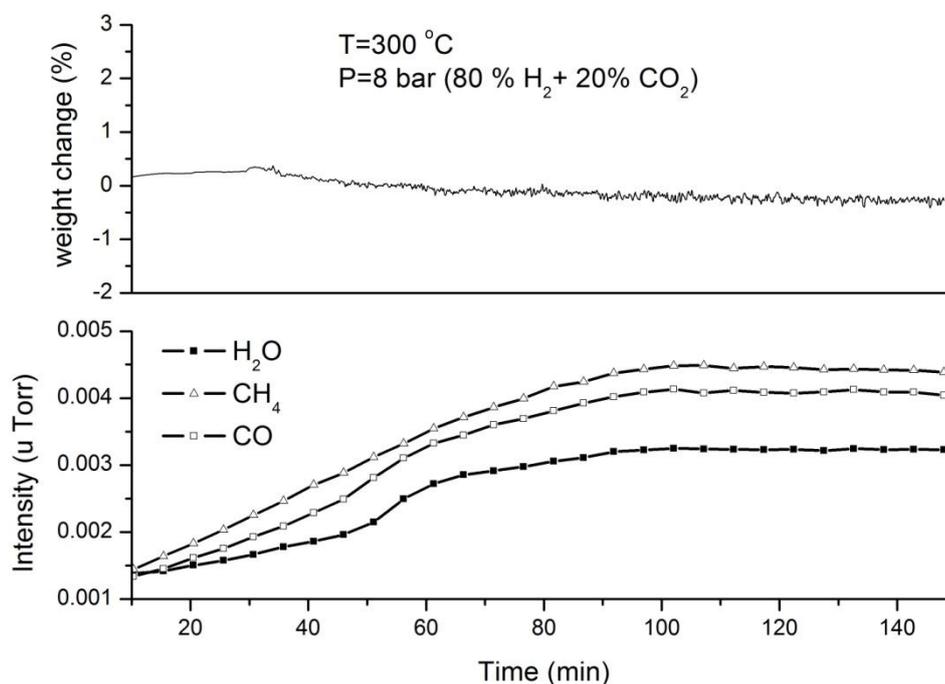
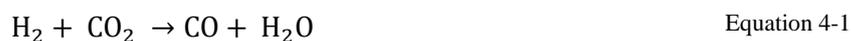


Figure 4-30 TG-MS of the empty sample holder, measured at 300 °C under 8 bar H₂+CO₂ pressure.

4.5.1 (H₂ + CO₂) absorption of dehydrogenated cryomilled MgH₂

The (H₂ + CO₂) absorption behavior of the dehydrogenated cryomilled MgH₂ from 80% H₂ + 20% CO₂ gas mixture is shown in Figure 4-31. The maximum of absorption was more than 8 wt % in 120 min, which even exceeded the theoretical hydrogen storage capacity of Mg (7.6 wt %). Thus, the reactions between dehydrated cryomilled MgH₂ and 80% H₂ + 20% CO₂ gas mixture at 300 °C were further studied due to its over-absorption. There are three possible reactions proposed as follows.



Higher temperature over 600 °C or catalyst (e.g. Pt) is required for the reaction between H₂ and CO₂ (Equation 4-1). The reaction doesn't contribute to the weight gain of the sample,

and there are no peaks occurred along the CO and H₂O traces from mass spectrometry analysis. The reaction between H₂ and CO₂ (Equation 4-1) is not possible under the present experimental conditions. The hydrogenation process of Mg (Equation 4-2) should happen at 300 °C under around 6.4 bar H₂ partial pressure. The weight gain is over 7.6 wt %- the theoretical value. Thus the third reaction (Equation 4-3) definitely happened. From Equation 4-3, it has been calculated that the weight gain can be theoretically increased to 71.4 wt %, if the reaction is carried out fully. But the surface of Mg/MgH₂ particles could be covered by MgCO₃ which stopped the inner Mg/MgH₂ interacting with the gases further. The reaction rate decreased greatly after 40 min, as shown in Figure 4-31. The CO, H₂O and CH₄ traces from the mass spectrometry analysis could be from the original flow gas of (H₂+ CO₂). MgO is always existing as an impurity in the Mg/MgH₂ samples and easy to react with CO₂. The interaction of CO₂ with MgO was studied by several research groups¹⁷⁸⁻¹⁸¹. The formation of magnesium carbonate from the reaction between CO₂ and MgO was detected by XPS, UPS, LEED.

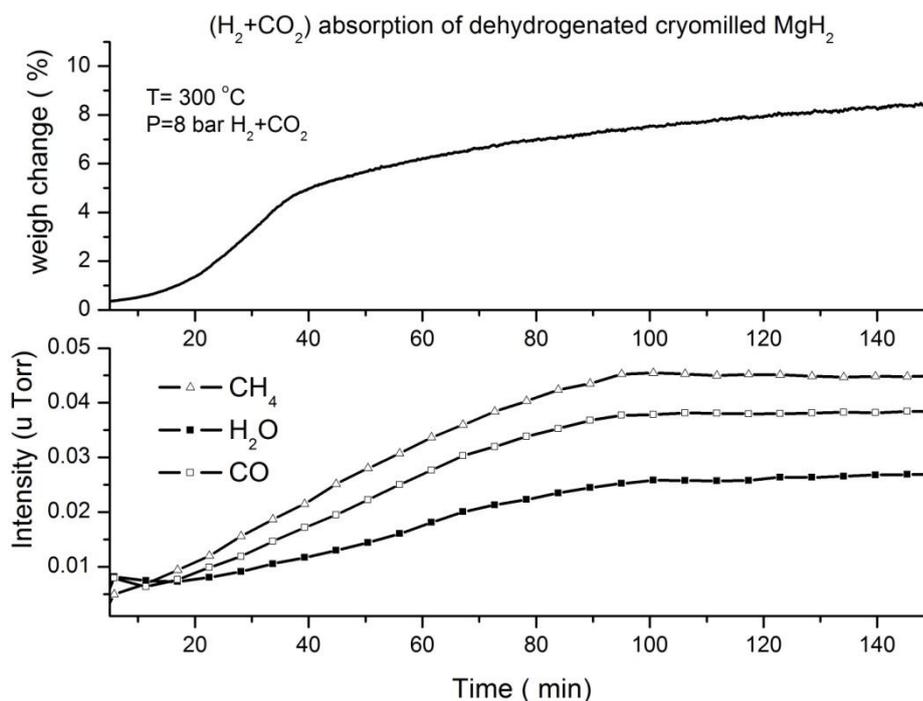


Figure 4-31 TG-MS of the dehydrogenated cryomilled-MgH₂, measured at 300 °C under 8bar H₂+CO₂ pressure. After (80 % H₂ + 20 % CO₂) absorption of dehydrogenated cryomilled-MgH₂, the sample was decomposed with the temperature range from room temperature to 500 °C at 1 bar helium pressure. The TG-MS curves are shown in Figure 4-32. The starting desorption temperature is about 360 °C, which is the same as that of cryomilled-MgH₂. The 1.5 % weight loss of dehydrogenated cryomilled-MgH₂ after (H₂+CO₂) absorption is corresponding to the dehydrogenation of MgH₂. MgO and MgCO₃ are stable from room temperature up to 500 °C in helium gas, which didn't have any weight loss. The ~ 6.5 % weight difference between absorption and desorption processes is due to the formation of MgO and MgCO₃. The reason that no peak of water appeared in MS curves is that H₂O further reacted with magnesium to form Magnesium hydroxide and hydrogen. The reason that there is no peak of H₂ in the MS analysis (Figure 4-32) is possibly due to the small quantity of hydrogen generated during the desorption, which is out of the detection range of MS.

