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DOCTORAL THESIS

Investigation on Catalytic Effect and Transformation Process in Mg/MgH₂ System

Author:

Tao MA

馬 涛

Supervisor:

Prof. Somei OHNUKI

大貫 惣明 教授

A thesis submitted in fulfilment of the requirements

for the degree of Doctor of Philosophy

in the

Laboratory of Advanced Materials

Graduate School of Engineering

August 2013

Declaration of Authorship

I, Tao MA, declare that this thesis titled "Investigation on Catalytic Effect and Transformation Process in Mg/MgH₂ System" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

"Yet a tree broader than a man can embrace is born of a tiny shoot; A dam greater than a river can overflow starts with a clod of earth; A journey of a thousand miles begins at the spot under one's feet."

Lao Zi, Tao Te Ching

“合抱之木，生于毫末；九层之台，起于累土；千里之行，始于足下。”

《老子·道德经·第六十四章》

HOKKAIDO UNIVERSITY

Abstract

Division of Materials Science and Engineering

Graduate School of Engineering

Doctor of Philosophy

Investigation on Catalytic Effect and Transformation Process in Mg/MgH₂ System

by Tao MA

Mg/MgH₂ system is a promising candidate for hydrogen storage materials due to its high hydrogen capacity (7.6 wt%) and low cost; Yet the main obstacle impeding its application lies in the limitation of kinetics and thermodynamics. In respect to these problems, two significant issues, the catalytic effect and Mg→MgH₂ transformation process, were studied in this thesis, as a contribution to further development on the system.

First, the catalytic effect of Nb₂O₅ was investigated in the MgH₂-Nb₂O₅ composites ball-milled for 0 (hand mixed), 0.02, 0.2, 2, and 20 h. An improvement on the desorption properties, in accordance with a decrease in the activation energy, was seen with the increase of ball-milling time. It was confirmed that the particle size of the additive was gradually refined during ball-milling, with the partial reduction occurred on the surface.

Next, the state of the catalyst in MgH₂-Nb₂O₅ composite was investigated during the full cycle. A transition of Nb₂O₅→NbH₂→Nb→NbH was confirmed during ball-milling, dehydrogenation, and rehydrogenation, respectively. It is suggested that the catalytic effect of Nb₂O₅ follows the Nb-gateway model, in which Nb facilitates the hydrogen transportation from MgH₂ to the outside, and accelerates the recombination of hydrogen molecules during the process. Nb crystals were observed to be highly dispersed in the sample, with 10–20 nm in size. As the essential catalyst, these tiny crystals worked as the gateway facilitating hydrogen transportation and hence improving dehydrogenation properties.

Finally, Mg→MgH₂ transformation process was observed by TEM. It was found that the hydrogenation took place along the specific orientation relationship, MgH₂(101)||Mg(002). A structural model, in which the Mg–Mg distance is adjusted according to the introduction of H, and the Mg layers shift slightly, correspondingly, was proposed to demonstrate the transformation.

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Tao MA
June 10, 2013

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Chapter 1

Introduction

1.1 Hydrogen

A symbol appearing at the first place of the periodic table, an element with the lightest weight, and a chemical substance constituting 75% of the Universe's baryonic mass, that is hydrogen, the most abundant chemical substance in the world. At standard temperature and pressure, hydrogen is a colorless, odorless, tasteless, nontoxic, nonmetallic, highly combustible diatomic gas, with the molecular formula H_2 . Hydrogen has been commonly used for the processing of fossil fuels in the petroleum industries. It is also used as a hydrogenating agent for oils, as well as a reducing agent for metal production.

Since John Bockris gave a talk in 1970 at General Motors Technical Center, the term *hydrogen economy* has been introduced, advocating the application of hydrogen as a potential fuel for motive power. The concept has been described in his later publication [1]. Hydrogen is the only energy carrier that can be produced easily in large amounts and in an appropriate time scale. Electric

Table 1.1: Energy densities of common energy storage materials

Storage material	MJ per kilogram	Direct uses
Uranium-235	79500000	Electric power plants (nuclear reactors)
Hydrogen (compressed at 70 MPa)	123	Experimental automotive engines
Gasoline (petrol) / Diesel	46	Automotive engines
Propane (including LPG)	46.4	Cooking, home heating, automotive engines
Fat (animal/vegetable)	37	Human/animal nutrition
Coal	24	Electric power plants, home heating
Carbohydrates (including sugars)	17	Human/animal nutrition
Protein	16.8	Human/animal nutrition
Wood	16.2	Heating, outdoor cooking
TNT	4.6	Explosives
Gunpowder	3	Explosives
Lithium battery	1.8	Portable electronic devices, flashlights (non-rechargeable)
Lithium-ion battery	0.72	Laptop computers, mobile devices, some modern automotive engines
Alkaline battery	0.67	Portable electronic devices, flashlights
Nickel-metal hydride battery	0.288	Portable electronic devices, flashlights
Lead-acid battery	0.17	Automotive engine ignition

energy, either from renewable energies, for example, solar and wind, or future fusion reactors, can be used to produce hydrogen from water by electrolysis. The combustion of hydrogen leads again only to water and the cycle is closed. Table 1.1 gives the energy densities of common energy storage materials [2]. Except the nuclear energy, the energy density of hydrogen is the highest, twice higher than gasoline, which is the main fuel for mobile applications. Therefore, hydrogen has been considered as the most desirable alternative energy carrier [3].

1.2 Approaches to hydrogen storage

Though hydrogen as the energy carrier has the outstanding energy density per unit mass, the volume density is low. Thus the storage of hydrogen at reasonable energy densities poses a technical and economic challenge. Conventionally hydrogen is stored as the pure form, using compressing or liquefying methods. The novel approaches based on the storage materials, either physically or chemically, are highly regarded and widely studied in the past decades.

1.2.1 Compressed hydrogen

Compressed gas is the most commonly used technology for all kinds of gases. The gas is usually compressed to pressures between 200 and 350 bar. Recently, storage pressures of 700 bar and even higher have been under trial, using a carbon-fiber-reinforced tank (Type IV). The design of such a vessel is shown in detail in Figure 1.1 [4]. However, the volumetric storage density is still rather low. For a hydrogen tank comprising a single vessel, the energy densities are about 0.048 kg H₂ per kg tank weight and 0.023 kg H₂ per liter tank volume [5]. Many automobile companies are currently researching the feasibility of commercially producing hydrogen cars, such as Honda and Nissan.

On the other hand, hydrogen has a tendency to adsorb and dissociate at material surfaces. The atomic hydrogen then diffuses into the material. When these hydrogen atoms re-combine in minuscule voids of the metal matrix to form hydrogen molecules, they create pressure from inside the cavity they are in. This pressure can increase to levels where the metal has reduced ductility

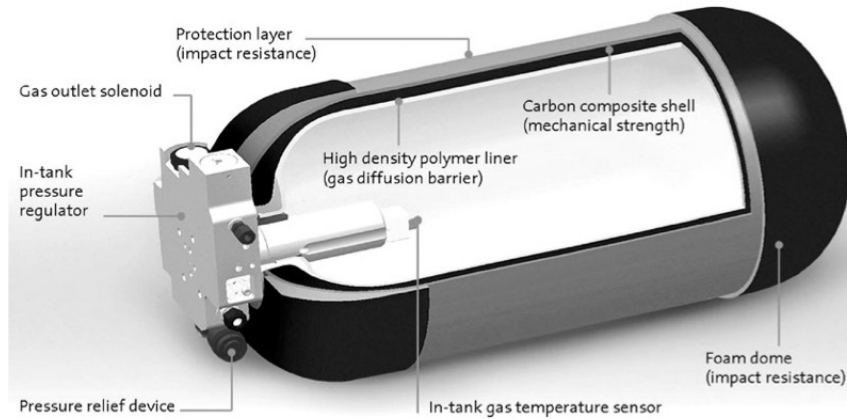


Figure 1.1: Type IV compressed gaseous hydrogen vessel. Reprinted from Ref [4].

and tensile strength up to the point where it cracks open. The phenomenon is known as hydrogen embrittlement. It causes potential problems in safety when hydrogen tanks are used in the automobiles.

1.2.2 Liquid hydrogen

To exist as a liquid, H_2 must be cooled to 20.28 K (-252.87 °C). Liquefaction increases the density up to 70.8 kg/m³, while raises other challenges to be solved. First, the low operation temperatures of 20–30 K require sophisticated cryogenic system and consume large amount of energy. Second, the large temperature difference to the environment (~ 300 K) causes the inevitable heat leakage. Thus hydrogen evaporates in the container, leading to an increase in pressure. Liquid hydrogen containers must therefore always be equipped with a suitable pressure relief system and safety valve. The continuously evaporated hydrogen is catalytically burnt with air in the overpressure safety system of the container or collected again in a metal hydride. Evaporation losses on today's tank installations are somewhere between 0.3% and 3% per day, though larger tank installations have an advantage as a result of their lower surface area

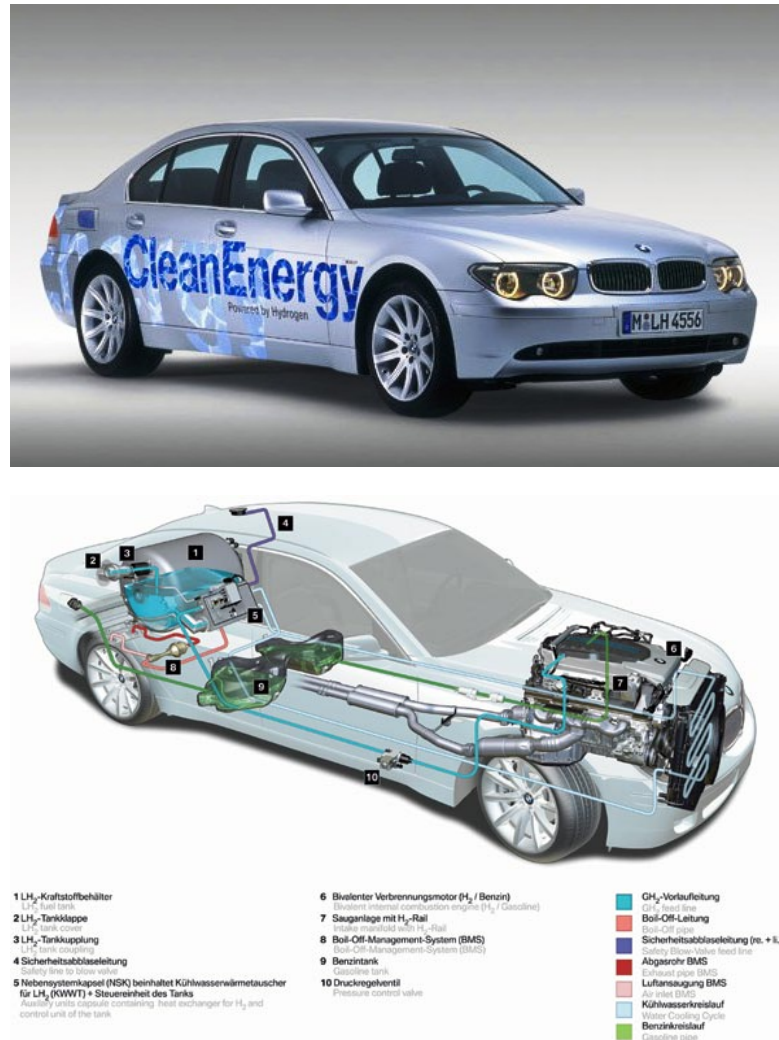


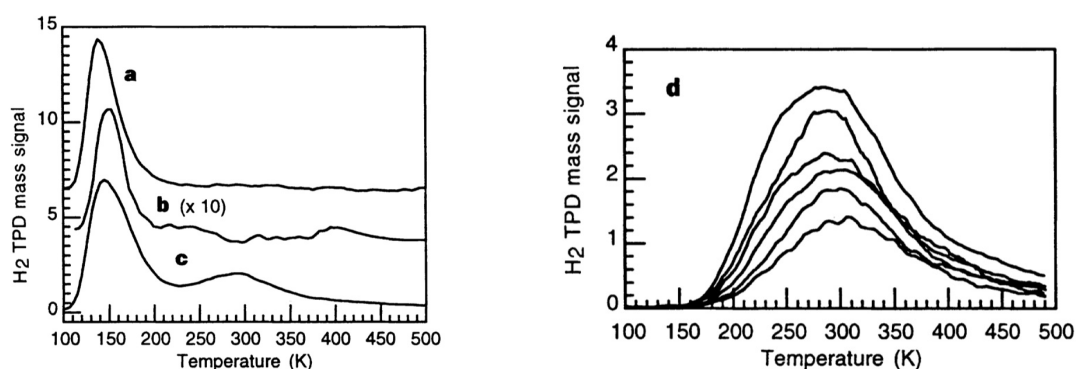
Figure 1.2: BMW Hydrogen 7.

to volume ratio [6]. In addition, liquid storage requires highly sophisticated tank systems. Heat transfer into the tank through conduction, convection and radiation has to be minimized.

The liquid storage system for the first small series hydrogen vehicle with internal combustion engine, BMW Hydrogen 7, was built by MAGNA STEYR in Graz (see Figure 1.2. The tank system for about 9 kg of hydrogen has a volume of about 170 dm^3 and a weight of about 150 kg, which allows a maximum driving range of about 250 km. However, the high cost entitles it as the luxury class and thus far from common use.

1.2.3 Physical storage

Hydrogen could be stored by physical adsorption on the surface of a solid material without dissociation. Responsible for the molecular adsorption of H_2 are van der Waals forces between the gas molecules and the atoms on the surface of the solid. Because there is not any change on both adsorbent and H_2 , physical adsorption is completely reversible and the activation energy is not involved. Therefore, kinetics of the adsorption and desorption is very fast. However, hydrogen capacity is usually very low at room temperature, which hinders its application.



(a) TPD spectrum from: a, as-produced SWNT sample; b, activated carbon; c, SWNT sample after heating in vacuum to 970K.

(b) Hydrogen desorption signals after exposures that populated only the high-temperature sites. Coverages range from 0.3 to saturation.

Figure 1.3: Temperature programmed desorption data of single-walled nanotube and activated carbon. Reprinted from Ref [7]).

Activated carbons and carbon nanotubes are well studied as physical adsorbent in the past decades. The porous structure with a long-range order entitles them the most promising adsorbent for physical storage. Dillon et al. reported that single-walled nanotubes adsorbed large amount of hydrogen under conditions that did not induce adsorption within a standard mesoporous activated

carbon [7], as shown in Figure 1.3. However, the results were hardly reproduced. Later reported reproduction showed that the hydrogen storage capacity of both purified single-walled carbon nanotubes and graphitic nanofibers does not exceed 0.6 wt% at room temperature [8–10]. In contrast, the capacity increases at low temperatures. Panella et al. reported that an activated carbon with a specific surface area of 2560 m²/g adsorbed 4.5 wt% of hydrogen at 77 K [11]. Due to this feature, carbon materials are better to be used as cryogenic hydrogen adsorbent rather than onboard hydrogen storage materials.

1.2.4 Chemical storage

In contrast with physical storage, hydrogen could be stored in a compound, where hydrogen binds with other elements chemically. When necessary, the hydrogen gas could be regenerated by letting the compound decompose under a certain condition, usually 100–300 °C in vacuum. Therefore, such kind of compound can be used as a storage medium for hydrogen, even reversibly.

A good storage medium requires following properties [12]:

- (1) High hydrogen capacity;
- (2) Hydrogen absorption/desorption reversibility at moderate temperature and pressure;
- (3) Low cost, abundant resource;
- (4) Easy handling.

According to the targets for onboard hydrogen storage systems for light-duty vehicles set by the Department of Energy (DOE), US, a capacity of more than 5.5 wt% and 4 vol% is desired in 2017, and 7.5 wt% and 7 vol% ultimately [13]. The system should release hydrogen under an ambient temperature lower than

Table 1.2: Standard formation enthalpy ($\Delta_f H^\ominus$) and entropy ($\Delta_f S^\ominus$), decomposition temperature range, and the hydrogen capacity for the selected metal-hydride systems

System	$\Delta_f H^\ominus$ (kJ·mol ⁻¹)	$\Delta_f S^\ominus$ (J·K ⁻¹ ·mol ⁻¹)	Temperature range (°C)	Hydrogen capacity (wt%)
Li–LiH	-158	-134.7	600–900	12.68%
Na–NaH	-114	-163.0	500–600	4.20%
K–KH	-118	-167.9	288–415	2.51%
Rb–RbH	-108	-169.6	246–350	1.17%
Cs–CsH	-114	-169.6	245–378	0.75%
Ca–CaH ₂	-182	-139.7	600–800	4.79%
Sr–SrH ₂	-198	-156.3	<1000	2.25%
Ba–BaH ₂	-174	-143	470–550	1.45%
Mg–MgH ₂	-74	-133	440–560	7.66%
Al–AlH ₃ ¹	-9.9	-130.7	~150	10.1%
La–LaH ₂	-208	-138.0	600–800	1.43%
Ti–TiH ₂	-130	-100	<300	4.04%
Zr–ZrH ₂	-188	-149.6	400–550	2.16%
V–VH ₂	-40	-149.6	50–120	3.18%
Nb–NbH ₂	-40	-133.0	25	2.12%
Mn–MnH	-22	-116*	<50	1.80%
Ni–NiH	-58	-116*	20	1.69%
Pd–PdH _{0.5}	-40	-83.1	-78–175	0.46%

¹Data were extracted from Ref [16]

*Estimated value and not verified.

85 °C, with more than 1500 times of cycle life. The targets are also acknowledged as the criteria for scientists to evaluate a potential material, not only in US but all around the world.

Metal hydride

Metal hydride, which can be defined as a concentrated single-phase compound between a host metal and hydrogen [14], is a promising candidate for hydrogen storage applications. Table 1.2 shows the basic thermodynamic information as well as the hydrogen capacity for some metal hydrides (Reconstructed from ref [15]).

Simple binary metal hydrides can be grouped into three basic types: ionic, covalent, and metallic hydrides, according to the nature of the metal-hydrogen

bond.

In the hydrides of all alkali metals and alkaline earth metals from calcium through barium, hydrogen exists as a negatively charged ion (H^-) [17]. Those hydrides are called ionic hydrides, representatively LiH , NaH , CaH_2 , etc. The ionic hydrides are thermodynamically too stable for hydrogen storage. For example, LiH with the standard formation enthalpy of -158 kJ/mol won't decompose until it is heated up to $600\text{--}900^\circ\text{C}$.

In the second group calling covalent hydrides, hydrogen holds the covalent bond with its host. The representative metal hydride in this category is aluminum hydride (AlH_3 , alane), which has a large gravimetric and volumetric capacity ($10.1 \text{ wt\%}$ and 149 kg/m^3 , respectively). Besides, it releases hydrogen at low temperature around 150°C , which makes it an attractive material for hydrogen storage. However, the direct hydrogenation of aluminum requires over 10^4 MPa of hydrogen pressure at room temperature. Such unfavorable hydrogenation thermodynamics plays as the main drawback for the practical application.

It should be pointed out that magnesium hydride (MgH_2) is partly ionic and partly covalent, thus is considered as a transition hydride between ionic and covalent hydrides. Given this particularity, MgH_2 "inherits" the stability as the ionic hydrides are, while this stability is weakened more or less towards the practical condition. Additionally, the hydrogen capacity of $7.66 \text{ wt\%}$ is high enough to meet the ultimate target of DOE. Thus MgH_2 exhibits great potential for an desirable storage media among all the metal hydrides, attracting investigations all around the world. As the main topic of this thesis, a state-of-the-art in Mg based materials for hydrogen storage will be reviewed in the

later sections.

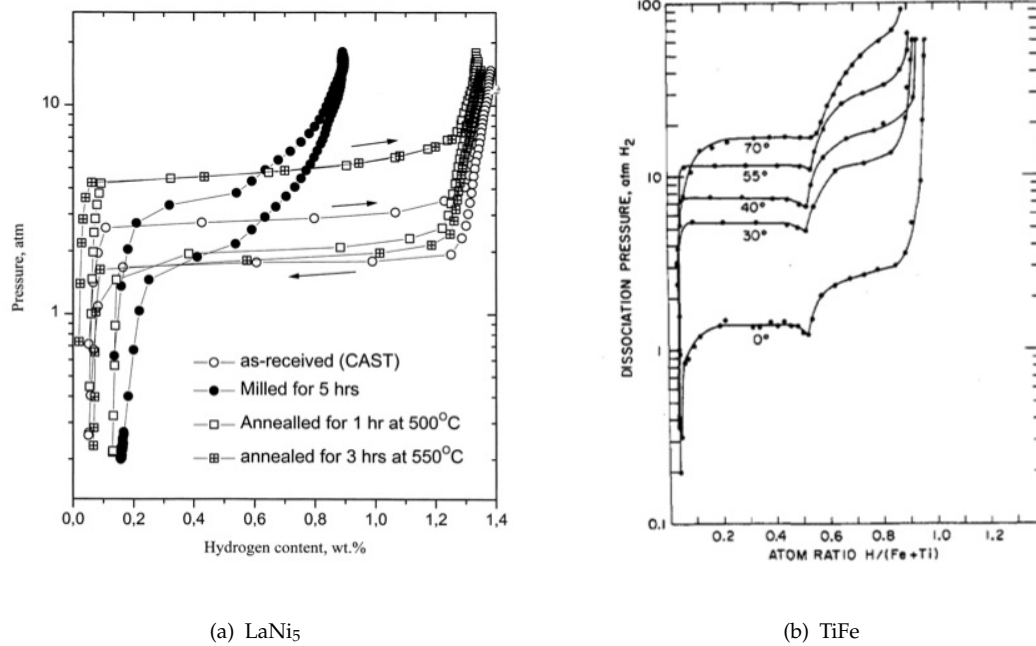


Figure 1.4: PCT curves of LaNi₅ (from Ref [18]) and TiFe (from Ref [19]).