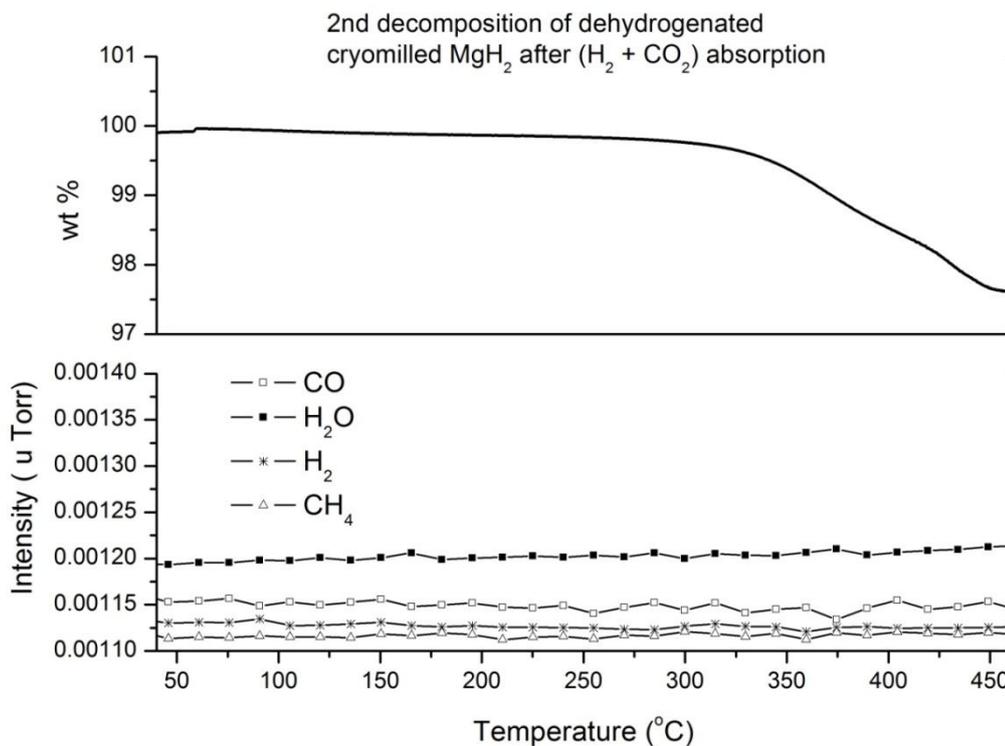


Figure 4-32 TG-MS of 2nd decomposition of dehydrogenated cryomilled MgH_2 after $\text{H}_2 + \text{CO}_2$ absorption, measured at 1 bar helium pressure.

From XRD patterns of the samples, Figure 4-33a, the peaks of Mg, MgO, MgH_2 , and MgCO_3 was detected after $(\text{H}_2 + \text{CO}_2)$ absorption of dehydrogenated cryomilled- MgH_2 . The obvious peaks of Mg are due to the incomplete reaction, which can be concluded from the weight gain, 8 wt%, which is much less than the theoretical value of 71.4 wt%. After the second decomposition, the peaks of MgH_2 were not detected and the main phases were Mg and MgCO_3 (Figure 4-33b). This also demonstrated that MgH_2 was dehydrogenated to Mg during heating. In conclusion, the possible reaction steps of the dehydrogenated cryomilled- MgH_2 with the (80% H_2 + 20 % CO_2) gas mixture at 300 $^{\circ}\text{C}$ are listed as follows. The calculated enthalpy changes show equation 4-2 and 4-4 are endothermic reactions or heat-absorbing processes, which mean the reactions need to absorb energy from the surroundings in the form of heat.

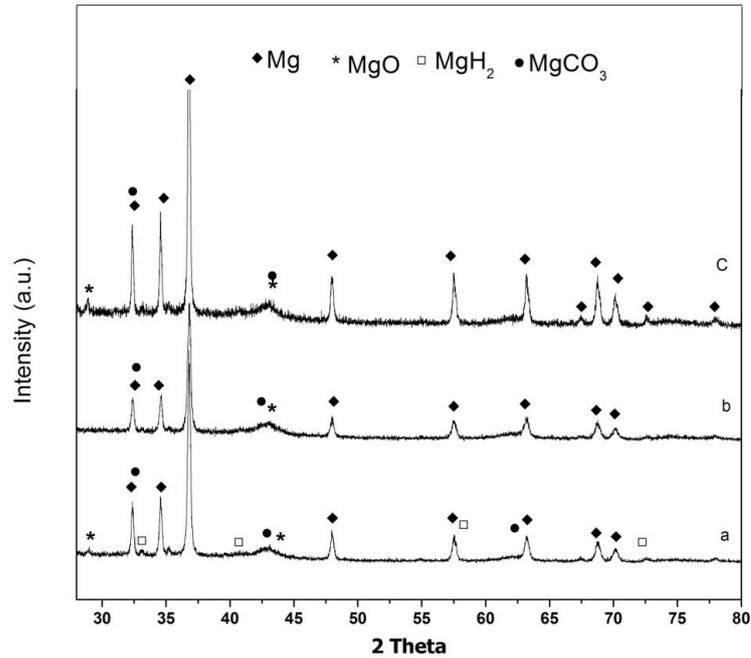


Figure 4-33 XRD patterns of the samples: a, ($\text{H}_2 + \text{CO}_2$) absorption of dehydrogenated cryomilled- MgH_2 ; b, 2nd dehydrogenation of dehydrogenated cryomilled- MgH_2 after ($\text{H}_2 + \text{CO}_2$) absorption; and c, CO_2 absorption of dehydrogenated cryomilled- MgH_2

4.5.2 ($\text{H}_2 + \text{CO}_2$) absorption of dehydrogenated milled-($\text{MgH}_2 + \text{TiC} / \text{Mo}_2\text{C}$)

From Figure 4-34, the weight of dehydrogenated as-received MgH_2 didn't increase after ($\text{H}_2 + \text{CO}_2$) absorption at 300 °C and 8 bar gas pressure. The weight gain of dehydrogenated 60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) after cryomilling was less than 1.5 ± 0.02 wt%, whereas that of milled ($\text{MgH}_2 + \text{TiC}$) was 5.5 ± 0.02 wt% in 230 min, which were less than weight gain of dehydrogenated cryomilled MgH_2 . Thus it indicates that cryomilled MgH_2 after dehydrogenation has strong ability to absorb or react with 80 % $\text{H}_2 + 20\%$ CO_2 gas mixture. TiC inserted in the inner space of grain boundaries of MgH_2 particles, which enhanced H_2

absorption rate of Mg and induced fast formation of MgCO_3 , therefore stopped the interaction between Mg/MgH_2 and H_2/CO_2 molecules and decreased reaction rate.

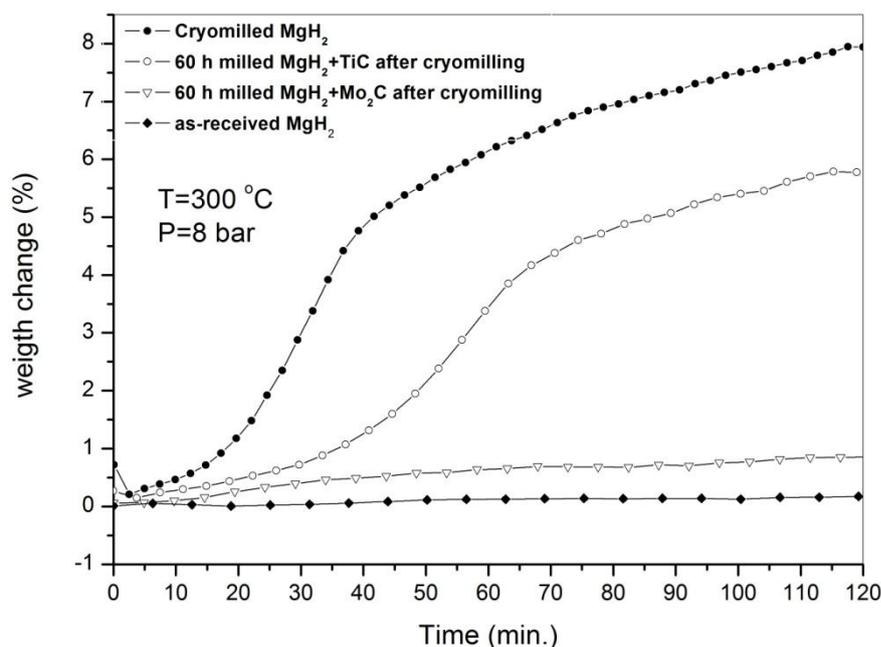


Figure 4-34 (H_2+CO_2) absorption of dehydrogenated MgH_2 with and without catalyst, measured at 300 °C under 8 bar ($\text{H}_2 + \text{CO}_2$) pressure.

4.5.3 Interaction between Mg/MgH_2 and CO_2 gas

To confirm the reaction between MgH_2 and CO_2 , both the dehydrogenated cryomilled- MgH_2 and the cryomilled- MgH_2 were subjected to a pure CO_2 atmosphere at 300 °C and 8 bar CO_2 pressure, shown in Figure 4-35 and Figure 4-36. The sample weight of the dehydrogenated cryomilled- MgH_2 almost increased 0.8 ± 0.02 wt%. From XRD analysis, Figure 4-33c, MgCO_3 and MgO are the new compounds formed during CO_2 absorption of dehydrogenated cryomilled MgH_2 adsorbed at 8 bar CO_2 atmosphere. The reaction of CO_2 with Mg was studied by XRS and EELS^{182, 183}. A mechanism for the carbonate formation observed above 100 K was put forward. It is suggested that dissociative absorption of oxygen takes place,

followed by the chemisorptions of CO_2 at oxygen sites. The reaction can be presented as follows:



This is an endothermic reaction with $\Delta H_{298} = 272.8 \text{ kJ/mol}$. Also, the MgO easily reacts with CO_2 under the experimental conditions to form MgCO_3 , Equation 4-5, which has been detected by XRD.

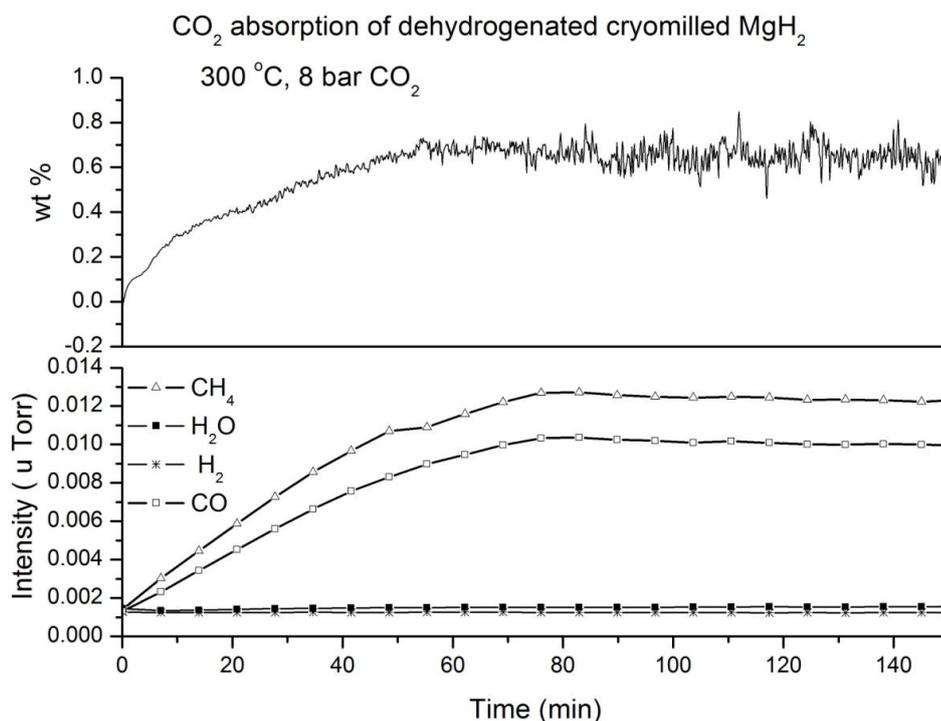


Figure 4-35 TG-MS of CO_2 absorption of dehydrogenated cryomilled- MgH_2 , measured at $300 \text{ }^\circ\text{C}$ under 8 bar CO_2 pressure.