In other hydrides, which are named metallic hydrides, hydrogen occupies the interstitial sites with a metallic bond with metals. The host metals are usually transition metals. The metallic hydrides have a wide variety of stoichiometric and non-stoichiometric compounds and are formed by direct reactions of hydrogen with the metal or by electrochemical reactions. Some transition metals, such as Pd and Nb, show quite active properties towards hydrogen, forming solid solutions easily and quickly. In addition, by combining metals with different hydrogenation properties, intermetallic compounds can be designed with reversible hydrogen-storage ability. The well known hydrogen-storage alloys, such as LaNi₅ and TiFe, have been well studied in the past decades and the literature is abundant. Figure 1.4 shows the typical PCT curves of LaNi₅ and TiFe. The materials can reversibly absorb hydrogen at low temperature with good kinetics under the control of pressure. However, because of

the heavy weight of these metals, the hydrogen capacity is usually below 3 wt%. Besides, the raw materials like La and Ti are quite expensive. Given all that, those materials are hardly the desirable media for the onboard hydrogen storage system.

Complex hydrides

Complex hydrides are salt-like materials in which hydrogen is covalently bonded to the central atoms. In this way a crystal structure consisting of so-called complex anions is formed. In general, complex hydrides have the chemical formula $A_xMe_yH_z$. Compounds where position A is preferentially occupied by elements of the first and second groups of the periodic table and Me is occupied either by boron or aluminum are well known and have been intensively investigated [20].

As a representative complex borohydride, $LiBH_4$, with a hydrogen capacity of 18.4 wt%, has been well studied. It was firstly prepared by Schlesinger et al. in 1939 [21]. The decomposition investigated by Züttel et al. was described in three steps [22]: First, a structure change accompanied with 0.3 wt% of hydrogen release occurred at 100–200 °C; After melting around 270 °C the first decomposition started at 320 °C, with 1 wt%; A second hydrogen release took place from 400 to 600 °C, giving a total amount of 9 wt%. The addition of a metal or metal hydride could destabilize $LiBH_4$ to some extent [23], as shown in Figure 1.5. The temperature programmed desorption (TPD) in panel a revealed that the peak of hydrogen release could be decreased by more than 100 °C and the desorption started even lower than 300 °C. The isothermal desorption data taken at 370 (MgH_2), 375 (Mg), 390 (TiH_2), 395 (Al, CaH_2), and 400 °C (Ti, Sc, V, Cr) in panel b showed hydrogen released with varied

amount and kinetics in each sample, where MgH_2 seemed to give the best performance, liberating ~ 11 wt% of hydrogen with fast kinetics.

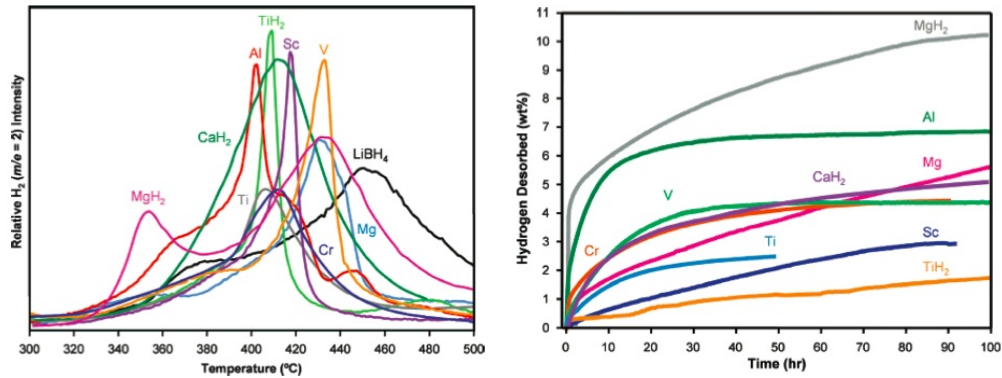
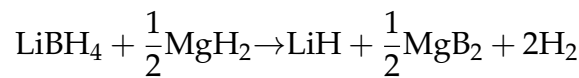


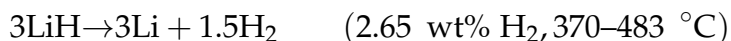
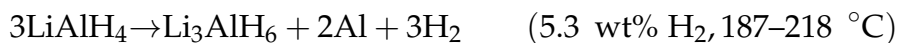
Figure 1.5: TPD-MS and PCT curves (370–400 °C) of destabilized LiBH_4 . Reprinted from Ref [23].

It was reported that LiBH_4 – MgH_2 mixture decomposes following the reaction:



and the formation of MgB_2 effectively destabilizes LiBH_4 [24]. However, the desorption temperature is still far from the practical range; and the rehydrogenation, though performed successfully, requires the H_2 pressure of as high as 100 bar. Other metal borohydrides such as NaBH_4 and $\text{Mg}(\text{BH}_4)_2$ similarly exhibit such high thermal stability and poor reversibility, thus could not be used for practical application at the present stage.

The complex metal aluminum hydrides or metal alanates are composed of an alkali or alkali earth metal and $[\text{AlH}_4]^-$. LiAlH_4 as the representative material in this group has a high capacity of 10.6 wt%, thus has been highly regarded. The thermal decomposition was investigated by Block et al., and described in three steps as follows [25]:



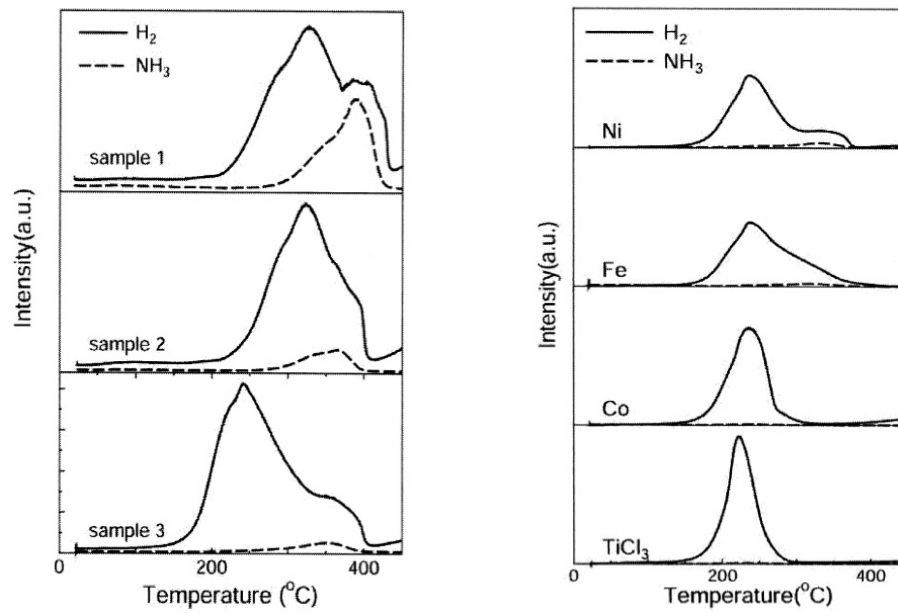
The addition of TiCl_3 followed by a mechanical ball-milling could significantly improved the desorption properties, as reported in several publications [26–28]. LiAlH_4 catalyzed by 2 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and ball-milled for 1 h decomposed from 100 °C, 60 °C lower than the un-doped sample [28]. The presence of TiAl_3 in the milled sample was confirmed by X-ray diffraction, rising the possibility that the alloy may be the catalytic active species [27]. Yet, the mechanism of Ti catalysts is still obscure so far. And the rehydrogenation of the material is far from the reasonable physical conditions, dimming the application of the material.

Amides and imides

Study on the amides and imides for hydrogen storage originates from the report that Li_3N can reversibly absorb/desorb hydrogen following a two step reaction [29]:



where lithium imide (Li_2NH) is generated in the first step and lithium amide (LiNH_2) in the second, with a total hydrogen capacity of 10.4 wt%. Since the hydrogenated mixture won't return to the initial state until it is heated above 320 °, only the second step is reversible under practical temperature and pressure, with a hydrogen capacity of 6.5 wt%. Therefore the further research

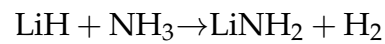
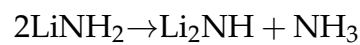


(a) Un-doped samples, where samples 1 and 2 were mixed using an agate mortar and pestle and sample 3 was mixed by ball milling.

(b) Doped samples, where 1 mol% Ni, Fe, Co, and TiCl₃ are added before ball-milling

Figure 1.6: Thermal desorption spectra of H₂ and NH₃ from LiNH₂-LiH ball-milled mixture. Reprinted from Ref [32].

has been focused on the amide-imide, rather than the nitride system. The mechanism of the reaction in amide-imide system was proposed by Hu et al. [30] and Ichikawa et al. [31] as follows:



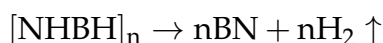
This mechanism explains the generation of NH₃, which poisons the downstream during the process.

It was reported that when doped by some catalysts, the kinetics of desorption could be drastically improved, and more important, the liberation of NH₃ could be suppressed [32]. Figure 1.6 gives the thermal desorption spectra of

un-doped (panel a) and doped (panel b) $\text{LiNH}_2\text{--LiH}$ ball-milled mixture. Compared to the un-doped samples, the temperature range of the hydrogen release was lowered to different extent. Especially, the TiCl_3 -doped sample desorbed a large amount of hydrogen (~ 5.5 wt%) in the temperature from 150 to 250 °C without NH_3 release at all. However, the capacity does not fulfill the expectation, and the temperature range is still too high for application. Later effort has been made on the substitution of Li by Mg [33, 34], and understanding the reaction mechanism fundamentally [35–37]. Either of them, if progress is made, may provide the solutions to the issues.

Ammonia borane and related compounds

Ammonia borane (NH_3BH_3 , AB), containing theoretically 19.6 wt% of H_2 , has been considered as one of promising candidates for hydrogen storage. Being nonflammable and nonexplosive under standard condition, it undergoes a two-step decomposition under low temperature range of 70–200 °C, releasing ~ 6.5 wt% of hydrogen at each step [38–40]: Polyaminoborane, $[\text{NH}_2\text{BH}_2]_n$, is yielded with hydrogen release in the first step, which reaches a maximum at ~ 130 °C; The second step, forming polyiminoborane, $[\text{NHBH}]_n$, occurs in the range of 150–200 °C. At much higher temperatures of 500–600 °C, the decomposition chain can be even carried all the way through to boron nitride with further hydrogen release. The decomposition process can be described as follows:



The technical challenges in the practical application of AB lie in some aspects: First, the decomposition temperature is still higher than the DOE target (85 °C). Second, some undesirable byproducts such as ammonia (NH₃), borazine (N₃B₃H₆) and diborane (B₂H₆) are generated during dehydrogenation. These byproducts may either poison the hydrogen production or cause safety problems. Third, the final product of decomposition, BN, is chemically too stable to be recharged at a reasonable energy expenditure. Concerning with these issues, the modification of AB has been pursued recently. Z. Li et al. confined AB by a metal-organic framework, JUC-32-Y, which is constructed with the rare-earth metal Y³⁺ and the rigid organic ligand 1,3,5- benzenetricarboxylate (BTC) through coordination bonding, and showed the improvement both on the kinetics and the elimination of the byproducts [41]. Figure 1.7 shows the TPD-MS spectra of neat and the modified AB. The dehydrogenation peak-temperature has been decreased to 84 °C, compared to 114 °C of neat AB. And the emission of ammonia, diborane and borazine were not detected. S. Li also reported the dehydrogenation properties of polyacrylamide (PAM) supported AB, which released hydrogen at 75 °C without producing boracic impurities [42]. Especially, a significant depression of NH₃ evolution was achieved by ZnCl₂ doping, as shown in Figure 1.8.

On the other hand, a number of substituted AB-compounds have been developed. A review of those compounds is listed in Table 1.3. Though progress has been made, unfortunately neither of them can fulfill the requirement for onboard hydrogen storage. Furthermore, the unfavorable recycling problem remains gloom. Still more effort should be made on the system.

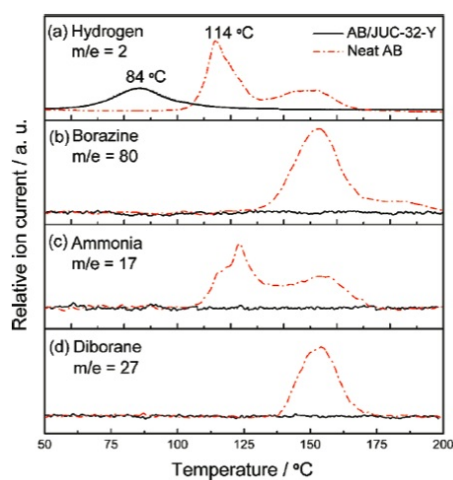


Figure 1.7: TPD-MS spectra of AB/JUC-32-Y and neat AB. Reprinted from Ref [41].

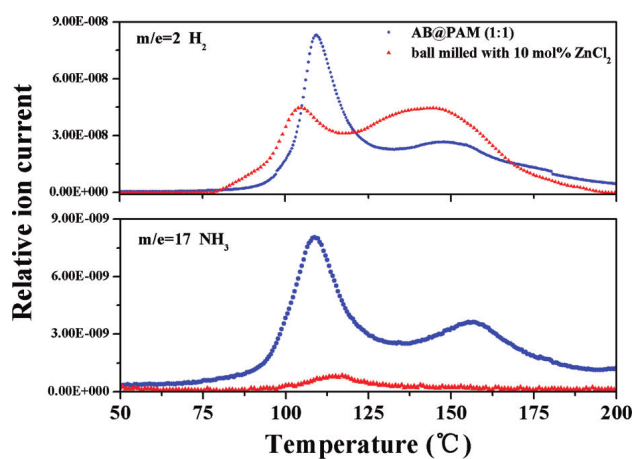


Figure 1.8: MS signals of NH_3 and H_2 evolved from PAM supported AB. Reprinted from Ref [42].

Table 1.3: Desorption temperature and the hydrogen capacity of some substituted AB-compounds.

AB-compounds	$T_{\text{Desorption}}$ (°C)	H_2 capacity (wt%)	Byrproduct(s)	Ref
$(\text{BH}_3\text{NH}_2)_2\text{-Ca}$	120–245	12	$\text{N}_3\text{B}_3\text{H}_6$, NH_3	[43]
$\text{BH}_3\text{NH}_2\text{-Li}$	92	10.9	No $\text{N}_3\text{B}_3\text{H}_6$ emitted	[44]
$\text{BH}_3\text{NH}_2\text{-Na}$	89	7.5	No $\text{N}_3\text{B}_3\text{H}_6$ emitted	[44]
$(\text{BH}_3\text{NH}_2)_2\text{-Sr}$	93	6.8	B_2H_6 , NH_3	[45]

1.3 Magnesium hydride for hydrogen storage

Magnesium is the lightest useful metal in the periodic table, commonly used for making alloys, electronic devices, aerospace construction metals, and so on. The main advantages of Mg are its light weight, high abundance, and low cost—all of them are desirable for a hydrogen storage material. Therefore, magnesium hydride has been considered as a promising candidate, and highly regarded. However, pure Mg is hard to activate, leading to the poor kinetics for hydrogen absorption/desorption. The first report on the thermodynamic properties of MgH_2 was published in 1955 [46]. The high operation temperature of 400–500 °C makes it impossible for application. Therefore, modifications, mainly categorized as nanocrystallization and catalysis, have been made in the past decades.

1.3.1 Nanocrystalline Mg

Nanocrystallization of Mg or MgH_2 was first achieved by mechanical ball-milling in the end of the last century [47, 48]. The kinetics of hydrogenation and dehydrogenation was reported to be significantly enhanced, compared to the bulk Mg. Figure 1.9 shows the dehydrogenation (panel a) and hydrogenation (panel b) isotherms of the milled (nanocrystalline) and unmilled ($\sim 20\ \mu\text{m}$) MgH_2 powder. The desorption kinetics was much faster for the milled sample compared to the unmilled one, while the hydrogen capacity did not change. Further investigations by other groups revealed that the reduced particle size and the increased surface area played an important role on the enhanced kinetics [49–51].

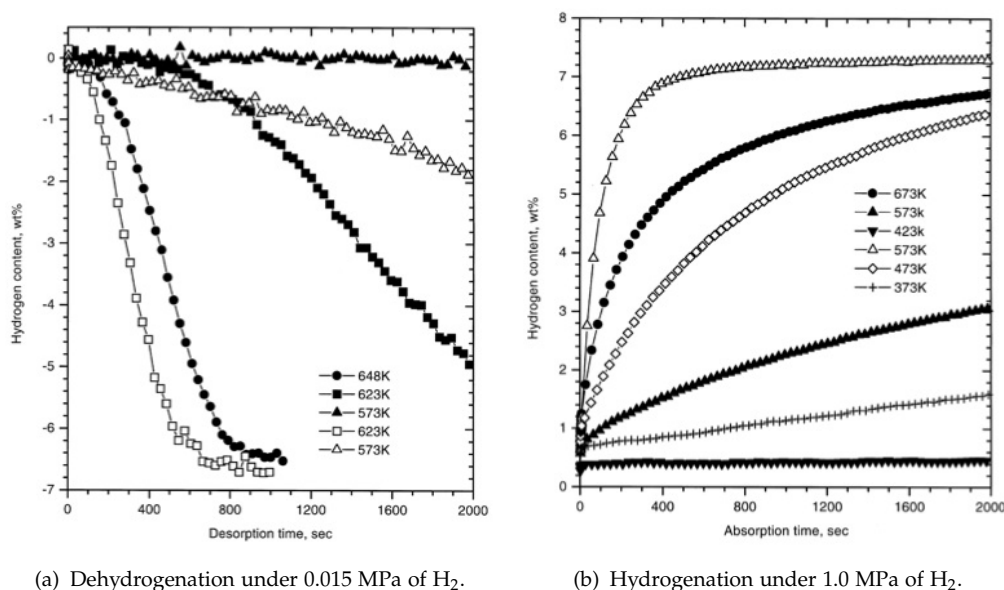


Figure 1.9: Dehydrogenation and hydrogenation isotherms of the unmilled MgH₂ (filled marks) and ball-milled (hollow marks) MgH₂. Reprinted from Ref [48].

Recently, new approaches were developed to prepare nanocrystalline Mg. W. Li et al. reported that 1D Mg nanowires with controllable shape fulfilled absorption and desorption at 573 K within 30 min [52]. Nanocrystallization in 2D, Mg thin films, also presents promising properties in hydrogen uptake and release. A Pd-Mg-Pd thin film was reported to absorb and release hydrogen at room temperature, with an activation energy deduced as $48 \text{ kJ}\cdot\text{mol}^{-1}$ [53]. Later, it was reported that Mg nanocrystals have been prepared in gram quantities via chemical approach, using the Rieke method [54]. Mg nanocrystals were generated through the reduction of magnesocene (MgCp_2), using potassium biphenyl, potassium phenanthrene, or potassium naphthalide as the reducing agent. The nanocrystals with the sizes from 25 nm to 38 nm (Figure 1.10), which could be controlled by the reagents, showed enhanced kinetics for desorption. K. Joen et al. improved this method by encapsulating the prepared nanocrystals by polymethyl methacrylate (PMMA) [55], as shown in Figure 1.11. The polymer acts as a gas selective membrane through which only

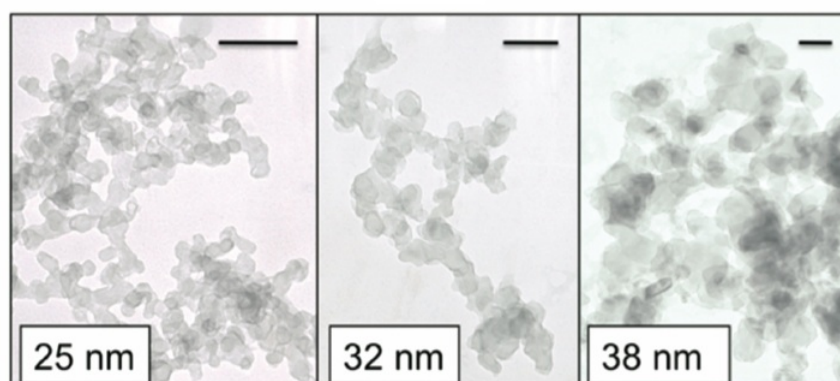


Figure 1.10: TEM images of the nanocrystalline Mg prepared by the Rieke method. Reprinted from Ref [54].