From Figure 4-36, the weight of cryomilled- MgH_2 increased to 5 wt% during the CO_2 absorption process, which is much higher than that of dehydrogenated cryomilled- MgH_2 (0.8 wt %). Thus MgH_2 can absorb CO_2 more easily than Mg . From the above, it can be confirmed that the main reaction steps of dehydrogenated cryomilled- MgH_2 with (H_2+CO_2)

gas mixture are hydrogenation of Mg to form MgH_2 , and then the reaction between MgH_2 and CO_2 to form MgO and gas mixtures. In the main reaction steps, the side reactions happened, such as Equation 4-5 and the reaction between MgO and H_2O .

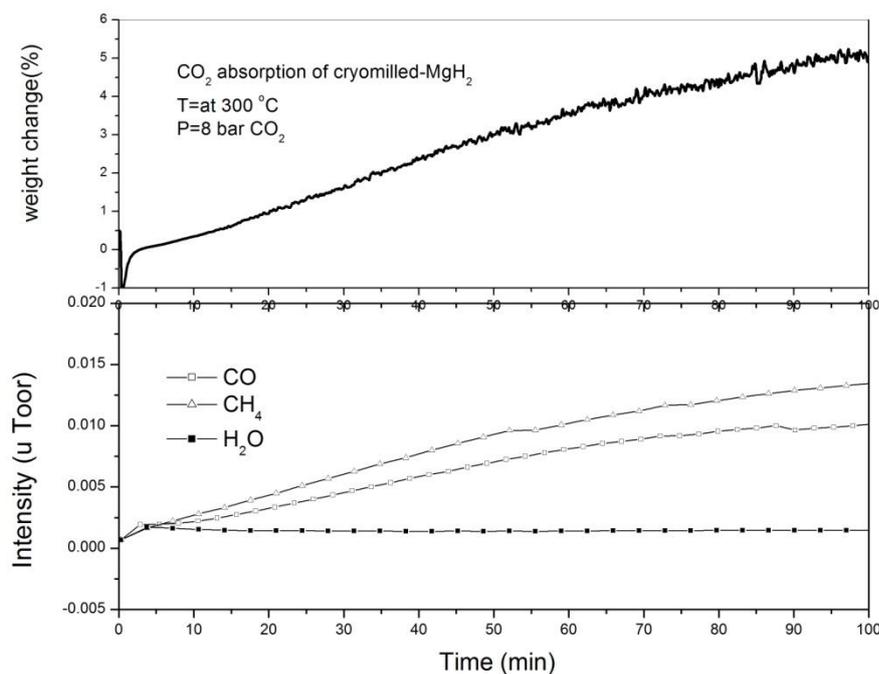


Figure 4-36 TG-MS of CO_2 absorption of cryomilled- MgH_2 , measured at 300 °C under 8 bar CO_2 pressure.

4.5.4 Summary

The reactions of Mg (from dehydrogenated MgH_2) with (80% H_2 + 20% CO_2) gas mixture at 300 °C have been proved to occur and is rather complex. Magnesium preferentially reacts with H_2 due to the high content of H_2 in mixture gas. Then MgH_2 reacts with CO_2 to form gas mixtures, such as CO and H_2O etc. and MgO, which makes further reaction with CO_2 to form MgCO_3 . Reaction mechanisms need to be studied further in the future work.

CHAPTER 5 GENERAL DISCUSSION

5.1 The Effect of Milling Conditions on Microstructure and Hydrogen Sorption Properties of Magnesium Hydride.

Magnesium hydride (MgH_2) shows great potential as a material for reversible hydrogen storage because it is abundant, inexpensive, environmentally benign, easy to handle and possesses a sufficient hydrogen storage capacity (7.6 wt %). It is well known that a breakthrough in the magnesium hydride technology has been achieved by using the high-energy mechanical (ball) milling technique to prepare nanocrystalline hydride powders^{77, 159}. Milling of MgH_2 instead of pure Mg produces nanocrystalline powders with larger surface areas beneficial to the hydrogen sorption process³⁰. Nanocrystalline magnesium hydride exhibits fast absorption and desorption kinetics at 300 °C when compared with its non-milled counterpart⁹⁵. This behavior has been attributed to the faster diffusion of hydrogen along grain boundaries and the higher number of heterogeneous nucleation sites for hydrogen during absorption or the pure magnesium phases during desorption. Unfortunately, the slow hydrogenation/dehydrogenation kinetics and the high desorption temperatures remain problematic. To overcome these problems further research is needed.

In my work, there are two types of millings, cryogenic milling and high energy ball milling, which are used for the engineering of MgH_2 in its nanocrystalline form in combination with different additives. The microstructural and hydriding/dehydriding properties of nanocrystalline MgH_2 prepared by cryogenic milling and ball milling have been investigated in the present work.

The estimates for the nanograin size of the as-received MgH_2 , calculated based on XRD patterns¹⁸⁴, is of the order of 65 ± 5 nm. After 8 h cryogenic milling, the grain size of MgH_2 has decreased greatly to 25 ± 3 nm. It has been suggested that the presence of liquid nitrogen during cryomilling has several advantages. For example, decreased oxygen

contamination¹⁸⁵ and enhanced deformation during milling¹⁶². In particular cryogenic milling offers an effective solution for achieving fine powders by enhancing the brittleness of the materials and reducing their tensile strength for materials²². With a further 60 h ball milling, the grain size of MgH₂ is only reduced slightly to 20 ± 3 nm. Therefore, the cryogenic milling process is very effective in reducing crystalline size of MgH₂ and further high energy ball milling only reduces the grain size by a nominal extent. Cryogenic milling provides significant process improvements in terms of the surface residual stresses and the effectiveness of grinding forces mainly due to substantial temperature reductions in the grinding zone, and a decrease in the magnitude of tensile residual stresses for all the materials¹⁸⁶. Despite this, peaks of the γ -MgH₂, which is known as a high-pressure orthorhombic phase, are observed in the ball-milled samples.

The 8 h cryogenically milled MgH₂ presents more granular surfaces as compared to the further 60 h ball-milled MgH₂. The cryomilled MgH₂ has irregular shapes resembling the popcorn structure and agglomerate together, which is typical for small particles, as seen in Figure 4-2. The nanoparticle size distributions show the long time ball-milled powders appear more heterogeneous, containing a large number of larger and smaller particles, presumably formed by the clustering and cold-welding of small particles (Figure 4-2, Figure 4-9 and Figure 4-18). The particle size distribution after 60 h ball-milling becomes broader compared with that of only 8 h cryomilling. This is explained by the continuous welding and fracture of particles caused by the collision with milling media balls¹⁸⁷. These results are in good agreement with the results reported by Varin et al.¹⁸⁸ and Reule et al.¹⁸⁹, who also observed a propensity for the clustering and cold-welding of commercial MgH₂ into larger particles during milling for durations longer than 10 h.

The desorption and absorption curves of MgH₂ after cryogenic milling and ball milling were compared to the as-received MgH₂ powder. The 8 h cryogenic milling leads to a visible

enhancement of both desorption and absorption kinetics. The pronounced differences are observed in the desorption kinetics profile (Figure 4-3 and Figure 4-4). There is a significant release of hydrogen under the pressure of 1 bar by all the cryomilled MgH_2 samples at 320 °C and ball-milled MgH_2 samples at 305 °C, while the desorption of as-received MgH_2 starts at 418 °C, Table 5-1. The absorption kinetics of as-received MgH_2 is much lower than the cryomilled and ball-milled samples. Previous reports have confirmed that the milling process is specially suited to the fabrication of nanocrystalline hydrides exhibiting very fast hydrogen sorption properties. It could be concluded that the most likely explanation for these findings is that milling has the effect of reducing the particle and crystallite size, increasing the specific surface area of the material. This hypothesis would match the results as there were no pronounced differences in the hydrogen desorption and absorption kinetics between the 8 h cryomilled MgH_2 and further 60 h ball-milled MgH_2 after cryomilling. Both the materials had very similar particle and grain sizes compared with those of the as-received MgH_2 .

Reducing the particle size and grain size of MgH_2 increases the kinetics of absorption while maintaining the hydrogen storage capacity. Cryogenic milling is effective in reducing the grain sizes and particle sizes. Unfortunately the decomposition of MgH_2 , even in its nanocrystalline form, is not possible below 300 °C. This internal (material) drawback of Mg/MgH_2 can be partially overcome by the addition of catalysts to further enhance the absorption and desorption kinetics of hydrogen.

Table 5-1 Hydrogen sorption parameters of all samples.

Sample	Grain Size of β -MgH ₂ (nm)	Mean particle size (μ m)	T _{Onset} (°C)	T _{Peak} (°C)	E' (KJ/mol)*	Absorption Rate (wt. %/min)
As-received MgH ₂	65 ± 5	30 ± 2	418	434	235 ± 10	0.008 ± 0.00004
8 h cryomilled MgH ₂	25 ± 3	0.19 ± 0.02	320	362	200 ± 9	0.06 ± 0.0001
60 h ball-milled MgH ₂ after cryomilling	20 ± 3	0.28 ± 0.02	305	360	199 ± 9	0.1 ± 0.0001
8 h cryomilled (MgH ₂ + 2%TiC)	27 ± 3	0.2 ± 0.02	280	332	157 ± 9	0.08 ± 0.0001
60 h ball-milled (MgH ₂ + 2%TiC) after cryomilling	23 ± 3	0.29 ± 0.02	190	275	104 ± 6	0.12 ± 0.0001
60 h ball-milled (MgH ₂ + 8%TiC) after cryomilling	20 ± 3	0.3 ± 0.02	175	264	89 ± 5	–
8 h cryomilled (MgH ₂ +Mo ₂ C)	27 ± 3	0.44 ± 0.02	320	360	217 ± 10	0.074 ± 0.0001 (40- 60 min) 0.021 ± 0.0001 (60-180 min)
60 h ball-milled (MgH ₂ +Mo ₂ C) after cryomilling	18 ± 3	0.53 ± 0.02	300	358	167 ± 9	0.074 ± 0.0001 (40- 60 min) 0.023 ± 0.0001 (60-180 min)
(MgH ₂ +2%Ni)	--	--	190	301	--	--
(MgH ₂ +2%Mo ₂ C+2%Ni)	--	0.54 ± 0.02	240	328	--	--
(MgH ₂ +2%TiC+2%Ni)	--	0.42 ± 0.02	195	282	--	--

5.2 The Catalytic Mechanism of TiC on Hydrogen Sorption Properties of Magnesium Hydride

The phenomenon of mechanical milling helps to pulverize the particles of MgH_2 into nanocrystalline phases and thus leads to lowering the activation energy of desorption¹⁵⁹. The height of the activation energy barrier depends on the surface elements¹². It can be concluded that the activation barrier has been drastically lowered by nanocatalyst doping, suggesting that the collision frequency between the H_2 molecules and transition metal nanoparticles increases with decreasing particle sizes for MgH_2 and the catalysts, shown in Table 4-1, Table 4-2 and Table 4-3. From the experimental results, two facts with regard to the thermal stability and the sorption kinetics can be extracted: (i) TiC nanoparticles reduce the temperature for hydrogen release from MgH_2 , while Mo_2C does not. (ii) TiC enhances the hydrogen absorption kinetics of Mg/MgH_2 ; Mo_2C shows almost no influence on that of Mg/MgH_2 . These results indicate clearly that the catalytic behaviors are distinct from each other, depending not only on the hydrides, but also on the transition metal carbides present. A correlation among them is discussed below.

5.2.1 Analysis of hydrogen sorption of MgH_2 catalyzed by TiC

Recently, it has been reported that metallic Ti could catalytically improve the hydrogen storage property of Mg-based hydrides. There are two different mechanisms reported for the enhancement of the reaction kinetics of MgH_2 with dopants. One believes the interactions between the hydrides and the Ti-containing agents weakens the Mg-H bonds and favors the recombination of hydrogen atoms toward the hydrogen molecules^{22, 190}. Examples include the classic Ti-halides (e.g. TiCl_3) reacting with MgH_2 to form TiH_x , which acts as the catalyst responsible for hydrogen dissociation/recombination at the surface of hydride after ball milling and hydriding/dehydriding processes. The other opinion is that Ti or metallic Ti acts as a classic catalyst for hydrogen dissociation/recombination on the surface of reacting

solids^{191, 192}. From XRD analysis, TiC didn't react with MgH₂ during the milling and dehydrogenation/hydrogenation processes. This means that TiC and MgH₂ maintain their original phase structures in different hydriding/dehydriding stages throughout, as shown from the XRD patterns in Figure 4-1, and Figure 4-7. These results prove that TiC had not reacted with MgH₂ in this study, and no TiH_x or other alloy was formed during the ball milling and hydriding/dehydriding processes. Combining the results of the above-mentioned hydrogen sorption properties of MgH₂ catalyzed by TiC composite and the results of our previous investigation, we believe that TiC nanoparticles are existing stably and separately around the MgH₂ matrix as the catalytically active species for the reversible hydrogen storage of the composite. Because TiC powder is thermodynamically more stable than other Ti-chloride catalysts^{193, 194}, utilization of this stable TiC catalyst can be identified as an effective way to catalytically enhance the hydrogen sorption properties of MgH₂ without generating any dead weight byproducts. This makes TiC's catalytic mechanism similar to that of TiN¹⁹⁵ and TiO₂¹⁹⁶.

The dehydrogenation of magnesium hydride consists of the following steps: decomposition of the hydride phase to form the magnesium phase, diffusion of hydrogen atoms, and combination of hydrogen atoms into molecules around the TiC active sites and desorption of hydrogen molecules^{191, 197}, as Figure 5-1. Similarly, the catalytic hydrogenation process in this system follows the reverse order of the above dehydrogenation reaction steps.