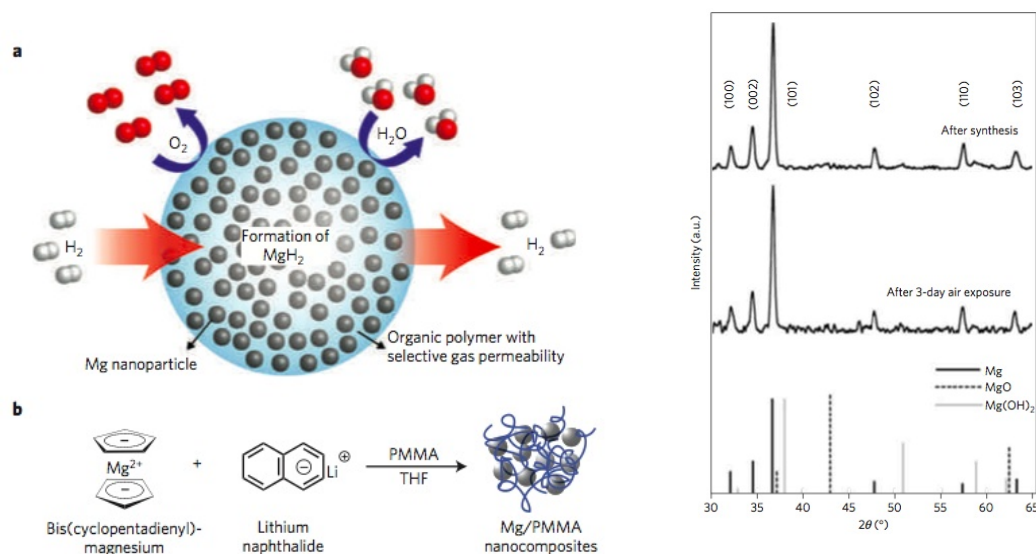


Figure 1.11: a, Schematic of Mg/P-MMA nanocomposite. b, Synthetic approach to formation of Mg/PMMA nanocomposites. Reprinted from Ref [55].

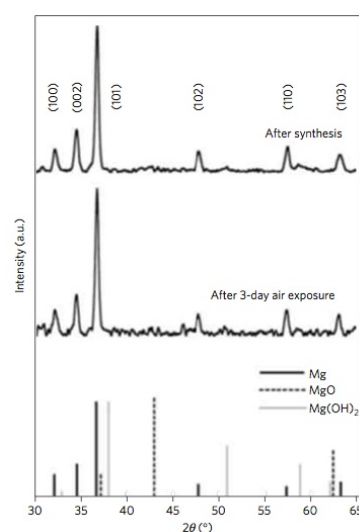


Figure 1.12: XRD spectra of the as-synthesized (top) and after three days of air-exposure (middle) of Mg-PMMA nanocomposites. Reprinted from Ref [55].

hydrogen can penetrate to react with Mg. Therefore, the material could remain good kinetics even under air exposure (see Figure 1.12). However, nanocrystallization is not able to break through the thermodynamics limitation of Mg. Thus these progress, though encouraging, is still far from the application level.

1.3.2 Catalyst modification

In order to further increase the desorption kinetics, a wide range of catalysts has been tested. In the late 70's, the additives were focused on Cu [56], Ni [57], Fe [58], Pd [47], as well as the rare-earth elements such as La, Ce [59]. Metal hydrides such as LaNi_5 [60] and TiFe [61] were also tried for the system. The mechanical alloying or also called ball-milling was mainly used for preparing such composites or alloys—The additives were mixed directly with Mg powder and mechanically milled. The kinetics could be somewhat improved. Due to the ductile feature of Mg, mechanical ball-milling is not so effective to reduce the size.

Later, MgH_2 instead of Mg was used as the starting material for ball-milling, and progress has been made. Liang et al. milled MgH_2 with 5 at%V and found out that the composite could desorb hydrogen at 473 K under vacuum and re-absorb hydrogen rapidly even at room temperature [62]. A systematic test of transition metals including Ti, V, Mn, Fe, and Ni was done subsequently by the same group [63]. Among those additives, Ti and V were seen to show better effect in both dehydrogenation and rehydrogenation, as shown in Figure 1.13. The activation energies during dehydrogenation were estimated as 71.1 and 62.3 kJ/mol for $\text{MgH}_2\text{-Ti}$ and $\text{MgH}_2\text{-V}$, respectively, compared to ~ 120 kJ/mol of pure MgH_2 . Later, Huot et al. added Nb as the catalyst and showed the result that $\text{MgH}_2\text{-5 mol\%Nb}$ completed full desorption within 300 s at 300 °C [64], even faster than the case of Ti and V. The activation energy was calculated as 62 kJ/mol, comparable with that of the V-doped MgH_2 .

The mechanism of Nb-addition was investigated by a synchrotron work [65]. Figure 1.14 shows a record of in-situ XRD data for $\text{MgH}_2\text{-Nb}$ heated up to

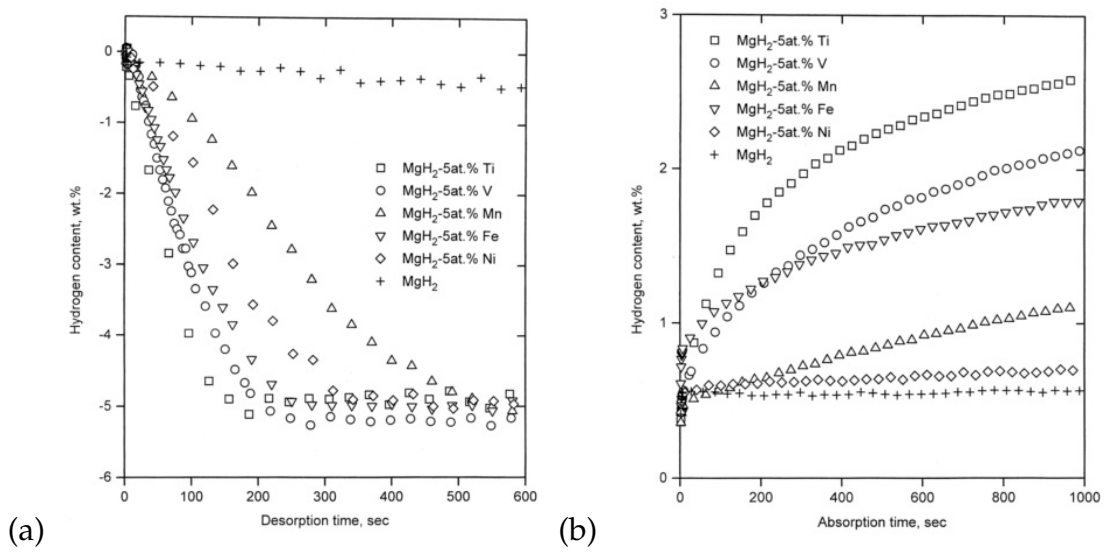


Figure 1.13: Dehydrogenation/rehydrogenation properties of MgH₂-TM composites. (a) Dehydrogenation at 573 K, 0.015 MPa H₂; (b) Rehydrogenation at 302 K, 1.0 MPa H₂. Reprinted from Ref [63].

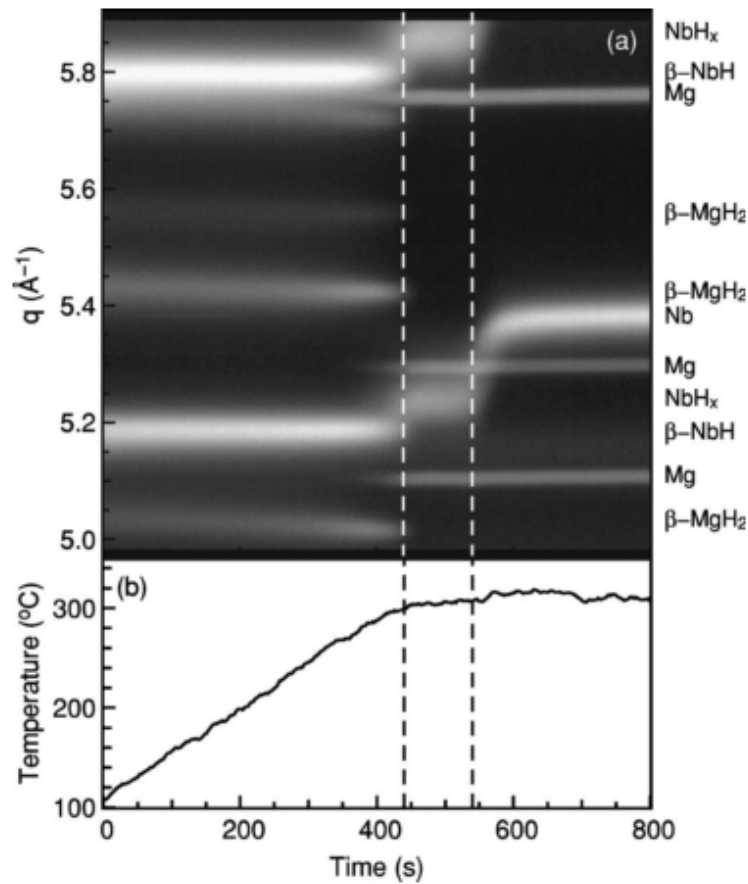


Figure 1.14: Synchrotron XRD profiles for MgH₂-Nb heated up to 310 °C. (a) X-ray scattering where intensity increases with lighter tones; (b) temperature profile. Reprinted from Ref [65].

310 °C. A short-lived metastable phase, NbH_x ($x \approx 0.6$) was seen during the dehydrogenation process. Thus it was concluded that it acted as a gateway through which hydrogen from MgH_2 released. The existence of Nb facilitates the transportation and recombination of H atoms during desorption. A similar mechanism was claimed later by Li et al. through a density functional theory calculation, in which the substitution of Nb at the Mg site followed by the clustering of H around Nb was a likely pathway for hydrogen desorption [66].

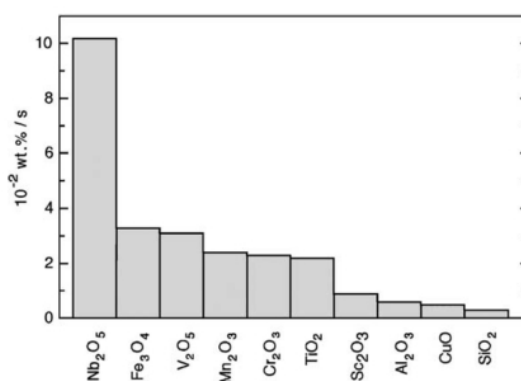


Figure 1.15: Comparison of the desorption rates of MgH_2 with different metal-oxide catalysts at 300 °C under vacuum. Reprinted from Ref [67].

Later attention has been put on the transition-metal oxides, such as TiO_2 [68], Fe_3O_4 [68], V_2O_5 [69], and Nb_2O_5 [67], since they were found to be more effective than their metallic counterparts. According the results of Oelerich et al., the addition of 5 mol% Fe_3O_4 or V_2O_5 accelerated the desorption rate as about ten times as that of the pure MgH_2 [68]. And Barkhordarian et al. made the first contribution on the discovery, characterization and investigation of the addition of Nb_2O_5 [67, 70–72], which is reckoned as the most effective metal-oxide catalyst to the author’s knowledge. A comparison of the desorption rate for different transition-metal oxides has been summarized, as shown in Figure 1.15. The desorption rate was as three times as the case of Fe_3O_4 in Oelerich’s work. The content of Nb_2O_5 was studied in the 20-hour-ball-milled

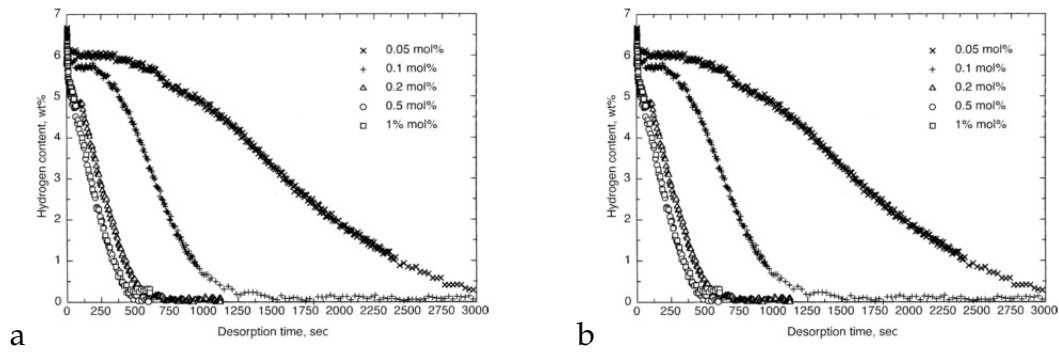


Figure 1.16: H₂ desorption properties of MgH₂ catalyzed by different content of Nb₂O₅ at (a) 250 and (b) 300 °C. Reprinted from Ref [70].

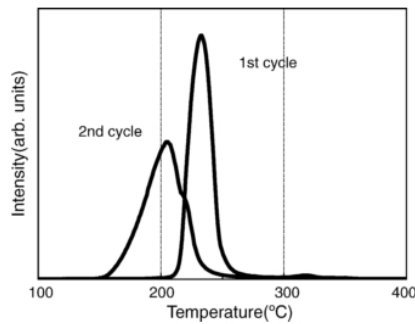


Figure 1.17: TPD-MS of H₂ for the 1st and 2nd cycle of MgH₂ catalyzed by 1 mol% Nb₂O₅ Reprinted from Ref [73].

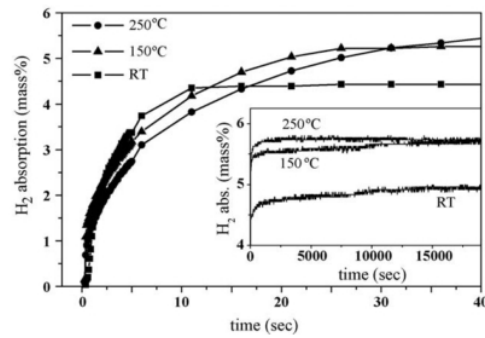


Figure 1.18: H₂ absorption properties of MgH₂ catalyzed by 1 mol% Nb₂O₅ after full desorption. Reprinted from Ref [74].

MgH₂–Nb₂O₅ composite at 250 and 300 °C, shown in Figure 1.16 [70]. The results revealed that the fastest kinetics were obtained when the content was 0.5 mol%, while further increasing to 1 mol% only resulted in a little improvement. Furthermore, the rate-determining step was confirmed as interface-controlled when the content was more than 0.2 mol%.

Hanada et al. also made effort on the MgH₂–Nb₂O₅ system. MgH₂ catalyzed by 1 mol% Nb₂O₅ and ball-milled for 20 h desorbed ~6.0 wt% of H₂ from 200 to 250 °C at a heating rate of 5 °C/min, and gave even better performance in the second cycle [73] (see Figure 1.17). The same composite even absorbed ~4.5 wt % of hydrogen after full desorption, under a pressure of 1.0 MPa within 15

s at room temperature [74] (see Figure 1.18). The exciting achievements reflect a glorious prospect for future application.

1.3.3 Mechanism of the catalytic effect

Though the superior catalytic effect of Nb_2O_5 in the MgH_2 system has been reported, the mechanism of this effect remains obscure. Through the intensive investigation on the issue in the past decade, several possibilities have been arisen.

Refinement of size

As is known to all, the mechanical ball-milling can decrease the size of the materials effectively. In the recent study on MgH_2 - Nb_2O_5 ball-milled composite, the size of both the hydride and the additive was found to be within nanoscale. Especially, the size of MgH_2 could be further refined at the presence of Nb_2O_5 , reported by Porcu et al [75]. Hanada et al. observed the MgH_2 -1 mol% Nb_2O_5 composite by the transmission electron microscope (TEM) and analyzed the composition by the energy-dispersive X-ray spectroscopy (EDS) at different positions [76], marked 3–8 in Figure 1.19. The content of Nb in all the positions was found to be around 2 mol%, in accordance with the starting ratio. Thus it was concluded that the catalyst, Nb_2O_5 , dispersed homogeneously in the MgH_2 matrix. The refinement of size and the consequently homogeneous distribution may lead to the fast kinetics.

Increased defects

It has been reported by Fromme that transition-metal ions on the surface and in the bulk of oxides may experience different crystal fields because of missing oxygen ions at the surface [77]. By increasing defects in the metal oxides,

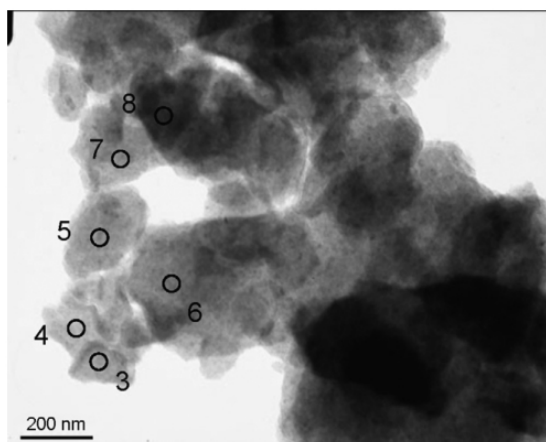


Figure 1.19: TEM image of MgH_2 catalyzed by 1 mol% Nb_2O_5 . Reprinted from Ref [76].

the electronic state of the transition-metal ions could be altered, hence may be responsible for the catalytic effect. The mechanical ball-milling herein is an effective way to introduce defects and create new surfaces in the material. Barkhordarian et al. ball-milled Nb_2O_5 with MgH_2 powder for varied time and tested the dehydrogenation properties separately [72]. The results showed that the kinetics were indeed improved as the increase of ball-milling time (see Figure 1.20). Because the MgH_2 powder was pre-milled for a long time, the effect of microstructure refinement of the MgH_2 could be safely excluded. Thus it was concluded that the defects introduced by the mechanical ball-milling played an important role in the catalytic effect. However, considering the conclusion reported in another paper by the same group that the rate-determining step might be interface-controlled [70], which is related to the dissociation and recombination of hydrogen at the interface, the diffusion of hydrogen atoms seems less significant. Anyhow, this contradicting issue needs more comprehensive investigation.

Reduction of the additive

It can be predicted thermodynamically that MgH_2 may react with Nb_2O_5 , and

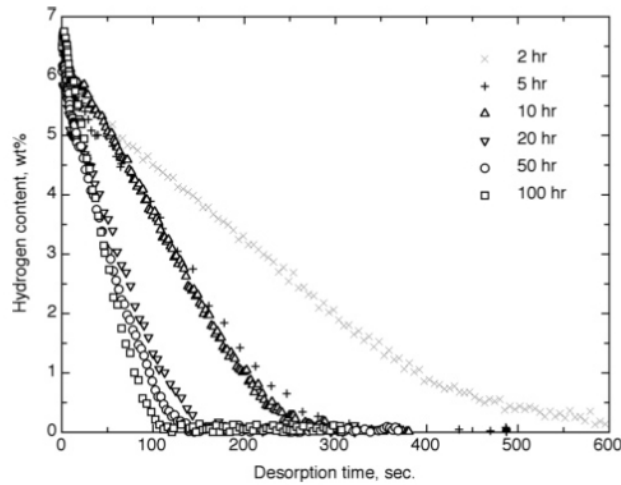


Figure 1.20: Dehydrogenation isotherms of MgH_2 catalyzed by 1 mol% Nb_2O_5 measured at 300 °C. Reprinted from Ref [72].

Table 1.4: Standard thermodynamics data for Nb and Mg family.

Formula	$\Delta_f H^\ominus / \text{kJ} \cdot \text{mol}^{-1}$	$S^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta_f G^\ominus / \text{kJ} \cdot \text{mol}^{-1}$
Mg	0	32.7	0
MgH_2	-75.3	31.1	-36.0
MgO	-601.6	26.9	-569.0
Nb	0	36.4	0
NbO	-405.8	48.1	-378.6
NbO ₂	-796.2	54.5	-740.5
	(398.1 per O)	(27.25 per O)	(370.25 per O)
Nb ₂ O ₅	-1899.5	137.2	-1766.0
	(379.9 per O)	(27.44 per O)	(353.2 per O)
NbH ₂	-40	34.1*	-0.37*
NbH	-18.4	46.4*	-21*

Data are from Ref [78] and [15].

* Estimated values.

the latter would be reduced to a lower oxidation state, or even the metal state, with the yielding of MgO which is more stable in thermodynamics. Table 1.4 lists the thermodynamic data for Nb and Mg family. One could expect such tendency by analyzing the data given.