It is believed that the greatly reduced particle size in the ball-milled composite would increase the hydrogenation/dehydrogenation reaction activity sites and hence it would be beneficial to the enhancement of hydrogen storage kinetics as shown in Table 5-1. It also can be found that the mean particle size of 60 h ball-milled (MgH₂+TiC) is larger than that of the 60 h ball-milled MgH₂ without TiC. This is because the TiC content of the (MgH₂+TiC) composite is hard and brittle, and take longer to pulverize into fine particles.

The SEM and TEM images of the (MgH₂+TiC) composite, Figure 4-9 and **Error! Reference source not found.**, show that some of TiC nanoparticles have been inserted into the MgH₂ grain boundaries. The onset and peak temperature of hydrogen desorption of the 60 h ball-milled (MgH₂+TiC) is much lower than the 60 h ball-milled MgH₂ without TiC. This is due to the shorter hydrogen diffusion distance within the (MgH₂+TiC) composite, making the diffusion of hydrogen atoms easier and quicker across MgH₂. Likewise the activation energy of desorption for the (MgH₂+TiC) decreased greatly. Throughout the 8 h cryogenic milling and a further 60 h ball milling MgH₂ mixed with the catalyst TiC to produce a favorable reactive composite with sufficient area for contacting hydrogen and a large amount of defects acting as reaction active sites. TiC active sites have a greater affinity for hydrogen than MgH₂, which reduces the bond strength between Mg-H. In addition, Xiao et al. believe¹⁹² that the smaller TiC particles inlaid on the surface of the larger matrix act not only as the catalytic active sites for the redox reaction of hydrogen but also as a source for hydrogen spillover, assisting hydrogen diffusion into the matrix. The spillover properties of noble metal catalyst have been proved by Xu et al¹⁹⁷.

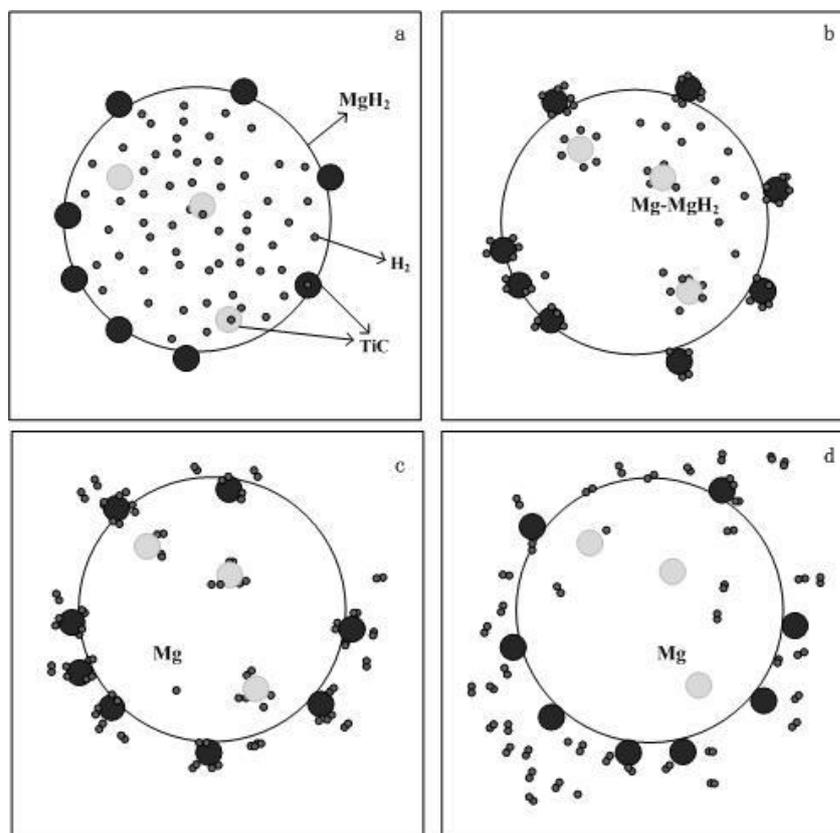


Figure 5-1 Scheme of the (MgH_2+TiC) mixture in different states of dehydrogenation. (a) Milled MgH_2 with TiC nanoparticles, (b) Decomposition of hydride phase to form magnesium phase, (c) Combination with hydrogen atoms into molecules, and (d) desorption of hydrogen molecules

From Figure 4-10 and Table 5-1, it is apparent there are no big differences between the sizes of the cryomilled and ball-milled nanoparticles of (MgH_2+TiC). However, the hydrogen sorption properties and kinetics of 60 h milled (MgH_2+TiC) are faster than 8 h cryomilled (MgH_2+TiC). This is because the high energy ball milling for 60 h forces TiC nanoparticles into the inner space or grain boundaries of Mg/ MgH_2 . Consequently the catalytic effect on transformation and growth of the inner phase is improved.

In addition, compared with the as-received MgH_2 sample, the onset and peak temperatures of hydrogen desorption decreased significantly from 418 °C to 190 °C and from 434 °C to 275 °C with 2 % TiC. The ($\text{MgH}_2+8\%$ TiC) showed a slightly greater effect on hydrogen sorption than ($\text{MgH}_2 + 2\%$ TiC), with an onset temperature of 175 °C and a peak

temperature of 264 °C. Whilst doping can lower the hydrogen desorption temperature, heavy doping can lower the hydrogen storage capacity, slow kinetics and increase the rate of hysteresis. Thus we can conclude that a low amount of TiC as a catalyst can improve the hydrogen sorption kinetics of MgH₂, but a large amount of TiC could block the hydrogen diffusion and lower the hydrogen capacity. Ranjbar et al.¹⁵ reported 2 wt % SiC doped MgH₂ shows the optimum desorption kinetics and too much SiC addition degraded the hydrogen absorption/desorption kinetics. Xie et al.¹³⁹ reported that the desorption kinetics enhance with increasing Ni nanoparticles when the quantity of catalyst is below 25 wt%. When the quantity of Ni nanoparticles exceeds 25 wt%, the improvement to the desorption kinetics is minor.

5.2.2 Structure of TiC to improve catalytic effect

TiC is a typical faceted crystal. Figure 5-2(a) shows its crystal structure. C atoms occupy the octahedral positions. If viewed along the axis perpendicular to the (111) planes, Ti and C atoms form a hexagonal shape as shown in Figure 5-2 (b). It has been reported that TiC has a simple-hexagonal structure¹⁹⁸. Chien et al.¹⁹⁹ reported that stress induced the transformation of TiC from cubic to hexagonal structures. As reported by Chien²⁰⁰, sub-boundary defect structures in single crystal TiC were observed. Because high-energy ball milling is known to introduce a high number of crystal lattice defects into a material, we have investigated in chapter 4.2 that some TiC nanoparticles are inserted into the grain boundaries of MgH₂ nanoparticles. The microstructure of MgH₂ was changed by not only high-energy ball milling but also the addition of TiC. The increasing structural defects effectively expedite hydrogen diffusion, which is the control step in the hydrogen sorption processes^{20, 192, 197}.