Reduction of Nb_2O_5 by Mg/ MgH_2 was indeed confirmed experimentally. Friedrichs et al. reported in 2007 that Nb_2O_5 was partially reduced during the milling process and was further reduced during the heating and cycling processes

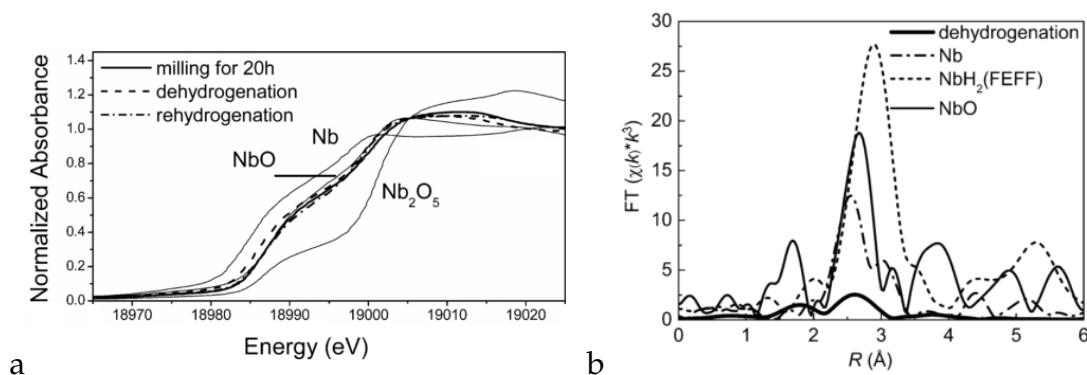


Figure 1.21: (a) XASNE profile and (b) Fourier transformation curves of EXAFS for MgH₂ catalyzed by 1 mol% Nb₂O₅. Reprinted from Ref [80].

[79]. During the cycling processes a repetitive Nb oxidation-reduction process was observed, which may improve hydrogen diffusion by the formation of metastable niobium hydrides. Hanada et al. later reported similar results obtained by the X-ray absorption spectroscopy (XAS) [80]. Figure 1.21a shows the profile of X-ray absorption near edge structure (XANES). The K-edge of Nb was seen between Nb and Nb₂O₅, indicating that the valence of Nb was between 0 and +5. The edge shifted to the lower energy side after dehydrogenation and returned to the same position as the ball-milled one after rehydrogenation, suggesting that an oxidation-reduction process was taken place during the cycling. From the Fourier transformation curves of the extended X-ray absorption fine structure shown in Figure 1.21b, they concluded that the state of the catalyst after dehydrogenation was close to NbO. The author believed that the metal oxides with lower oxidation state could provide pathways for hydrogen, while the details of how it works in the sample was not mentioned.

Formation of Mg–Nb–O ternary phase(s)

Friedrichs et al. first reported the existence of A Mg–Nb–O ternary phase with

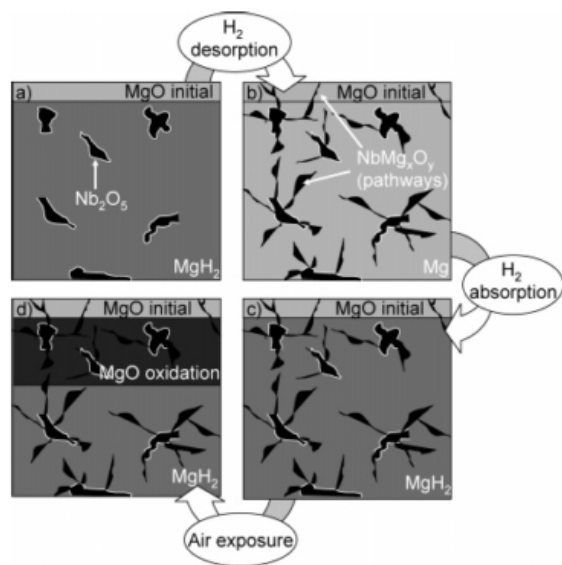


Figure 1.22: The scheme of the “pathway” model in $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite. Reprinted from Ref [81].

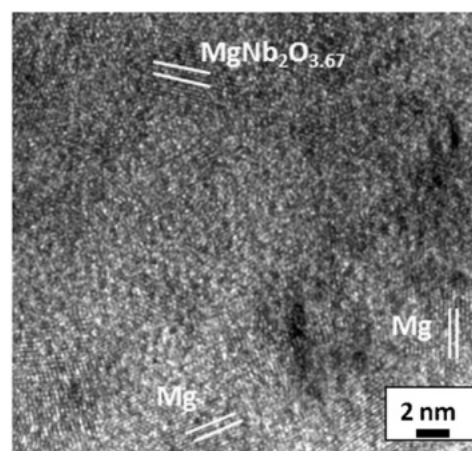


Figure 1.23: HRTEM image of $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite after dehydrogenation. Reprinted from Ref [75].

the stoichiometric composition of $\text{MgNb}_2\text{O}_{3.67}$ in the $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite after cycling [82]. Though the direct evidence is still missing, the author ascribed the catalytic effect to the formation of such phase. In their later publication, a “pathway” model was proposed to explain the mechanism [81]. Figure 1.22 illustrates the scheme of the “pathway” model: During ball-milling Nb_2O_5 is embedded in the MgH_2 matrix covered by and an outer surface oxide layer, which impedes hydrogen diffusion (Figure 1.22a); During the first hydrogen desorption, the Nb_2O_5 reacts with the liberated Mg and the originating products disperse in the sample and emerge to the surface, forming pathways for hydrogen diffusion (Figure 1.22b); Thus hydrogen can enter the sample easily through these pathways, and hence the kinetics is improved (Figure 1.22c). When the sample is exposed to the air, the pathways can also facilitate the diffusion of oxygen, so that the oxidation of the sample occurs and further hydrogen diffusion is suppressed (Figure 1.22d). The existence of $\text{MgNb}_2\text{O}_{3.67}$ was also observed in a TEM observation, reported by Porcu et al

[75], as shown in Figure 1.23, yet still no direct prove was provided to correlate the catalytic effect to such ternary phase.

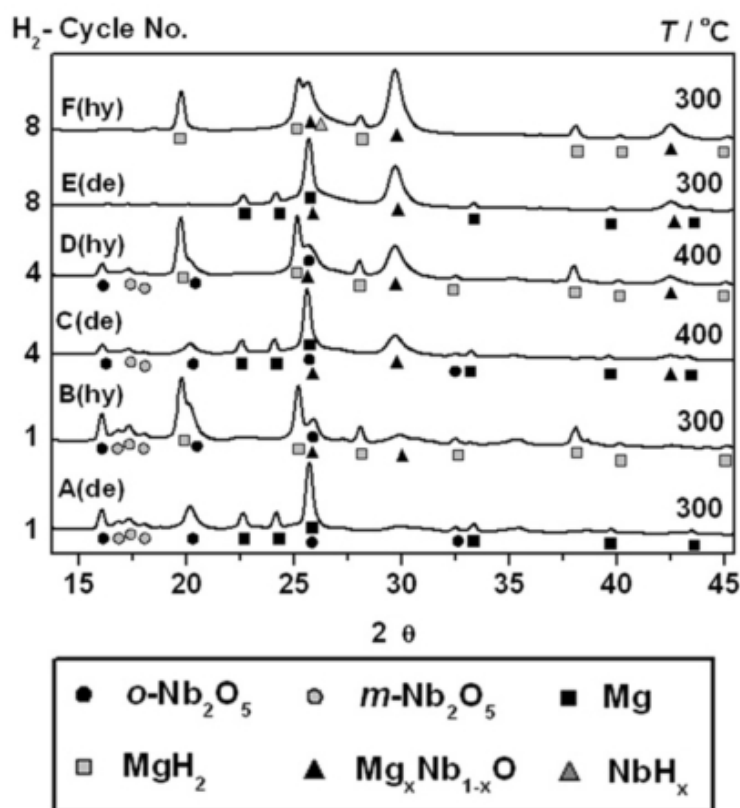


Figure 1.24: XRD patterns of MgH_2 -8 mol% Nb_2O_5 composite during the 1st, 4th, and 8th cycle. Reprinted from Ref [83].

In an in-situ XRD measurement on MgH_2 -8 mol% Nb_2O_5 done by Nielson et al., ternary oxides, $\text{Mg}_x\text{Nb}_{1-x}\text{O}$ was found to appear during heating [83]. Especially, the amount of the ternary phase increased when the sample was cycled, as shown in Figure 1.24. Such phase has a unit expansion up to 4.6% compared to the binary oxides, MgO and NbO , and may lead to formation of cracks and hydrogen diffusion pathways in MgO layers on the surface. Thus the fast kinetics could be achieved by the formation of the ternary phase(s). However, the author failed to associate the fast kinetics with the producing of Mg-Nb-O phase(s). After all, though the amount of the ternary phase(s)

increases during cycling, the kinetics is not improved further according to the existing literature. Thus it is still too early to jump to the conclusion that Mg–Nb–O ternary phase is responsible for the catalytic effect of Nb₂O₅ in MgH₂.

1.3.4 Orientation relationship of Mg/MgH₂ during transformation

Understanding the transformation process of $\text{Mg} \leftrightarrow \text{MgH}_2$, as the fundamental study of the material, can provide us with the hint to further developing the material. Several works have been made to investigate the preference in orientation during the transformation, reviewed as follows.

The transformation from MgH₂ to Mg during dehydrogenation can conveniently be observed by transmission electron microscopy (TEM); so far a few analyses have been conducted, in which the orientation relationship between MgH₂ and Mg was found to be $\text{MgH}_2(110) \parallel \text{Mg}(0001)$ [84–86]. In the case of the hydrogenation process, it is not easy to observe the phase transition directly by TEM because of the difficulty in introducing hydrogen. So far only the report from Schober was seen, in whose work a relationship of $\text{MgH}_2(110) \parallel \text{Mg}(0001)$ was observed [87].

On the other hand, using X-ray diffraction (XRD), Kelekar et al., who hydrogenated epitaxial Mg thin films grown on Al₂O₃ and LiGaO₂, found the orientation relationships that $\text{MgH}_2(110)[001]$ parallels to $\text{Mg}(001)[100]$, and $\text{MgH}_2(200)[001]$ parallels to $\text{Mg}(110)[\bar{1}11]$, respectively [88]. Figure 1.25 demonstrates the probable epitaxial growth mode of MgH₂ on Mg(001). There was a symmetry mismatch between the sixfold symmetric Mg(001) surface and

the twofold symmetric $\text{MgH}_2(110)$ surface, thus no big rearrangement of Mg atoms is required during the transformation. Léon et al. reported that during the hydrogenation of a Mg thin film that highly oriented along (002), (110) and (101) of MgH_2 formed at the very beginning and then grew along these preferred orientations [89], as shown in Figure 1.26. These preferred orientation relationships, suggesting the physical and chemical feature of Mg/ MgH_2 , could help with improving the absorption/desorption properties, if been employed in the design of the materials. However, before doing that, a systematic understanding of the phase-transition process is necessary.

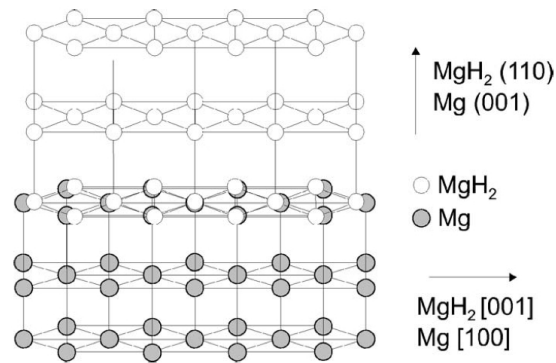


Figure 1.25: Schematic drawn to scale of the probable epitaxial growth mode of MgH_2 on $\text{Mg}(001)$. Reprinted from Ref [88].

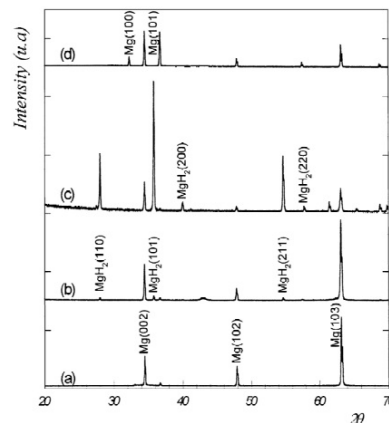


Figure 1.26: XRD profiles of magnesium film (a) Before hydrogenation; (b) At a H concentration of 0.4 wt%; (c) At a H concentration of 6 wt%; (d) After dehydrogenation. Reprinted from Ref [89]

1.4 Objective of this thesis

As described in the previous section, MgH_2 is the most promising metal hydride for hydrogen storage, since its capacity and reversibility all fulfill the DOE target. Besides, Mg is abundant on the earth, thus the cost is low. To use MgH_2 into the industrial application, the only barrier that needs to be conquered is its absorption/desorption properties. Specifically, the desorption temperature is above 300 °C, far from the maximum delivery temperature, 85 °C, set by DOE. When the most effective catalyst, Nb_2O_5 , was found in the last decade, future of MgH_2 seemed to be enlightened. Unfortunately, the addition of Nb_2O_5 still doesn't meet the target, thus further development is necessary. In the following years, such research reached a low point, since an obvious improvement has hardly been achieved.

Coming down to earth, further developing the system requires comprehensive understanding of the fundamental science in two aspects: (a) the mechanism of catalysis; (b) the transformation process of $\text{MgH}_2 \leftrightarrow \text{Mg}$. This thesis was put on these critical issues, aiming at contributing to the development of Mg/ MgH_2 system for future hydrogen storage. The objective of the thesis lies in the following points:

- (1) To trace the Nb_2O_5 in the MgH_2 – Nb_2O_5 composite milled for varied time, investigating the desorption properties, microstructure, and chemical state of the catalyst during the mechanical ball-milling;
- (2) To clarify the interaction between MgH_2 and the catalyst during ball-milling, dehydrogenation, and rehydrogenation processes, and discuss the mechanism of the catalytic effect based on it;

(3) To investigate the orientation relationship during the transformation of $\text{Mg} \rightarrow \text{MgH}_2$, and demonstrate the process in the atomic scale.

In the following chapters, those issues will be targeted on the basis of a series of experiments. Discussions will be carefully made to draw the conclusion.

Chapter 2

Experimental Procedures

2.1 Sample preparation

2.1.1 Starting materials

Magnesium hydride powder was purchased from *Alfa Aesar* with a purity of 98%. The impurities are mainly the unreacted Mg and MgO. Powder of Nb₂O₅ (99.99%), NbO (99.9%), and Nb (99.9%) was purchased from the *Kojundo Chemical Laboratory*. The size of all the powder materials is within micro-scale. Mg turnings, ~5 mm in size, with a purity of 99.98% were purchased from *Aldrich*. All materials were used directly as purchased.

2.1.2 Mechanical ball-milling

High-energy mechanical ball-milling method was used to prepare the catalyzed MgH₂ composites. The milling pot is made by an alloy tool steel (JIS SDK-11), with 30 cm³ in volume. Steel balls used in the milling process are

made by a Cr steel (JIS SUJ-2), with 7 mm in diameter. The pot was specially designed, where a quick connector is equipped for introducing several kinds of gases. A picture of the ball-milling set can be seen in Figure 2.1.

When doing ball-milling, 300 mg mixture of MgH_2 and the catalyst were sealed into the pot together with 20 steel balls. Milling was performed using a planetary ball-milling apparatus (Fritsch P7) at a rotation speed of 400 rpm, under 1 MPa of H_2 (99.9%) or Ar (99.99%). If H_2 was used, the pot was degassed below 1×10^{-4} Pa for 12 h before poring the gas into the pot, in order to eliminate Ar in the pot, since all the operations were done in a Ar-filled glovebox, where the purity of Ar is 99.99%. During ball-milling, the apparatus was set to automatically pause for 30 min in every 1 h, in order to release the inner heat and protect the samples from thermal decomposition.



Figure 2.1: A picture of the set of ball-milling pot and balls.

In the case that the catalyst was pre-milled used in chapter 4, the atmosphere was set to 1 atm of Ar. Several droplets of ethanol was added into the pot in order to prevent the material from adhering on the wall of the pot. The milled material was dried naturally in the glovebox overnight after the process.

2.1.3 Thermal evaporation

Thermal evaporation was employed to prepare the Mg–Nb₂O₅ evaporated composite. Mg turnings with ~ 5 mm in size were put in a resistively heated tungsten boat, connected with a current-control system. A 150-mesh copper TEM grid on which single crystals of Nb₂O₅ were dispersed was put about 20 cm beneath the evaporation source. The chamber was evacuated for 1 h before operation, so that the pressure could reach to 1×10^{-4} Pa. Because it is hard to monitor the amount of the evaporated Mg, trial tests were made, where the power-on time and the maximum current were recorded separately. The optimized combination was finally set as 30 A for 10 s, empirically, since the evaporated Mg on Nb₂O₅ existed isolated like islands, with the average size of ~ 200 nm. After evaporation, a custom designed container, with a lid that can be controlled by the lever outside the chamber, was used to prevent air exposure of the sample during transport from the evaporator into the glovebox (see Figure 2.2).

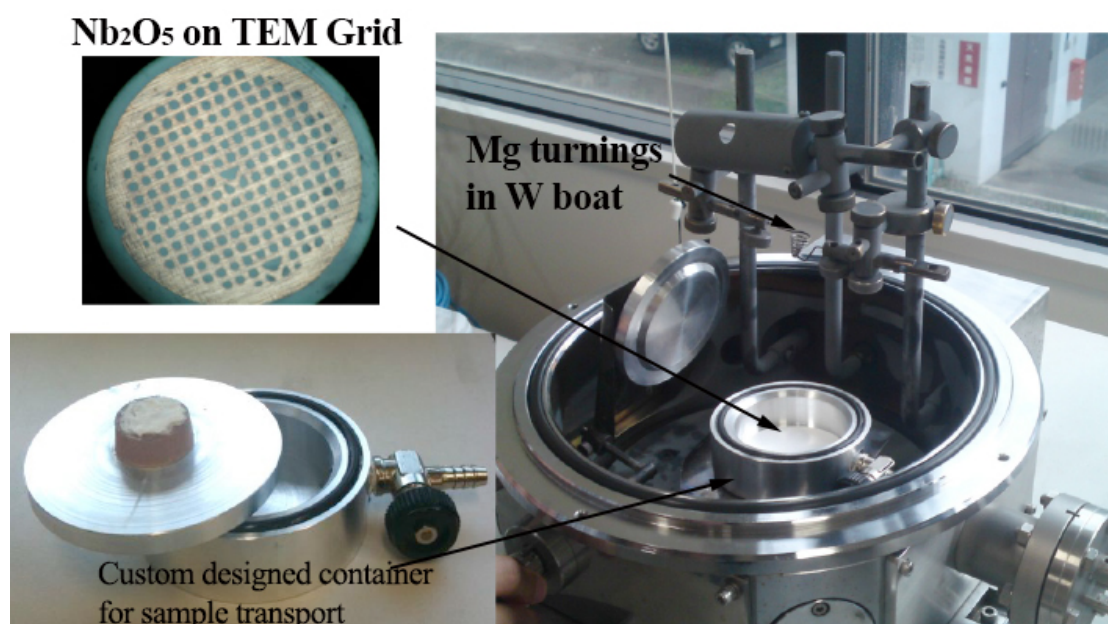


Figure 2.2: Thermal evaporator for sample preparation.

2.2 Sample characterization

2.2.1 Powder X-ray diffraction

Powder X-ray diffraction (XRD) was used to identify the phases of the samples and estimate the crystallite size. The method is based on the phenomenon that the crystalline atoms cause a beam of X-rays to diffract into many specific directions. The diffraction on different crystal planes follows the Bragg's law, shown in Equation 2.1:

$$2d \sin \theta = \lambda \quad (2.1)$$

where λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. By measuring the angles and intensities of these diffracted beams, the phases can be identified in reference to the standard spectra.

The crystallite size can be derived from the broadening of the XRD peaks, based on the Scherrer equation as follows:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (2.2)$$

where K is the shape factor, typically 0.89, λ is the X-ray wavelength, β is the full width at half-maximum (fwhm), θ is the Bragg angle, and τ is the mean size of the crystallites [90]. It should be pointed out that the equation is limited to nano-scale particles and not applicable to grains larger than about 0.1 to 0.2 μm . And it has to be realized that a variety of factors can contribute to the

width of a diffraction peak, such as inhomogeneous strain and crystal lattice imperfections. Therefore, Equation 4.3 provides a lower bound on the particle size.

In this work, XRD measurement was performed using a Philips X'Pert Pro powder diffractometer with Cu K α radiation. The wavelength of the incident X-ray is 1.54 Å. The sample was set on a glass plate, and covered by a kapton sheet of 8 μm thickness sealed by the vacuum grease, in order to prevent oxidation during the measurements.

2.2.2 Thermal desorption spectroscopy

Thermal desorption spectroscopy (TDS) was used to examine the dehydrogenation properties of the samples. During a temperature-programmed desorption, the amount of the released gas, specifically H₂ in this work, can be detected by mass analysis.

The principle of TDS can be described as follows: First, the gas molecules from sample ionize by conflicting electron beam in ionization part. If generated molecules have excess internal energy, they split to fragment ions. Second, the molecular ions are divided by an electromagnetic field according to the difference of the mass in the mass spectrometer. Finally the divided molecular ions reach the detector and detected by different mass. Recording such signals as the function of time or temperature gives the TDS spectra, where the release of gases shows up with peaks in the curve.

The activation energy of the desorption can be extracted from the TDS spectra, using Kissinger method, proposed by Kissinger in 1957 [91]. In most of

solid→solid+gas reactions, the reaction rate can be described as:

$$\frac{dx}{dt} = Ae^{-\frac{E_a}{RT}} f(x) \quad (2.3)$$

where

x is the fraction already reacted,

t is the time since the reaction starts,

T is the temperature,

A is the pre-exponential factor,

R is the gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ typically,

E_a is the activation energy for the reaction,

$f(x)$ is related to the empirical reaction model, listed in Table 2.1.

Here A , E_a , and $f(x)$ are defined as the kinetic triplets.

In a nonisothermal process, where temperature is increased at constant speed,

β ,

$$\beta = \frac{dT}{dt} \quad (2.4)$$

thus

$$\frac{dx}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} \cdot f(x) \quad (2.5)$$

When $T = T_p$, which is the peak temperature during desorption, the rate of the reaction reaches the maximum value. Therefore,

$$\frac{d^2x}{dT^2} = 0 \quad (2.6)$$

Table 2.1: Empirical models for solid reactions. Reconstructed from Ref [92].

Model	$f(x)$
Nucleation models	
Power law (P2)	$2x^{1/2}$
Power law (P3)	$3x^{2/3}$
Power law (P4)	$4x^{3/4}$
Avrami-Erofe'ev (A2)	$2(1-x)[- \ln(1-x)]^{1/2}$
Avrami-Erofe'ev (A3)	$3(1-x)[- \ln(1-x)]^{2/3}$
Avrami-Erofe'ev (A4)	$4(1-x)[- \ln(1-x)]^{3/4}$
Geometrical contraction models	
Contracting area (R2)	$2(1-x)^{1/2}$
Contracting volume (R3)	$3(1-x)^{2/3}$
Diffusion models	
1-D diffusion (D1)	$1/2x$
2-D diffusion (D2)	$[- \ln(1-x)]^{-1}$
3-D diffusion (D3)	$3(1-x)^{2/3}/2(1-(1-x)^{1/3})$
Glinstling-Brounshtein (D4)	$3/2((1-x)^{-1/3}-1)$
Reaction-order models	
Zero-order (F0)	1
First-order (F1)	$1-x$
Second-order (F2)	$(1-x)^2$
Third-order (F3)	$(1-x)^3$

Substituting dx/dT in Equation 2.5 and simplifying, then

$$-f'(x) \cdot \frac{A}{\beta} e^{-\frac{E_a}{RT_P}} = \frac{E_a}{RT_P^2} \quad (2.7)$$

Taking the natural logarithms and simplifying, then

$$\ln \frac{\beta}{T_P^2} = -\frac{E_a}{RT_P} + \ln \frac{AR}{E_a} - \ln f'(x) \quad (2.8)$$

Differentiating Equation 2.8 and neglecting small quantities, then

$$\frac{d(\ln \frac{\beta}{T_P^2})}{d(\frac{1}{T_P})} = -\frac{E_a}{R} \quad (2.9)$$

Equation 2.9 is the common equation used for calculating the activation energy

of a reaction, regardless of the reaction model. By plotting $\ln \beta / T_p^2$ versus $1/T_p$, called as Kissinger curve, the activation energy can be extracted from the slope.

The pre-exponential factor could be extracted only when the reaction model is known. Table 2.1 lists the main models in the solid reactions. For example, for a first-order reaction, $f(x) = 1 - x$. Then Equation 2.8 can be written as:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \ln \frac{AR}{E_a} \quad (2.10)$$

In this case, the pre-exponential factor, A , can be further extracted from the intercept of the Kissinger curve.

In this work, the desorption properties of the samples were examined by Qulee BGM-102. Roughly 5–10 mg sample was set in an electric furnace equipped with thermal couples which recorded the time-resolved temperature of the sample. The equipment was specially designed and installed in a Ar-filled glovebox, thus the thermal desorption could be carried out without exposing the sample to the air. When the sample was heated, a highly pure helium (99.99995%) was flowed from the heating chamber to the mass detector so that the release of hydrogen could be monitored.

In order to estimate the activation energy, the thermal desorption was measured at different heating speed, that was, 1 °C/min, 5 °C/min, 10 °C/min, and 20 °C/min in Chapter 3, and 2 °C/min, 5 °C/min, 10 °C/min, and 20 °C/min in Chapter 4. According to the peak temperature at each heating speed, $\ln \beta / T_p^2$ was calculated and plotted as the function of $1/T_p$. Then the activation energy for the desorption was calculated from the slope of the plot.

2.2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was adopted to check the chemical state of the samples. The method is based on the interaction between an electromagnetic wave and a material (atoms). Since the XPS spectrum directly reflects the electronic structure of a material, it provides formation on electron configuration and energy levels within atoms. The process of photoelectron emission from a solid is divided into 3 stages: First, X-rays are absorbed by atoms, and photoelectrons are emitted; Next, part of the photoelectrons generated within a solid move toward the surface; Then, the photoelectrons which have reached the surface are emitted into a vacuum.

The emission of the photoelectrons obeys the following equation:

$$E_k = h\nu - E_b - \Phi \quad (2.11)$$

where E_k is the kinetic energy of the emitted photoelectrons, $h\nu$ expresses the energy of the excited X-rays, E_b is the electron binding energy, Φ is the work function which depends on both the material and spectrometer. By measuring the kinetic energy of the emitted photoelectrons, the binding energy of the atoms can be obtained. Because the binding energy differs depending on the chemical environment of atoms, the XPS allows the chemical state analysis of a material.

Only those photoelectrons that are generated near the top surface of the solid are emitted from the surface, otherwise the photoelectrons will lose the energies inside the solid material. Therefore, only the photoelectrons generated near the top surface, usually 2 to 5 nm thick, can be received and measured by

the detector. In other words, XPS is only sensitive to the chemical state near the very top surface of the materials.

In this work, the chemical state of the catalyst in the samples were measured using a JPS-90MX photoelectron spectrometer with Mg K_{α} radiation. The powder samples were dispersed onto a carbon tape adhered on the sample stage and measured under vacuum. After wide scan, O1s (524–540 eV) and Nb3d (195–213 eV) were scanned in detail in the narrow scan mode. The energy scale of the spectrometer was calibrated by setting oxygen (O1s) peak to 532 eV. The spectra were smoothed and background-subtracted according to the Shirley method. Peak separation was performed using Gaussian-Lorentz routines with the ratio of 0.8. The area ratio was fixed to 2/3 due to spin-orbit coupling and the distance 2.7 eV between Nb3d_{3/2} and Nb3d_{5/2} peaks.

2.2.4 Scanning electron microscopy observations

A scanning electron microscope (SEM) produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected. The types of signals produced by a SEM include secondary electrons, back-scattered electrons, characteristic X-rays, and so on. Imaging with secondary electrons provides information about morphology and surface topography. The contrast is dominated by the so-called edge effect: more secondary electron can leave the sample at edges leading to increased brightness there (see Figure 2.3). Back-scattered electron imaging is fully based on the atomic number (Z) of the sample. A high mean Z material will produce more back-scattered electrons than a low mean Z one, forming the brighter contrast in the image.

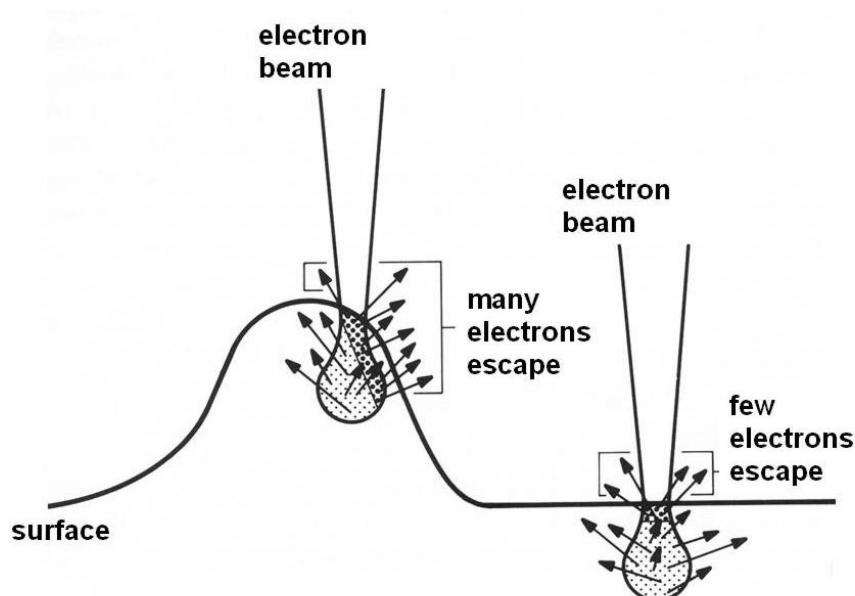


Figure 2.3: Scheme of the edge effect in secondary electron imaging. Reprinted from Ref [93].

In the present work, a field emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) was used to observe the morphology of the samples. The secondary electron image was captured. The powder samples were dispersed onto a conductive carbon tape, which was adhered directly onto the stage for SEM observations. When setting the samples, air exposure was inevitably occurred. However, considering the oxidation would not severely change the morphology, the influence was neglected.

2.2.5 Transmission electron microscopy observations

Transmission electron microscopy (TEM) is a powerful method to characterize materials in micro or nano scale. The instrument enables users to examine fine detail — even as small as a single column of atoms, owing to the small de Broglie wavelength of electrons. In a TEM observation, a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as

it passes through. An image is formed from the interaction of the electrons transmitted through the specimen.

The TEM provides many imaging modes, among which the bright field image, dark field image, and diffraction are the most commonly used. In the bright field imaging mode, the direct beam of electrons will be gathered to form the image (Figure 2.4a). In this case, the contrast is mainly determined by the mass and thickness of the sample, known as mass-thickness contrast. The regions with high mass, that is, the high atomic number (Z), will scatter more electrons than low- Z regions. Similarly, thicker regions will scatter more electrons than thinner regions of the same average Z . Thus thicker and/or higher- Z areas will appear darker than thinner and/or lower- Z areas. In the diffraction mode, the scattered electrons, which are dispersed into discrete locations in the back focal plane by the interaction with crystals, are recorded. By analyzing the diffraction pattern, the phase, crystal structure, as well as the crystal orientation, can be known. If the objective aperture is placed in the back focal plane (Figure 2.4b), the desired Bragg reflections can be selected, thus only parts of the sample that are causing the electrons to scatter to the selected reflections will end up projected onto the imaging apparatus. That is called the dark field image, which is usually used with pair of the bright field image.

Another important imaging mode is the high-resolution transmission electron microscopy (HRTEM), which I realized via a 1250 kV high-voltage electron microscope in this work. As opposed to conventional microscopy, HRTEM does not use amplitudes, i.e. absorption by the sample, for image formation. Instead, contrast arises from the interference in the image plane of the electron wave with itself, thus is named the phase-contrast. When the electrons pass

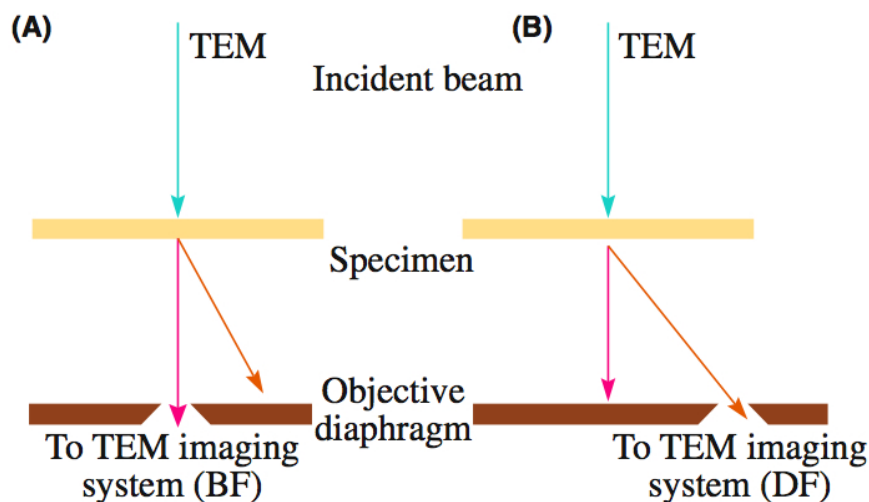


Figure 2.4: The use of an objective aperture in TEM to select (A) the direct or (B) the scattered electrons forming bright field and dark field images, respectively. Reprinted from Ref [94].

through the sample, they are diffracted by the atoms, causing diffraction contrast in addition to the already present contrast in the transmitted beam. The interference of the transmitted and diffracted beams result in the periodical fringe, whose distance is inversely related to the lattice spacing.

In this work, the microstructure of the samples were observed by a 200 kV TEM (JEOL JEM-2010). The high-resolution images of the samples were captured using a 1250 kV HVEM (JOEL JEM-ARM1300). The powder sample was directly dispersed onto a copper TEM grid, which is then set into the TEM holder. In order to prevent the oxidation of the samples during transport into the instruments, the plastic bag method was used [95]. Image analysis, including measuring, editing, fast Fourier transform (FFT), and inverse fast Fourier transform (IFFT) were carried out using *Gatan Digital Micrograph*™ 3.7.0.

Chapter 3

Catalytic Effect and Trace of Nb₂O₅ in MgH₂-Nb₂O₅ Composite

3.1 Background and purpose

Since the superior catalytic effect of Nb₂O₅ in both absorption and desorption processes of Mg/MgH₂ was discovered, many contributions have been made to figure out the mechanism of such effect. Some possible factors have been proposed in the recent literature, as mentioned in Chapter 1. In this chapter, these factors were reconsidered based on a study of MgH₂-Nb₂O₅ composites milled for varied time. The desorption properties were investigated versus the increase of the ball-milling time. Meanwhile, the microstructure, and especially the chemical state of the catalyst, were examined to correlate to the desorption properties. On the basis of those results, the possibly essential factors for the catalytic effect were discussed.

3.2 Experimental procedures

The mixtures of MgH₂ and 1 mol% Nb₂O₅ were ball-milled for 0.02 h, 0.2 h, 2 h, and 20 h, under 1 MPa of H₂ atmosphere. Also, the hand-mixed (HM) sample with the same composition was prepared by agate mortar in a Ar-filled glovebox. TDS, XRD, TEM and XPS were used for the characterization of the samples.

3.3 Results and discussions

3.3.1 Desorption properties of MgH₂-Nb₂O₅ composites milled for varied time

Figure 3.1 shows the profiles of TDS of hydrogen for the composites with a heating rate of 5 °C/min. It can be seen that as the ball-milling time increased, the peak temperatures of hydrogen desorption are decreasing, meaning the catalytic effect was gradually activated and improved during ball-milling.

By measuring TDS at different heating rates, 1 °C/min, 5 °C/min, 10 °C/min, and 20 °C/min separately, the activation energy (E_a) of desorption could be estimated by Kissinger method, as the theory was described specifically in Chapter 2. By plotting $\ln \beta / T_p^2$ versus the inverse of the peak temperatures, the Kissinger curves could be obtained, shown in Figure 3.2. It can be seen that the data points exhibit good linearity, validating the applicability of the method. From the slope of the straight lines, E_a for the HM sample and those ball-milled for 0.02 h, 0.2 h, 2 h and 20 h was estimated to be 147, 138, 82,

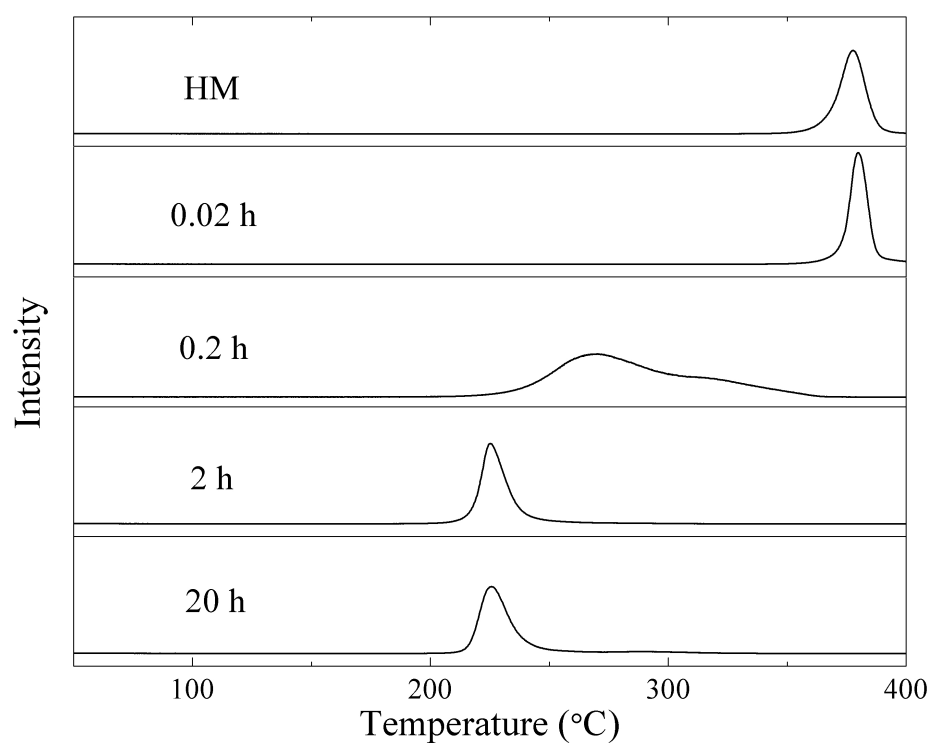


Figure 3.1: Profiles of TDS of H₂ for the HM sample and those ball-milled for 0.02 h, 0.2 h, 2 h and 20 h.

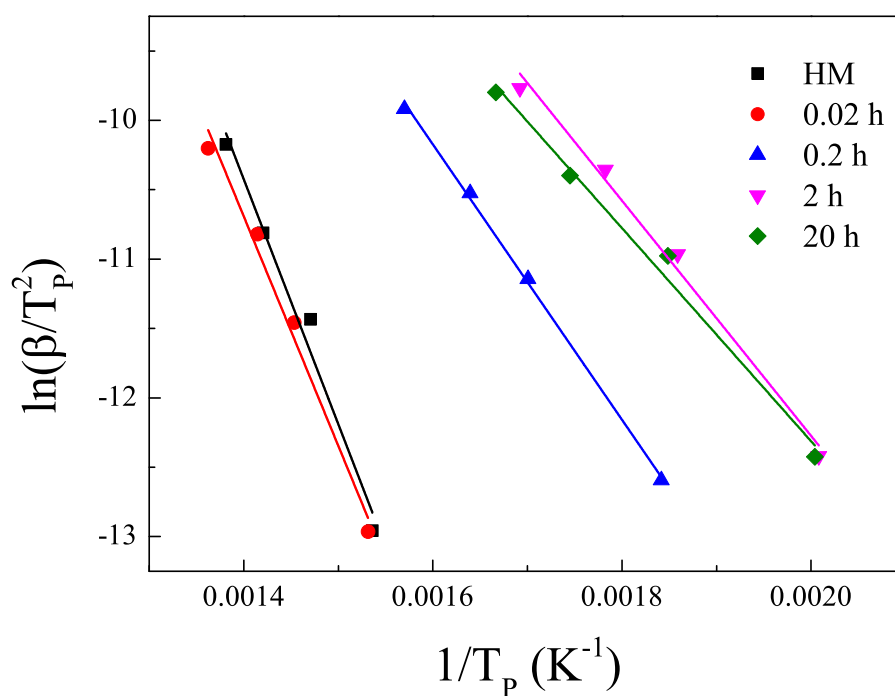


Figure 3.2: Kissinger curves of the samples derived from the desorption data.

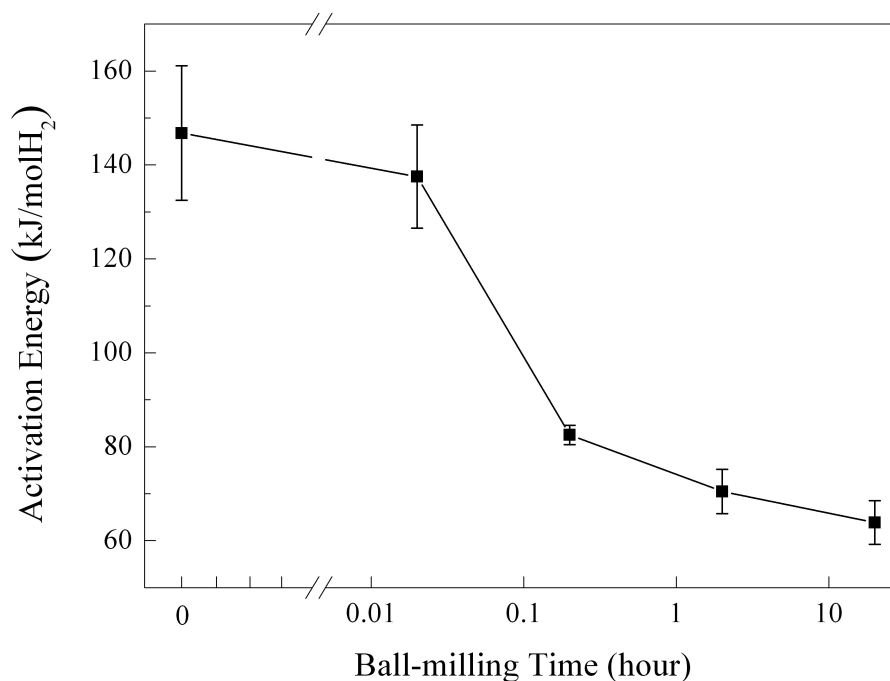


Figure 3.3: Correlation between E_a and ball-milling time for the HM sample (0 h) and those ball-milled for 0.02 h, 0.2 h, 2 h and 20 h.