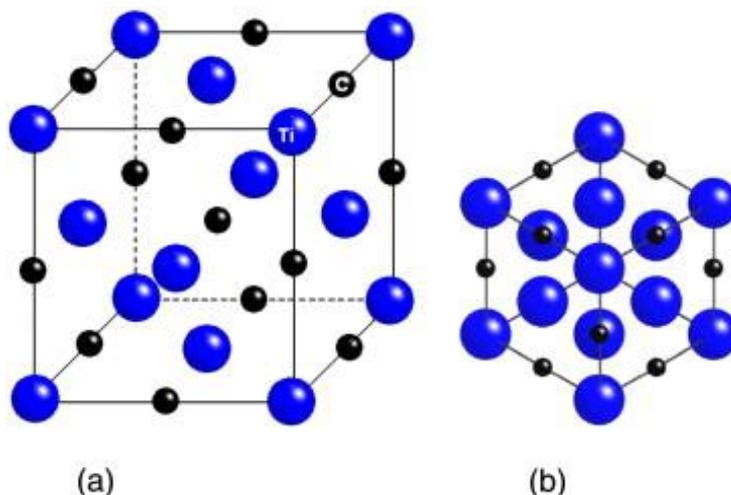


Figure 5-2 (a) Crystal structure of TiC, and (b) projection of Ti-C atoms along [111] direction. The smaller atoms are C atoms.¹⁵¹

Titanium alloys have a high affinity for hydrogen¹⁰⁸. The research from Barkhordarian²⁰ indicates that strong transition-metal-hydrogen reaction energies will improve the catalytic activity on hydrogen sorption reactions. In our reaction system, the interaction between Ti ions and hydrogen atoms is due to the high affinity of Ti for the hydrogen. This attraction improves the hydrogen sorption kinetics of our materials.

5.2.3 Thermodynamic stability of TiC for catalysis

Barkhordarian et al.²⁰ proposed a transition metal compound, such as Nb_2O_5 , V_2O_5 and TiO_2 , as an effective catalyst and stated that the compound should have a low thermodynamic stability to allow a chemical interaction with the magnesium support. The enthalpies of formation for TiCl_3 and TiCl_4 are -240 and -201 kJ per Cl atom respectively, this makes TiCl_3 more stable than TiCl_4 . Therefore, Mg atoms will require less energy to change the electronic structure of the Ti in TiCl_4 rather than TiCl_3 ²⁰. However, if the stability is too low, like Re_2O_7 (-180 kJ/mol), the compound reacts completely with magnesium and its catalytic activity is diminished. TiC is a stable compound with formation enthalpies of -190.4 ± 17.0

kJ/mol^{201} , which is a optimum stability of the transition metal compounds that have higher catalytic activity, comparing TiCl_3 and Re_2O_7 .

5.2.4 Summary

On the basis of the above discussion, the following mechanisms are proposed for the TiC catalyst influences upon the hydrogen sorption of MgH_2 . During absorption, hydrogen molecules disassociate on the Ti ions of TiC resulting in the formation of a Ti-H bond. The Ti ions dissociate hydrogen molecules and pass hydrogen atoms to the surrounding magnesium atoms leading to the formation of MgH_2 . In the case of desorption, Mg-H bonds are thermodynamically unstable, leading to dissociation from MgH_2 . The Ti ions of TiC then form a bond with hydrogen atoms, they act as an intermediate state which allows easier recombination for hydrogen atoms toward the molecular state.

5.3 Effect of Mo_2C and Ni on Hydrogen Sorption Properties of MgH_2

Comparing the particle size of ($\text{MgH}_2 + 2\% \text{TiC}$), the particle size of both 8 h cryomilled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) and 60 h ball-milled ($\text{MgH}_2 + \text{Mo}_2\text{C}$) after cryomilling is bigger, $0.44 \pm 0.02 \mu\text{m}$ and $0.53 \pm 0.02 \mu\text{m}$ respectively (Table 5-1). Most of the Mo_2C nanoparticles are dispersed on the surface on MgH_2 in the milling process, seen in Figure 4-18. The catalytic effect on the inner phase transformation and growth is limited. L. Xie et al.¹³⁹ have suggested that one principle of choosing a catalyst is according to the catalysts ability for enhancing the combination of H atoms. It has been suggested that during the dissociation of a H molecule, the σ electron of hydrogen first donates to a vacant metal d orbital. Then the bond is stabilized by back-donation of electrons from the filled d orbital to the anti-bonding orbital σ^* of the H_2 . Increasing the back-donation to σ^* facilitates to break the H-H bond to form H atoms. The combination of H atoms depends on the electron distribution and orbital structure of the transition metals²⁰². The atomic number of Mo in periodic table is 42, bigger

than Ti (22) and Ni (28). The valence electrons of Ti and Ni are on 3d and 4s orbital (Table 5-2), which have a stronger nuclear attraction to H atoms than Mo. It can explain the catalytic effect of TiC and Ni on hydrogen sorption of Mg/MgH₂ than that of Mo₂C.

It has been reported that Ni nanoparticles enhance the combination of hydrogen atoms to improve the desorption kinetics of MgH₂¹³⁹. In the study, Ni, as an additive mixing, with 60 h ball-milled (MgH₂+ Mo₂C) for 15 min reduces the hydrogen desorption temperature of MgH₂. However, the 60 h ball-milled (MgH₂+TiC) without Ni has better performance on hydrogen desorption than (MgH₂+TiC+Ni), shown in Table 5-1. It further confirms that TiC has a very effective catalyst on hydrogen sorption of MgH₂.

Table 5-2 Atomic Structure of Ti, Ni and Mo²⁰³

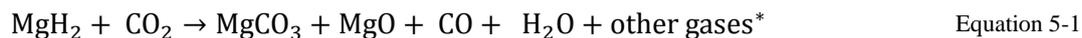
Element	atomic number	electron configuration	Valence Electrons
Ti	22	1s ² 2s ² p ⁶ 3s ² p ⁶ d ² 4s ²	3d ² 4s ²
Ni	28	1s ² 2s ² p ⁶ 3s ² p ⁶ d ⁸ 4s ²	3d ⁸ 4s ²
Mo	42	1s ² 2s ² p ⁶ 3s ² p ⁶ d ¹⁰ 4s ² p ⁶ d ⁵ 5s ¹	4d ⁵ 5s ¹

5.4 Interaction of Mg/MgH₂ with (H₂+CO₂) Gas Mixture

Studies of the reactions of Mg/MgH₂ in a gas mixture of (H₂+CO₂) are rather scarce. Interaction between (80 % H₂+ 20 % CO₂) and Mg/MgH₂ at 8 bar pressure and 300 °C is reported in this work. From the results in Section 4.5, (80 % H₂+ 20 % CO₂) reacts with Mg can be equal to the reaction of CO₂ with MgH₂, because the first step of sequenced reactions is hydrogenation of Mg.