70 and 63 kJ/molH₂, respectively. Those values were plotted versus the ball-milling time, as shown in Figure 3.3. It can be seen that E_a decreases with the increase of ball-milling time. Especially between the samples ball-milled for 0.02 h and 0.2 h, a large reduction of E_a (~ 56 kJ/molH₂) has been reached, which is worth discussion. This indicates that some changes were brought by ball-milling and hence improved the catalytic effect of Nb_2O_5 . To understand the mechanism of the catalytic effect, these changes should be investigated.

3.3.2 Trace of Nb_2O_5 in the ball-milled composites

XRD patterns of the samples were obtained to evaluate the crystalline information, as shown in Figure 3.4. The width of the peaks widened and the intensity

drastically decreased when the samples were milled for a long time. It indicates that the grain size of both MgH_2 and Nb_2O_5 becomes smaller during ball-milling. This refinement of grains may suggest the decrease of size for both MgH_2 and Nb_2O_5 particles, leading to a better distribution of catalyst in the samples.

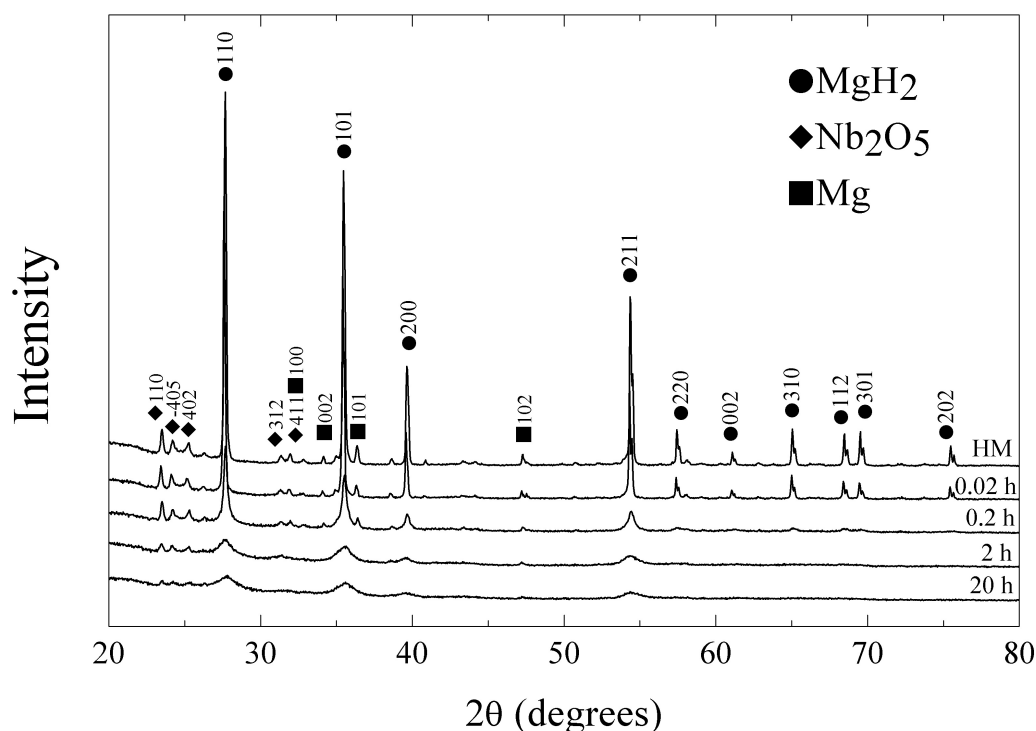


Figure 3.4: X-ray diffraction profiles of the HM sample and those ball-milled for 0.02 h, 0.2 h, 2 h and 20 h.

TEM observation provides evidence for the inference above. In the bright field images shown in Figure 3.5a–e (all of them were in the same scale), two kinds of particles could be distinguished by different contrast. The selected area diffraction was applied for both of them (see area A and B in Figure 3.5b). In Figure 3.5g the spots with streak (obtained from area B) are recognized as Nb_2O_5 , while in Figure 3.5f the Debye rings (obtained from area A) are confirmed as Mg and MgO. Therefore, in the bright field images the particles with

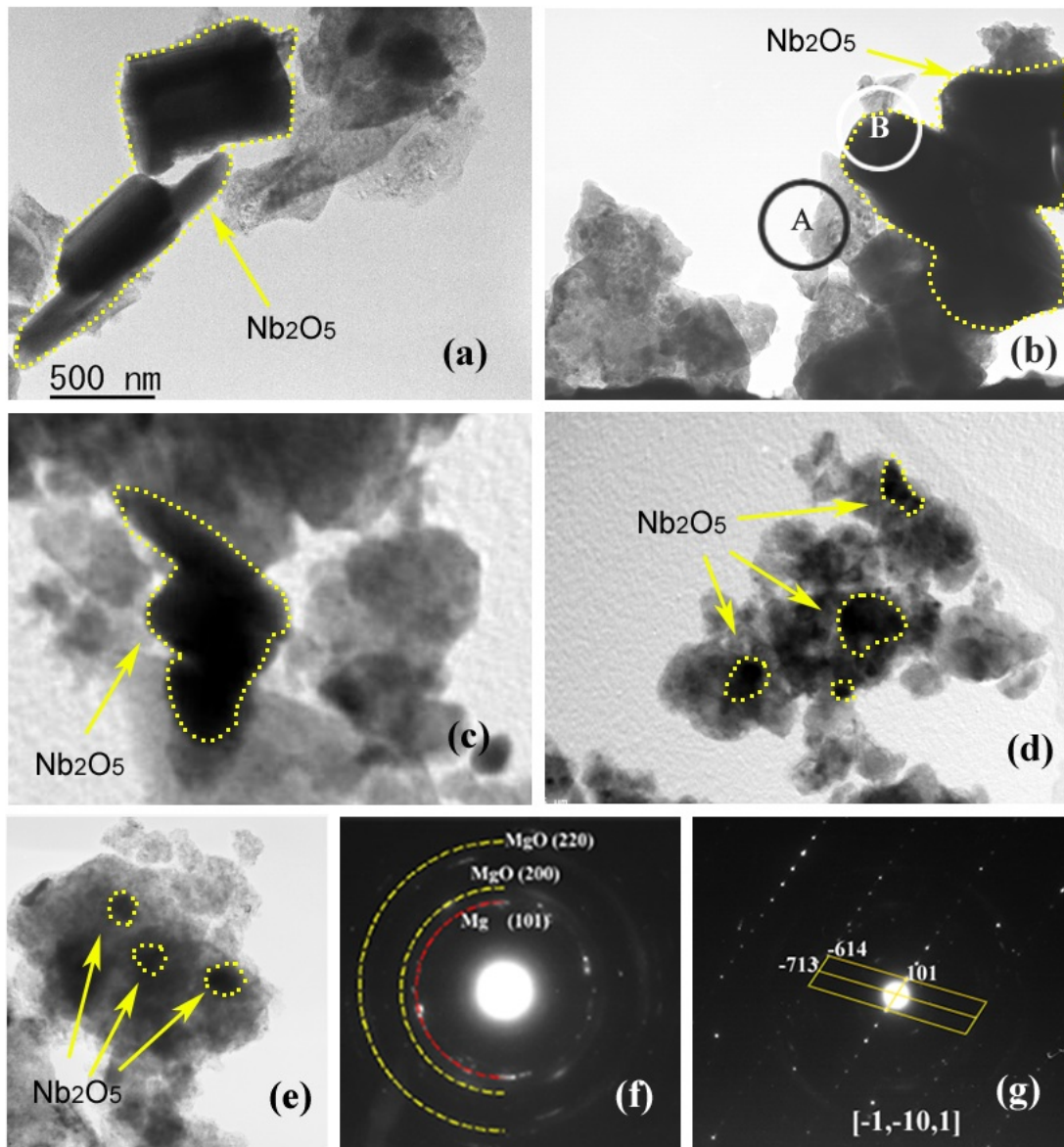


Figure 3.5: TEM micrographs of the HM and ball-milled samples: bright field images of (a) HM, (b) 0.02 h, (c) 0.2 h, (d) 2 h, (e) 20 h and the selected area diffraction from area (f) A and (g) B.

very dark contrast should be Nb_2O_5 while the others are Mg related phases. MgH_2 was not found because of the fast decomposition under the electron beam, as discussed in other papers [75, 76]. When comparing the images, it can be seen that the Nb_2O_5 particles were gradually attenuated by ball-milling and a homogeneous distribution was reached in the samples milled for long time. In Figure 3.5e, e.g., the Nb_2O_5 particles imbed homogeneously in the

Mg related phases. The size of the Nb₂O₅ particles was estimated to be less than 100 nm. This gradually improved distribution of the catalyst with the refined size should be one factor responsible for the decreased E_a and improved desorption properties.

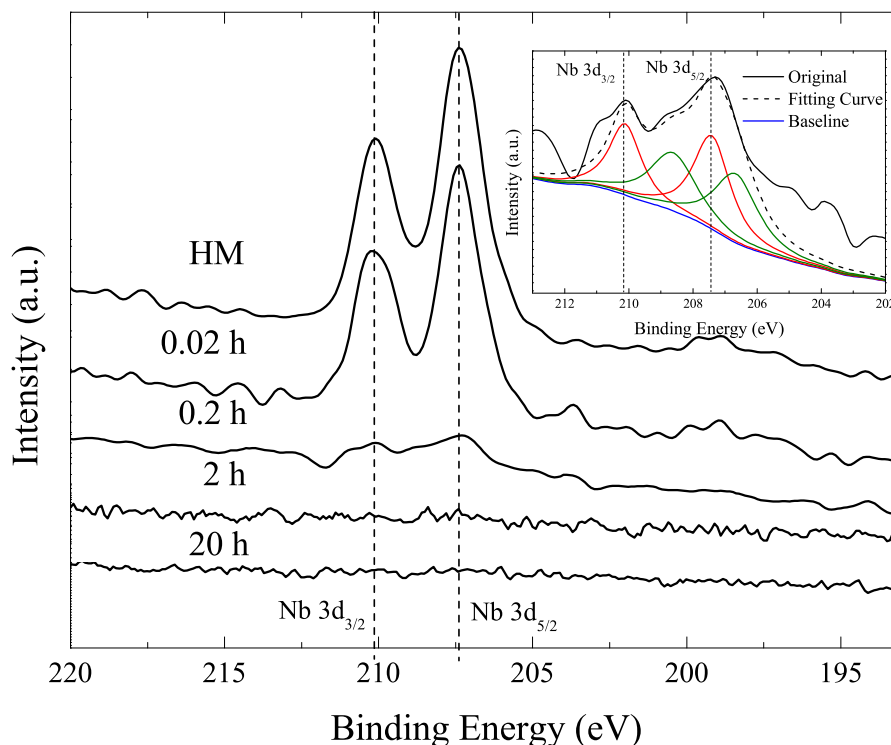


Figure 3.6: XPS spectra of the HM sample and those ball-milled for 0.02 h, 0.2 h, 2 h, and 20 h. The insert graph shows the Nb3d peak separation of the sample milled for 0.2 h.

However, we noticed that E_a decreased not gradually but in fact drastically when the sample was milled for 0.2 h. Thus there should be other factors that affect the kinetics more essentially. Under this consideration, XPS measurements were carried out for further investigation. The niobium (Nb3d) spectra were drawn in Figure 3.6 after calibration. A decrease of the Nb3d signal with ball-milling can be seen, reasserting the results from elsewhere [81, 82]. The decrease could be explained as the milled MgH₂ particles covered the surface of Nb₂O₅, preventing the detector from getting enough signal from inside. It

can be seen that the position of the Nb3d peaks detected almost remain the same, even after the sample was milled for a substantial period. However, the obviously widened peaks were obtained in the sample milled for 0.2 h. Further separation of those peaks shown in the inserted graph resulted in a coexistence of 4 peaks. There are two peaks at 210.2 eV and 207.5 eV, which are corresponding to Nb3d_{3/2} and Nb3d_{5/2} (210.1 eV and 207.4 eV respective in reference to [96]), and two new peaks appearing to the right. Though the signal is not strong enough to identify the exact phase for the new peaks, the shift to lower energy infers that the chemical state of Nb has changed at least on the surface of the sample. A certain or a complication of reduced Nb compound(s) appeared in the sample milled for 0.2 h. The compound(s) on the surface with the valence of Nb less than +5 may act as a more effective catalyst that decreases E_a and also improve the desorption properties.

3.4 Summary

In this chapter, a study on the HM MgH₂-Nb₂O₅ composite as well as those ball-milled for 0.02 h, 0.2 h, 2 h and 20 h under 1 MPa H₂ atmosphere was performed. Improved desorption kinetics was reached by ball-milling with Nb₂O₅. E_a of HM, 0.02 h, 0.2 h, 2 h and 20 h samples was estimated to be 147, 138, 82, 70 and 63 kJ/molH₂, respectively, thus decreasing in accordance with the improved kinetics. XRD and TEM results showed a decrease of particle size for both MgH₂ and Nb₂O₅ occurred with ball-milling. In the sample milled for 20 h, the Nb₂O₅ particles were found imbedding homogeneously in Mg related phases, with a size of less than 100 nm. The better distribution and the refined size of the Nb₂O₅ may be responsible for the decreased E_a and

improved desorption properties. Most importantly, the chemical state of Nb was found changed at least on the surface, as evident by XPS results. The peak separation was performed on the XPS spectrum of the sample milled for 0.2 h, indicating that a certain or a complication of reduced Nb compound(s) appeared, which may play an essential role in decreasing E_a and improving desorption properties of MgH₂.

Chapter 4

Mechanism of the Catalytic Effect in MgH₂-Nb₂O₅ Composite

4.1 Background and purpose

In the previous chapter, the catalytic effect of Nb₂O₅ in MgH₂ was discussed, and the reduction of the catalyst was confirmed. The reduced Nb compound(s) rather than Nb₂O₅ itself, therefore, has been considered as the essential catalyst responsible for the catalytic effect. In order to clarify the mechanism of how Nb₂O₅ works in the composite, the reduction and the reduced product should be intensively studied. In this chapter, clarifying the exact state of the catalyst during a full cycle was targeted. First, as a groundwork for the issue, the catalytic effect of Nb₂O₅ was compared to its metallic counterpart, Nb, as well as the lower oxidation state, NbO. The desorption properties and the morphology of MgH₂ doped by those additives were studied and compared. Next, the reactions between MgH₂ and three kinds of Nb-contained catalysts,

Nb, NbO, and Nb_2O_5 , were investigated and compared, in order to figure out the mechanism of the catalytic effect. The amount of the additives were increased to 50 wt% so that the state of the additives could be identified exactly at each stage. The morphology and the microstructure of the samples were observed and compared. Based on those results, the mechanism of the catalytic effect in $\text{MgH}_2\text{-Nb}_2\text{O}_5$ was discussed.

4.2 Experimental procedures

In order to compare the desorption properties, MgH_2 catalyzed by 1 mol% Nb_2O_5 , 2 mol% Nb, 2 mol% NbO, as well as 2 mol% Nb and 5mol% MgO, were prepared by ball-milling for 20 h. The atmosphere inside the milling pot was chosen to be 1 MPa Ar due to the fact that H_2 can react with metallic Nb directly during the process. Specially, the composite of $\text{MgH}_2\text{-Nb-MgO}$ was prepared under the consideration that MgO was always found in the $\text{MgH}_2\text{-Nb}_2\text{O}_5$ ball-milled composites. Here the ratio of Nb:O was set to 2:5 in order to make a comparison with the addition of Nb_2O_5 . To exclude the effect of different sizes of the starting materials, all additives were pre-milled for 20 h under 1 atm Ar atmosphere. Several droplets of ethanol was added into the pot so that the sample would not agglomerate and adhere onto the wall of the pot during the process. Dehydrogenation properties of the composites were examined by TDS under He flow. The activation energies were also estimated by the Kissinger method. The morphology of the samples was observed by FE-SEM.

Next, MgH_2 with 50 wt% additives were prepared in order to figure out the interaction between them. 150 mg MgH_2 and 150 mg additives (Nb_2O_5 , NbO or Nb) were ball-milled for 20 h under 1 MPa Ar atmosphere. Dehydrogenation was performed by annealing the milled composites for 1 h at 300 °C under vacuum. Rehydrogenation was carried out at 200 °C for 2 h, under a 1 MPa H_2 atmosphere. X-ray diffraction (XRD) was performed at each stage, in order to identify the composition of the composites. The morphology of the samples was observed via FE-SEM, and the microstructure was observed by TEM and HVEM.

4.3 Results and discussions

4.3.1 Comparison on the effect of Nb, NbO and Nb_2O_5

Figure 4.1 presents the TDS profiles of MgH_2 milled with different additives, under a heating rate of 5 °C/min. It can be seen that the desorption properties of the samples have been improved to different degrees (The data of the HM $\text{MgH}_2\text{-1 mol}\%\text{Nb}_2\text{O}_5$ sample in Chapter 3, in which the catalytic effect was not activated yet, could serve as a reference; see Figure 3.1). Nb_2O_5 gave the best performance among those catalysts studied here, as an overwhelming low peak-temperature (207 °C), appeared in the spectrum of the Nb_2O_5 -doped sample. It suggests the fast kinetics in the sample during dehydrogenation. It has been noticed that the peak-temperature is even lower than the 20-h-ball-milled sample in Chapter 3 (see Figure 3.1). It seems that the pre-milling on Nb_2O_5 could further improve the catalytic effect, perhaps due to the amorphization and destabilization of the additive during the process. The

peak-temperatures in Nb-doped and Nb-MgO-doped samples are almost the same (254°C and 257°C , respectively). It indicates that the addition of MgO, though makes the same composition as in the Nb_2O_5 -doped sample, cannot improve the dehydrogenation properties at all. The spectrum of NbO-doped sample exhibits a peak at 239°C , suggesting that the dehydrogenation property, though not as good as the Nb_2O_5 -doped sample, is better than Nb-doped and Nb-MgO-doped ones.

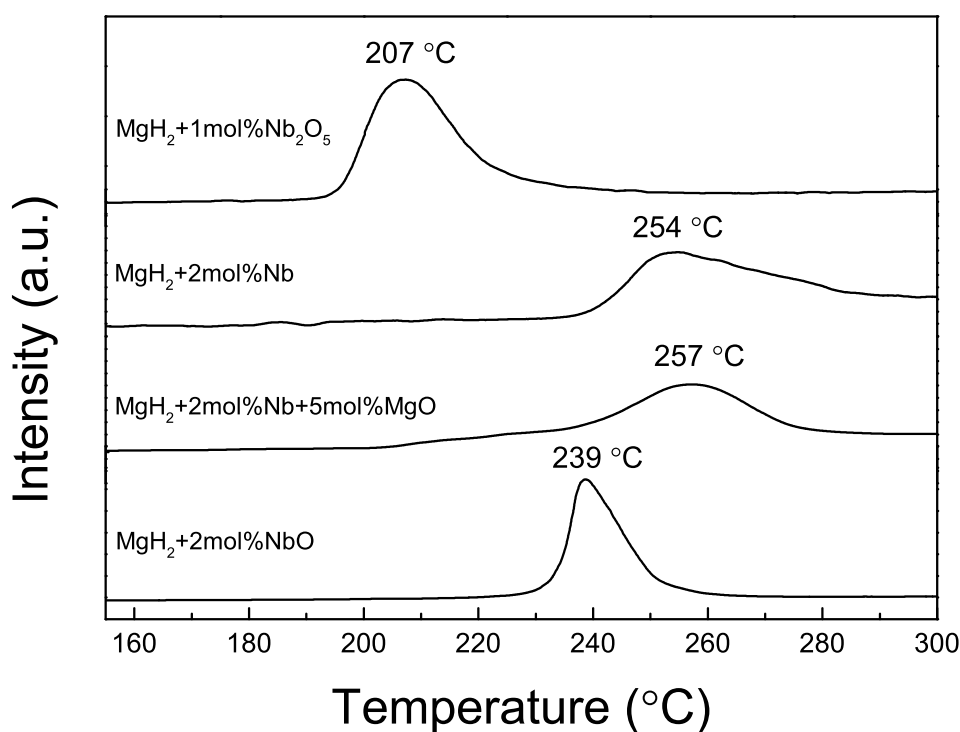


Figure 4.1: Hydrogen desorption spectroscopy of the $\text{MgH}_2\text{-Nb}_2\text{O}_5$, $\text{MgH}_2\text{-Nb}$, $\text{MgH}_2\text{-NbO}$, and $\text{MgH}_2\text{-Nb-MgO}$ ball-milled composites.

The activation energies (E_a) were estimated by measuring the TDS data at different heating rates, 2°C/min , 5°C/min , 10°C/min , and 20°C/min , separately. The Kissinger curves, $1/T_p$ as the function of $\ln \beta/T_p^2$, were plotted in Figure 4.2. E_a for each sample was extracted from the slope of the Kissinger

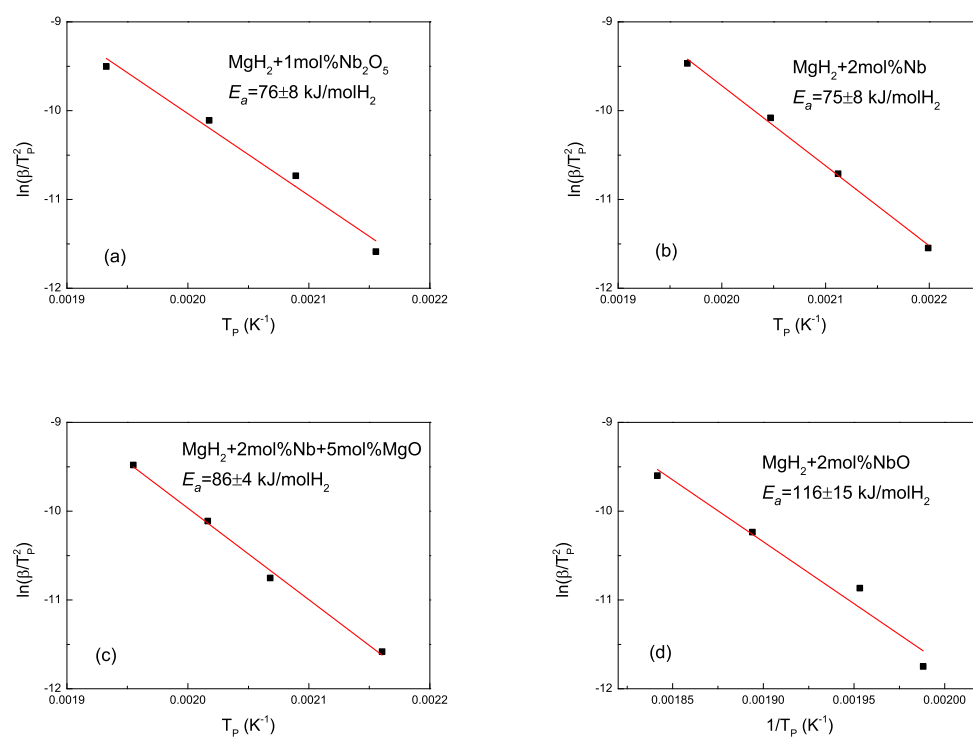


Figure 4.2: Kissinger curves of of the $\text{MgH}_2\text{-Nb}_2\text{O}_5$, $\text{MgH}_2\text{-Nb}$, $\text{MgH}_2\text{-NbO}$, and $\text{MgH}_2\text{-Nb-MgO}$ ball-milled composites.

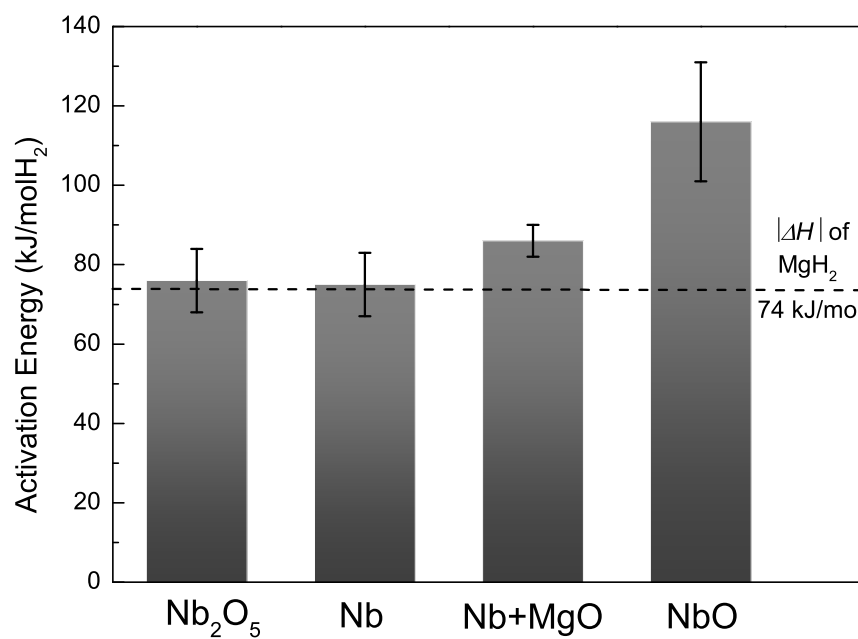


Figure 4.3: A comparison of E_a in MgH_2 doped by different additives.

curve, summarized in Figure 4.3. It can be seen that E_a for Nb_2O_5 -doped sample was quite low, in accordance with its good desorption properties. However, the value was a little larger than that of the 20-h-ball-milled sample in Chapter 3. The possible reason for this disagreement may be due to the system error brought by the TDS device, since the measurements were carried out via different devices. In the Nb-doped sample, though the peak-temperature was a little higher than that in others, E_a was unexpectedly comparable with that of Nb_2O_5 -doped one. Actually, both of them are close to the decomposition enthalpy of MgH_2 , 74 kJ/mol. If subtracted this value from the E_a calculated here, the net activation energy is closed to 0. It suggested that the catalysts already gave the maximum effect in the samples. On the other hand, the addition of MgO seemed to lead to an increase in E_a , again indicating that MgO was effectless. E_a for the NbO-doped sample turned out to be the highest among them, inconsistent with its relatively low desorption peak-temperature.

SEM observations on the ball-milled composites are shown in Figure 4.4. It can be seen that the size of the particles in the Nb_2O_5 -doped sample is smaller than those in the others, suggesting that the size tended to be refined under the addition of Nb_2O_5 . This tendency partially explains the good dehydrogenation property in the Nb_2O_5 -doped sample, since the refinement of the size can lead to the increase in the specific area that is quite related to the kinetics in solid reactions. In addition, the size of the particles in the Nb-doped and Nb-MgO-doped samples are comparable, indicating that MgO did not contribute to the size refinement either. The result claimed by Aguey-Zinsou that MgO helped to reduce the particle size and hence improved the desorption properties [97] were not seen.

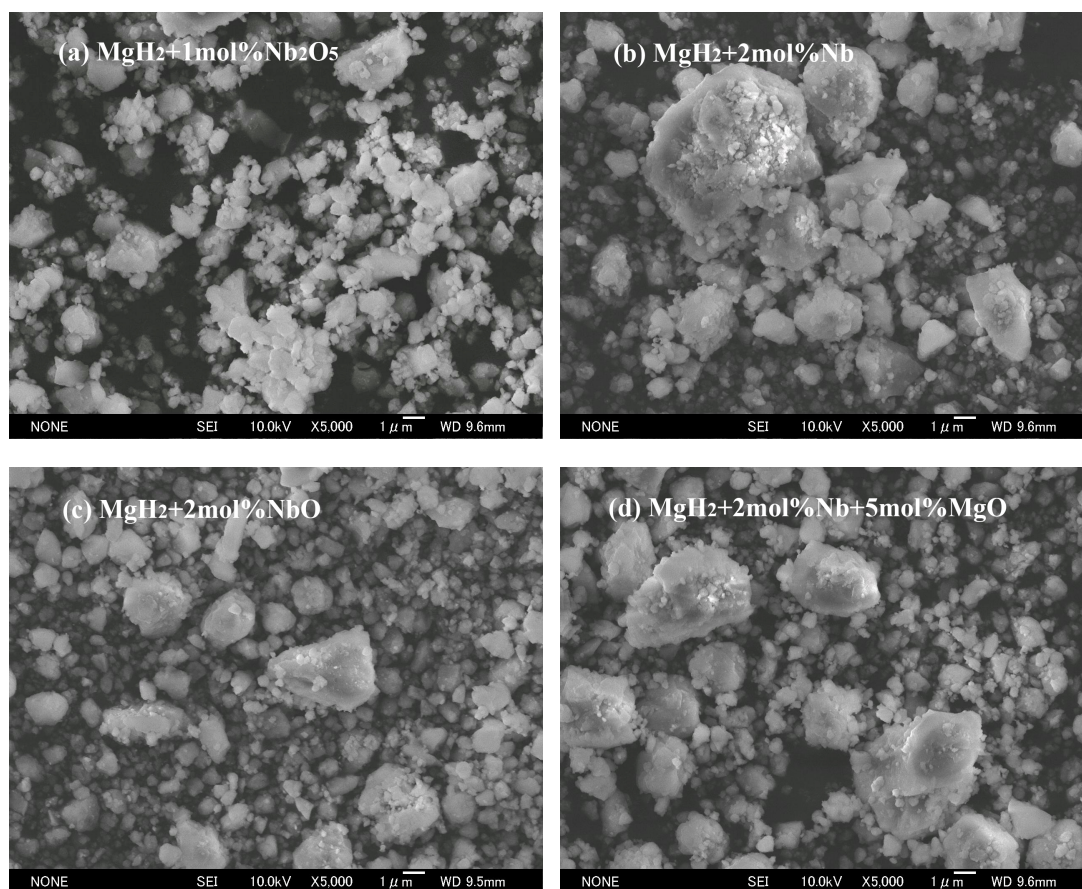


Figure 4.4: SEM images of the ball-milled MgH_2 nanocomposites doped by (a) 1 mol% Nb_2O_5 , (b) 2 mol% Nb, (c) 2 mol% NbO, as well as (d) 2 mol% Nb and 5 mol% MgO.

4.3.2 State of the additives during the absorption/desorption cycle

$\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite

Figure 4.5 shows the XRD profiles of $\text{MgH}_2\text{-Nb}_2\text{O}_5$ nanocomposite during the full cycle. In the as-milled sample, Nb_2O_5 was not detected. Instead, the peaks from NbH_2 and MgO can be seen, indicating that Nb_2O_5 reacted with MgH_2 during the ball-milling process. Nb (II) hydride and MgO as the products of the reaction were generated then. The reaction equation can be written as

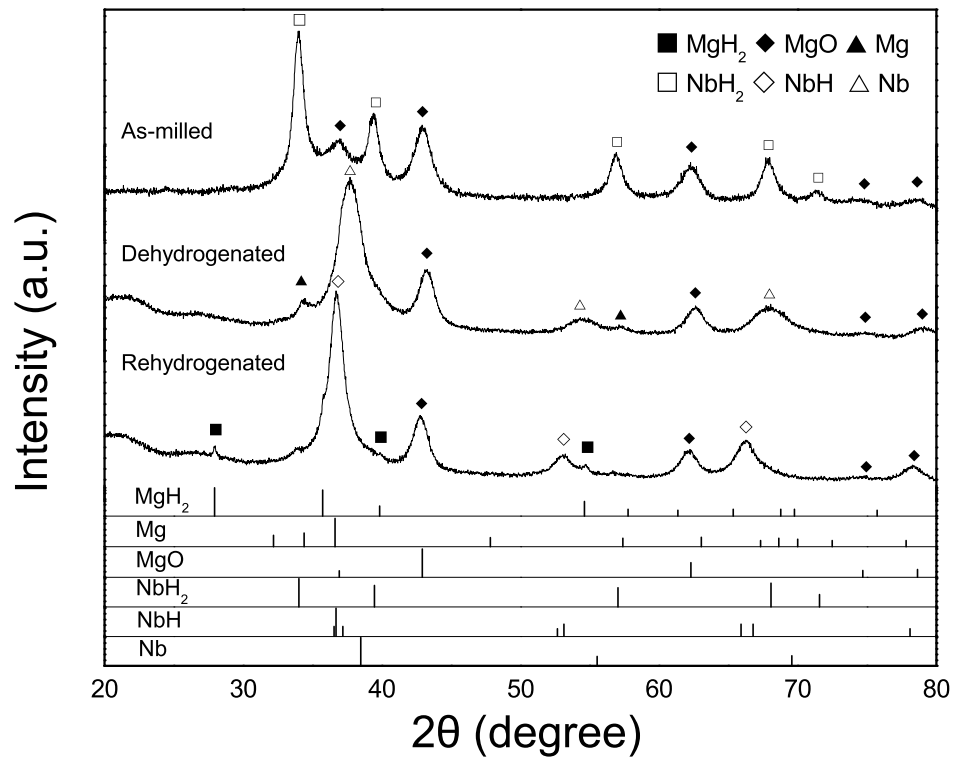
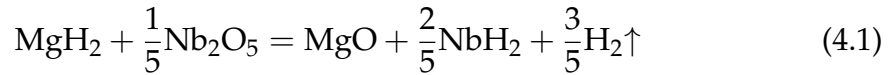


Figure 4.5: XRD profiles of $\text{MgH}_2\text{-Nb}_2\text{O}_5$ nanocomposites.

follows:



Equation 4.1 explains the common phenomenon that MgO is always found in the milled $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite. Additionally, the reduction of Nb_2O_5 agrees with the results shown in Chapter 3, implying that the reduction product, NbH_2 , may be the essential catalyst that improves the desorption kinetics. According to the mole ratio of the reactants, a small amount of MgH_2 should remain after ball-milling. The absence of the peaks of MgH_2 suggests that the residual MgH_2 is microcrystalline. In the dehydrogenated sample, since both MgH_2 and NbH_2 have decomposed, the XRD profile shows the coexistence of Mg , Nb , and MgO . After rehydrogenation, the peaks of MgH_2 and NbH were confirmed in the XRD profile. It indicates that, after one cycle, the initial additive, Nb_2O_5 , was converted into the niobium (I) hydride state.

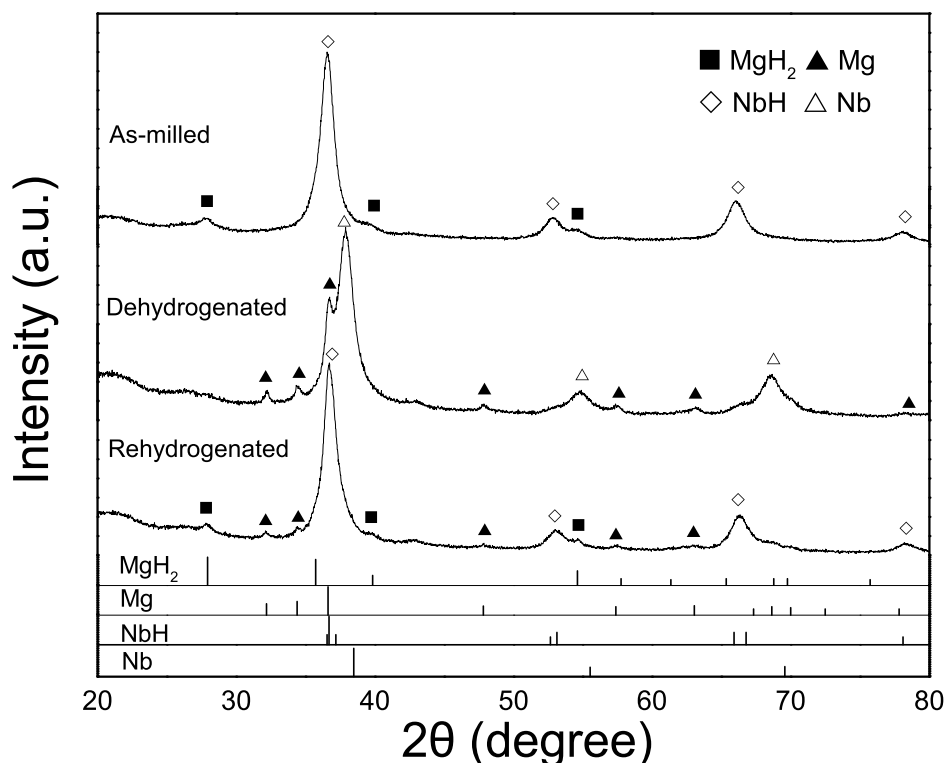


Figure 4.6: XRD profiles of $\text{MgH}_2\text{-Nb}$ nanocomposite.

$\text{MgH}_2\text{-Nb}$ composite

Similar as the case of Nb_2O_5 , reactions were also found between the MgH_2 and Nb. Figure 4.6 shows the XRD profiles of Nb-doped MgH_2 during the full cycle. Peaks from NbH were found in the spectrum of the as-milled sample, indicating that the initial additive was changed into NbH following the equation below:



This result is consistent with the work of Huot et al., in which NbH was also found in the 5 mol% Nb catalyzed MgH_2 nanocomposite [64]. The dehydrogenation resulted in the formation of Mg and Nb. Finally, the metals returned to MgH_2 and NbH state after rehydrogenation, and the composite gave a composition the same as the Nb_2O_5 -doped sample (if the byproduct MgO is ignored).

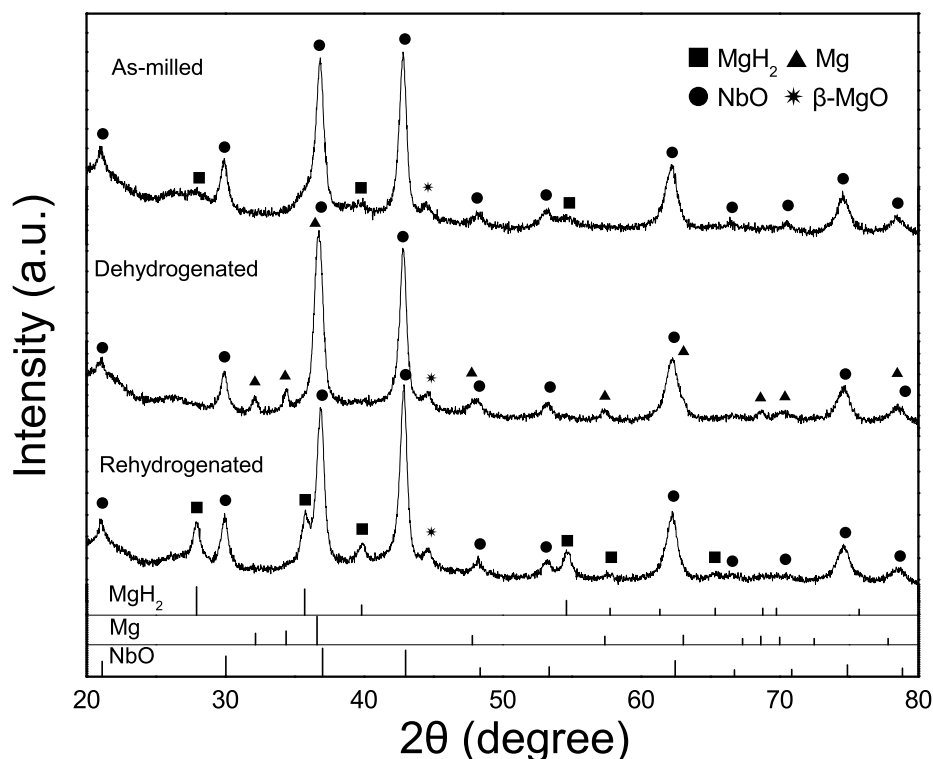


Figure 4.7: XRD profiles of $\text{MgH}_2\text{-NbO}$ nanocomposite.

$\text{MgH}_2\text{-NbO}$ composite

Figure 4.7 shows the XRD profiles of the NbO-doped sample during the full cycle. Unlike the obvious interactions between MgH_2 and the additives in the previous ones, no obvious reactions between MgH_2 and NbO were seen, as both of them remained after ball-milling. After dehydrogenation, the peaks of Mg were seen, due to the decomposition of MgH_2 . And the peaks of MgH_2 reappeared after rehydrogenation. During the whole process, the peaks of NbO remained unchanged, except for a slight change on the intensity. As an aside, an unknown peak at $2\theta = 44^\circ$, which is close to $\beta\text{-MgO}$ (400), appeared during the full cycle. We have not found any description about this metastable $\beta\text{-MgO}$ in the literature. Whether it helps the dehydrogenation or not is unclear.

4.3.3 Mechanism of the catalytic effect in $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite

It must be pointed out that in both Nb_2O_5 -doped and Nb-doped samples, the peaks of Nb in the XRD spectra of the dehydrogenated samples were a little shifted toward the lower angle (see Figure 4.8). The positions, however, quite match the metastable NbH_x phase, which is a solid solution described in the references [65, 98]. For one thing, it reaffirms the gateway model that NbH_x facilitates the hydrogen transportation in $\text{MgH}_2\text{-Nb}$ composites, described elsewhere [64, 65]. For another, it suggests the possibility that the Nb_2O_5 -doped sample may also undergo a dehydrogenation process following the Nb-gateway model, resulting in the formation of NbH_x solid solution as it does in the Nb-doped sample. This inference could be also supported by the estimation of E_a in the $\text{MgH}_2\text{-1 mol\%Nb}_2\text{O}_5$ and $\text{MgH}_2\text{-2 mol\%Nb}$ samples given in Section 4.3.1, since the values were quite comparable.