It is well known that dissociative absorption of CO₂ occurs on a number of metals^{181, 204}. In these cases, the presence of hydrogen anions at the surface promotes the deoxidization of CO₂ to form carbon monoxide and methane. It is suggested here that the reduction of CO₂ on MgH₂ occurs in three steps: initially, the CO₂ dissociates on the surface and (Mg-O) bonds are formed. The second step is the formation of methane based on the reaction of atomic

hydrogen with C ions. Finally, the interaction of CO₂ with MgO produces MgCO₃. The content of MgH₂, MgO and MgCO₃ formed during the reaction varies with different ratio of H₂: CO₂ in the flow gas stream and the measurement pressure. Thus the reaction between MgH₂ and CO₂ can be presented as follows.



* other gases to be further confirmed

Due to the interaction of Mg/MgH₂ with (H₂+ CO₂) mixed gas. Mg, as a H₂ storage media, cannot tolerate the CO₂ impurities in a hydrogen flow gas, seen Section 4.5. It is of interest to note that the reactions of CO₂ on MgH₂ are of great importance for several reasons: (i) CO₂ is of interest as a reactant in hydrocarbon synthesis. (ii) CO₂ is to a large extent responsible for the green house effect and therefore contributes to global warming; the reduction of CO₂ or, alternatively, its conversion into more valuable chemicals, such as hydrocarbons, methanol and others, is therefore of considerable interest. (iii) The activation of CO₂ at biological surfaces involves metal complexes.^{179, 181, 182}

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

A systematic investigation was carried out on the sorption properties and structural stability of MgH_2 modified by a range of mechanical milling conditions and chemical additions. The influences of cryogenic milling and ball milling on particle size and grain size, microstructure and phase composition of materials were characterized using X-Ray diffraction, SEM and TEM. The effects of selected transition metal carbides on dehydrogenation/hydrogenation of MgH_2 were evaluated by TG and DTG. The findings are very useful in the development of new Mg-based hydrogen storage materials with rapid kinetics and lower desorption temperature, and the exploitation of an effective and stable catalyst to improve hydrogen sorption properties. The following conclusions were drawn from the investigation.

- 1) Cryogenic milling is very effective in reducing the grain and particle sizes of MgH_2 . The smallest mean powder particle size achieved in this work by 8 h cryogenic milling was 190 ± 20 nm.
- 2) The onset and peak desorption temperatures of MgH_2 were substantially reduced to 320 and 362 °C, respectively, by 8 h cryogenic milling, due to smaller and more uniform nano-scaled particles achieved under the cryogenic condition. The hydrogen absorption of dehydrogenated MgH_2 is also enhanced by both cryogenic milling and ball-milling.
- 3) Hydrogen sorption of MgH_2 catalysed with 2 mol % and 8 mol % TiC by cryomilling and ball-milling was investigated. The formation of $\gamma\text{-MgH}_2$ during high energy ball milling of MgH_2 was observed from XRD patterns. The crystallite sizes of MgH_2 decreased significantly after cryomilling. TiC, which is a very stable

compounds under the testing temperature and pressure (< 500 °C, 1 bar He or 8 bar H_2), and retained original form during milling and after dehydrogenation, there is no reaction found between Mg/MgH₂ and TiC. From SEM-BSE and TEM observations, the nanometer-sized TiC particles were either distributed on the surface of MgH₂ particles or inserted between grains of MgH₂, which enhanced the interaction between MgH₂ and TiC.

- 4) TiC shows an effective catalyst for H₂ sorption of Mg/MgH₂. It was also found that a higher TiC content of 8 mol % reduced the onset desorption temperature further to 175 °C, compared with 2 mol % TiC (190 °C). The Mo₂C shows no catalytic effect on hydrogen sorption of MgH₂.
- 5) A preliminary study of hydrogen sorption using a (H₂ + CO₂) mixture strongly indicates that CO₂ poisons the hydrogen sorption process of Mg due to chemical reactions that generate solid phases and other gaseous species, such as MgO, MgCO₃, CO, CH₄ and H₂O.

6.2 Future Work

From the present findings, a number of issues should be investigated further, including the in-depth understanding of the current systems and development of new gas sorption systems.

In particular, the following lines of development should be pursued further:

- 1) The cyclability (stable H₂ storage capacity and microstructure upon cycling) of a hydrogen storage material is very important for reversible hydrogen charge/discharge in practical applications. The cyclic tests of the optimized materials, e.g. (MgH₂+TiC) mixture, should be carried out in future investigation.
- 2) To synthesize MgH₂ with higher content of TiC to reduce the desorption temperature and improve the absorption kinetics further. The optimum TiC content

in MgH_2 for lower desorption temperature, fast sorption kinetics and high capacity should be investigated.

- 3) To investigate the effect of other transition metal carbide, such as VC, WC and FeC, on hydrogen sorption properties of MgH_2 .
- 4) To further study the reaction mechanism of Mg/MgH_2 with H_2/CO_2 mixture at different temperatures. The results should provide valuable information for gas separation in syngas stream and CO_2 capture/storage, where H_2 could be effectively stored in Mg catalyzed by transition metal carbide at one range of temperature, CO_2 at another; it will be also interesting to study capture or separation of H_2 from other gas mixtures, e.g. H_2/CH_4 , $\text{H}_2/\text{CO}_2/\text{CO}$.

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PUBLICATIONS AND PRESENTATIONS

1. **Mi Tian** and Congxiao Shang, 'Nano-structured MgH_2 catalyzed by TiC nanoparticles for hydrogen storage', *Journal of Chemical Technology & Biotechnology*, Article first published online: 20 Aug, 2010. DOI: 10.1002/jctb.2479
2. **Mi Tian** and Congxiao Shang, 'Nano-structured MgH_2 catalyzed with TiC nanoparticles for hydrogen storage', *Oral Presentation* at The 16th Joint Annual Conference of The Chinese Society of Chemical Science and Technology in the UK (CSCST) & The Society of Chemical Industry—Chinese UK Section (SCI—CS), University of London, UK, October, 2009.
3. **Mi Tian** and Congxiao Shang, 'Synthesis and characterization of nano-structural $\text{MgH}_2/\text{Mo}_2\text{C}$ mixtures for hydrogen storage', *Poster Presentation* at UK NanoForum & Emerging Technologies, London, UK, November, 2009.