Comparing the XRD results of Nb_2O_5 -doped and Nb-doped samples, it can be noticed that the composition was the same after one cycle, except that MgO as the byproduct of the reaction existed in the former. The role of MgO was investigated in the previous section, indicating that the existence of MgO is meaningless for the desorption properties. Therefore, we can safely conclude that the catalytic effect in $\text{MgH}_2\text{-Nb}_2\text{O}_5$ nanocomposites is attributed to the existence of Nb, as it does in the Nb-doped composite. In both samples, the catalytic effect follows the same mechanism during dehydrogenation, which is based on a Nb-gateway model for hydrogen release. The scheme for the Nb-gateway model is shown in Figure 4.9. First, niobium (di)hydride decomposes rapidly (because niobium hydride is thermodynamically unstable) and

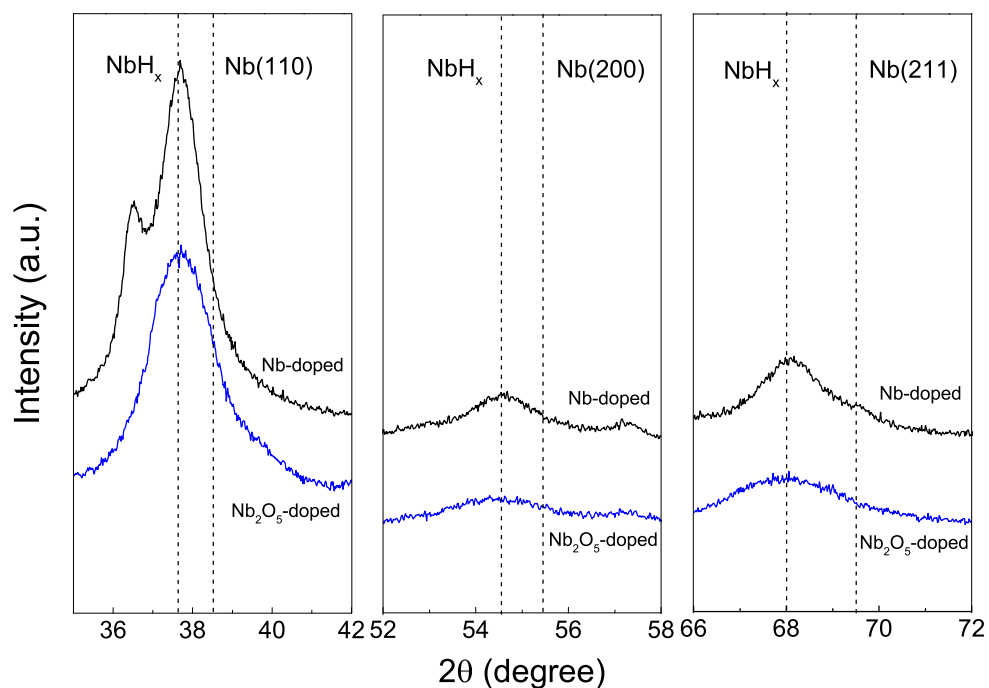


Figure 4.8: XRD profiles of the dehydrogenated Nb_2O_5 -doped and Nb-doped samples: Zoomed on the region of Nb peaks.

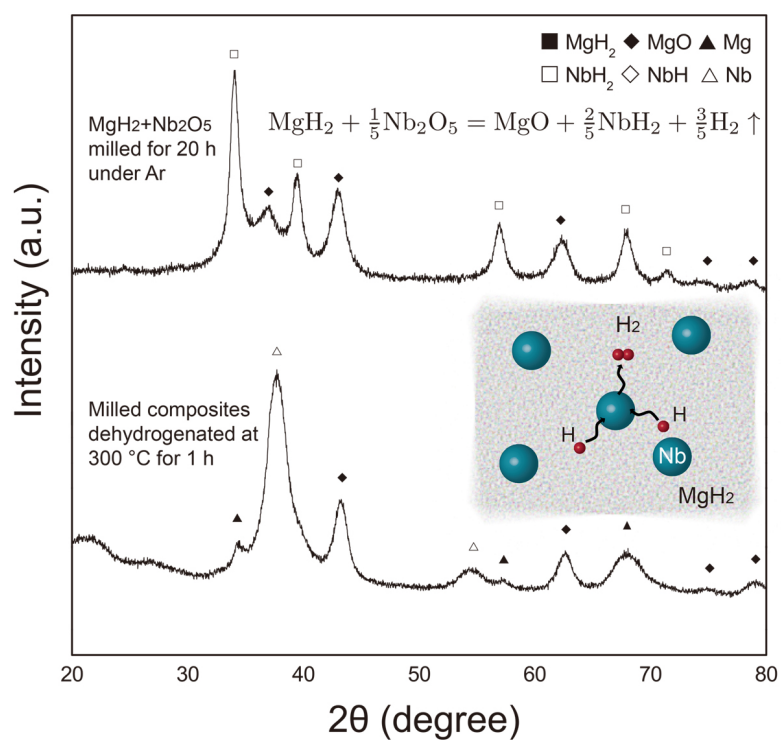


Figure 4.9: Scheme of the Nb-gateway model in $\text{MgH}_2\text{-Nb}_2\text{O}_5$ composite.

Nb forms. Then, hydrogen diffuses from MgH_2 to Nb, forming the NbH_x solid solution. The recombination of hydrogen molecules can be accelerated on the surface of NbH_x , which is stabilized by the hydrogen flow from MgH_2 to the outside, until MgH_2 exhausts finally. In both samples, Nb plays an important role in hydrogen transportation and recombination, acting as an essential catalyst and improving the kinetics during dehydrogenation.

4.3.4 The size effect in the desorption

As we stated that the catalytic effect of Nb_2O_5 and Nb follows the same mechanism, the Nb-gateway model, one would doubt why Nb_2O_5 -doped and Nb-doped samples exhibited different desorption properties (see Figure 4.1). In order to figure out the differences between them, we estimated the crystallite size of MgH_2 in the as-milled samples, as well as that of Mg and Nb after dehydrogenation, using the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (4.3)$$

where K is the shape factor, typically 0.89, λ is the X-ray wavelength, 1.54 Å for Cu radiation, β is the full width at half-maximum (fwhm), θ is the Bragg angle, and τ is the mean size of the crystallites [90]. For the estimation of MgH_2 , we selected the strongest peak, MgH_2 (110), to apply Equation 4.3. In the case of Mg and Nb, (110) and (200), respectively, rather than the strongest peaks were chosen, in order to avoid the peak overlapping. The measured fwhm and corresponding crystallite size are listed in Table 4.1. The size of MgH_2 in the Nb-doped and NbO-doped samples after ball-milling was around 70 Å, while that in the Nb_2O_5 -doped sample was microcrystalline, since the

Table 4.1: Crystalline size (τ ; in Å) of MgH_2 , Mg and Nb in each samples

Peak	Nb_2O_5 -doped		Nb-doped		NbO-doped	
	FWHM ($^\circ$)	τ (Å)	FWHM ($^\circ$)	τ (Å)	FWHM ($^\circ$)	τ (Å)
MgH_2 (110)	undetectable	microcrystalline	1.086	76	1.121	73
Nb (200)	2.367	38	1.232	68	–	–
Mg (110)	1.029	88	0.487	190	0.639	143

peak was not detected in the XRD spectrum. Therefore, the size of MgH_2 in the Nb_2O_5 -doped sample is extremely smaller than those in the others. The size of Nb and Mg in the Nb_2O_5 -doped sample after dehydrogenation was evaluated as 38 Å and 88 Å respectively, roughly half those in the Nb-doped sample (68 Å and 190 Å, respectively). It was suggested that when MgH_2 is milled with Nb_2O_5 , the crystallites tend to be refined. The decrease in size can lead to a fast decomposition, thus partially explaining the better desorption property of the Nb_2O_5 -doped sample, compared to the others. On the other hand, being comparable in size compared to the Nb-doped sample, the NbO-doped sample showed better desorption property. It implies that there are other factors determining the desorption kinetics in the NbO-doped sample.

In order to compare the morphology of the composites, we observed the as-milled and hydrogenated samples by SEM. The typical images are shown in Figure 4.10. It can be seen that for all the composites, the morphology hardly changed after dehydrogenation. On the other hand, the difference in size can be seen obviously. The Nb_2O_5 -doped sample shown in Figure 4.10a,d is distinctly small in size, while the particle size in the other two is much bigger than the former. It indicates that both MgH_2 and the additive could be pulverized more easily in the Nb_2O_5 -doped composite. This tendency agrees with the aforementioned results in 1 mol% Nb_2O_5 -doped and 2 mol% Nb-doped, as well as 2 mol% NbO-doped samples, as shown in Figure 4.4. The phenomena

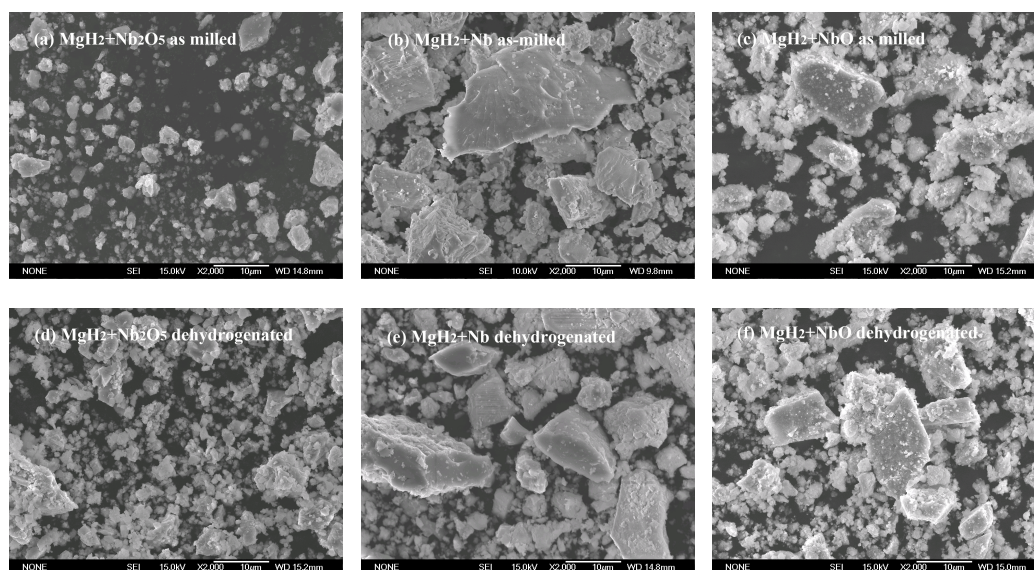


Figure 4.10: SEM images showing the morphology of the as-milled and dehydrogenated composites.

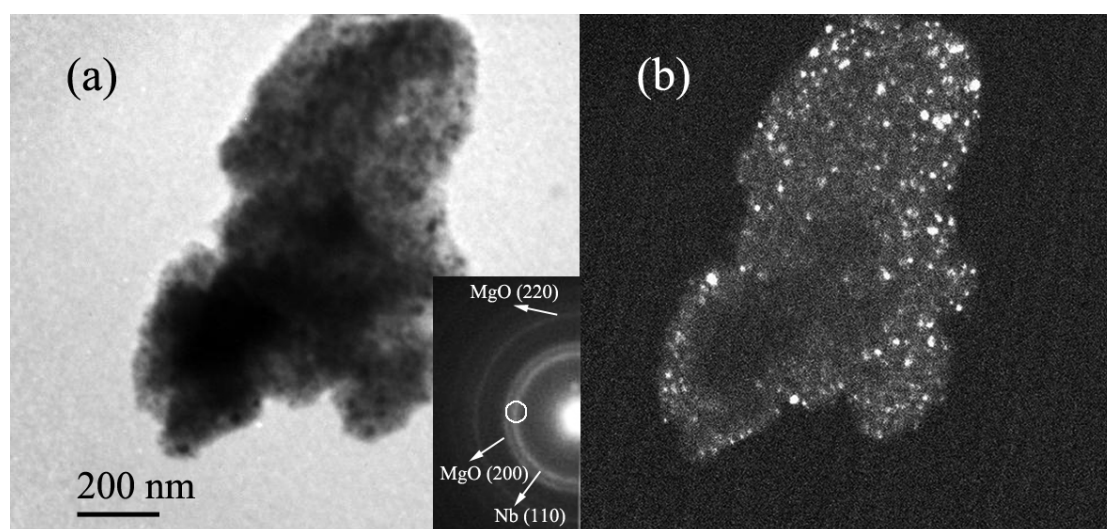


Figure 4.11: Typical TEM micrograph of the Nb_2O_5 -doped composite after dehydrogenation. (a): Bright field image. (b): Corresponding dark field image taken from the circled area.

could be explained by the physical properties of the additives. As a ceramic, Nb_2O_5 exhibits hard and brittle character, while Nb metal and NbO, which show metallic properties, are ductile and not easy to be pulverized. Therefore, the particles tend to be reduced in size when Nb_2O_5 is added, compared to its counterparts, NbO and Nb. This difference in size may play an important role during the catalyst-promoted dehydrogenation.

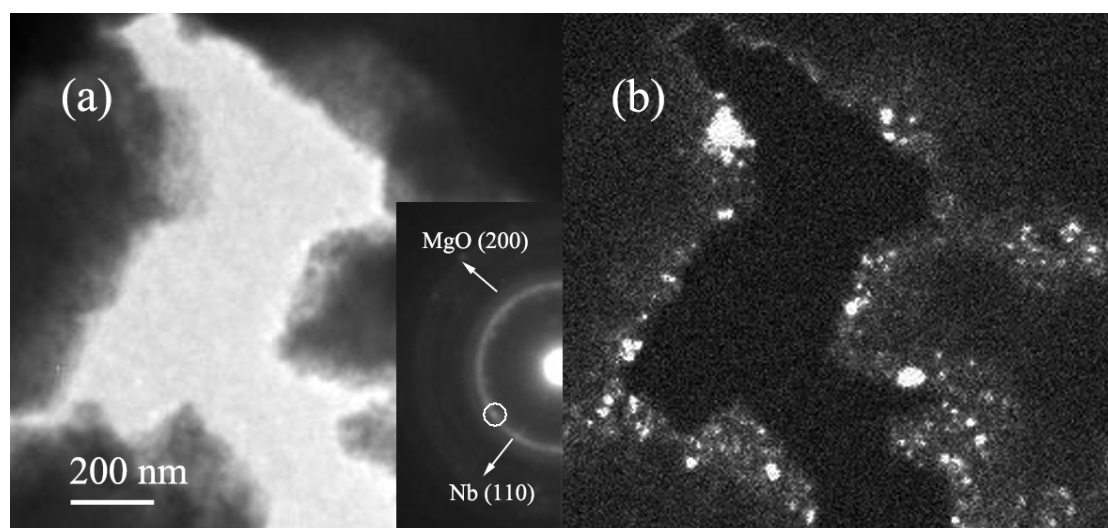


Figure 4.12: Typical TEM micrograph of the Nb-doped composite after dehydrogenation. (a): Bright field image. (b): Corresponding dark field image taken from the circled area.

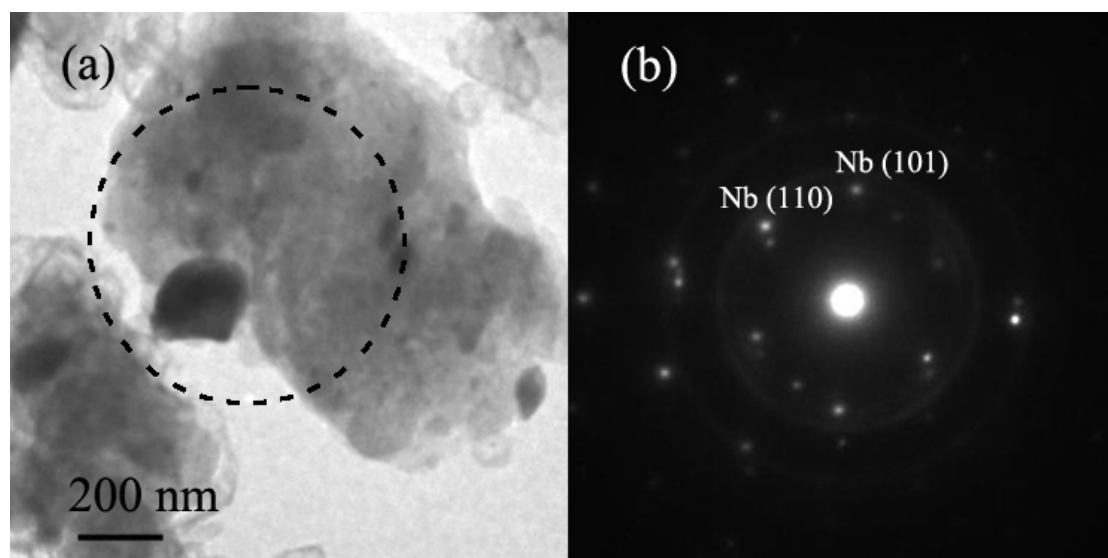


Figure 4.13: TEM images showing Nb particles in the Nb-doped composite after dehydrogenation. (a): Bright field image. (b): Diffraction pattern from the circled area.

Figure 4.11 and Figure 4.12 show the typical TEM images of the Nb_2O_5 -doped and Nb-doped composites after dehydrogenation. The insets in both figures show the Debye rings of Nb, meaning that Nb is polycrystalline. Nb crystals can be seen in the dark field images taken by selecting parts of Nb (110) rings marked by the white circles in the diffraction pattern. For the Nb_2O_5 -doped sample as shown in Figure 4.11b, it can be seen that Nb crystals, with a size

around 10–20 nm, dispersed homogeneously in Mg matrix. However, in the case of the Nb-doped sample, Nb crystals with a size of ~ 100 nm can be observed, as shown in Figure 4.12b. We also found Nb single-crystals with a size around 200 nm, shown in Figure 4.13. The inhomogeneity in the size of the Nb catalyst could hinder the catalytic effect and deteriorate the desorption properties.

Given all the observations above, the difference in the desorption properties between Nb_2O_5 -doped and Nb-doped samples could be explained. As the SEM and TEM observations all revealed that the size of both MgH_2 and the catalyst was quite smaller in the former than that in the latter, the contribution of such size refinement should be taken into account in the desorption process. As is well known to all, the smaller the particle size is, the more the surface area will be. By decreasing the size of both MgH_2 and the catalyst, the surface area can be significantly increased. Thus, there are more chances MgH_2 and the catalyst contact with each other. As a result, the sites for reactions are increased, hence the reaction rate can be increased drastically. Therefore, even following the same mechanism during desorption, the smaller size in the Nb_2O_5 -doped sample definitely leads to faster kinetics compared with the Nb-doped one.

Taking advantage of high-resolution electron microscopy, we were able to confirm the existence and the size of NbH_2 and Nb in the 1 mol% Nb_2O_5 -doped composite. Figure 4.14a shows the high-resolution image of the 1 mol% Nb_2O_5 -doped composite before dehydrogenation. In the FFT image (Figure 4.14b) taken from the selected area, a pair of spots corresponding to NbH_2 (111) was identified. The size of NbH_2 was around 20 nm, as can be seen in the IFFT image shown in Figure 4.14c. The high-resolution image of the dehydrogenated sample is presented in Figure 4.15a. Similarly the spots

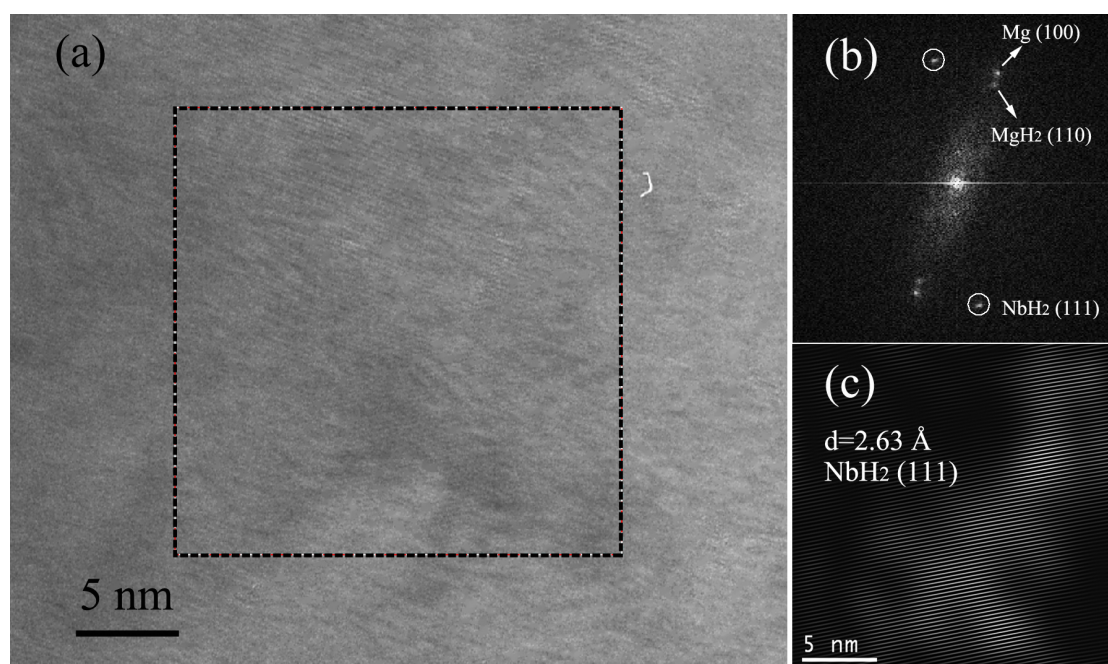


Figure 4.14: (a) High-resolution image, (b) FFT, and (c) IFFT images of the MgH_2 and 1 mol% Nb_2O_5 composite after ball-milling. The FFT area is marked by the square in (a).

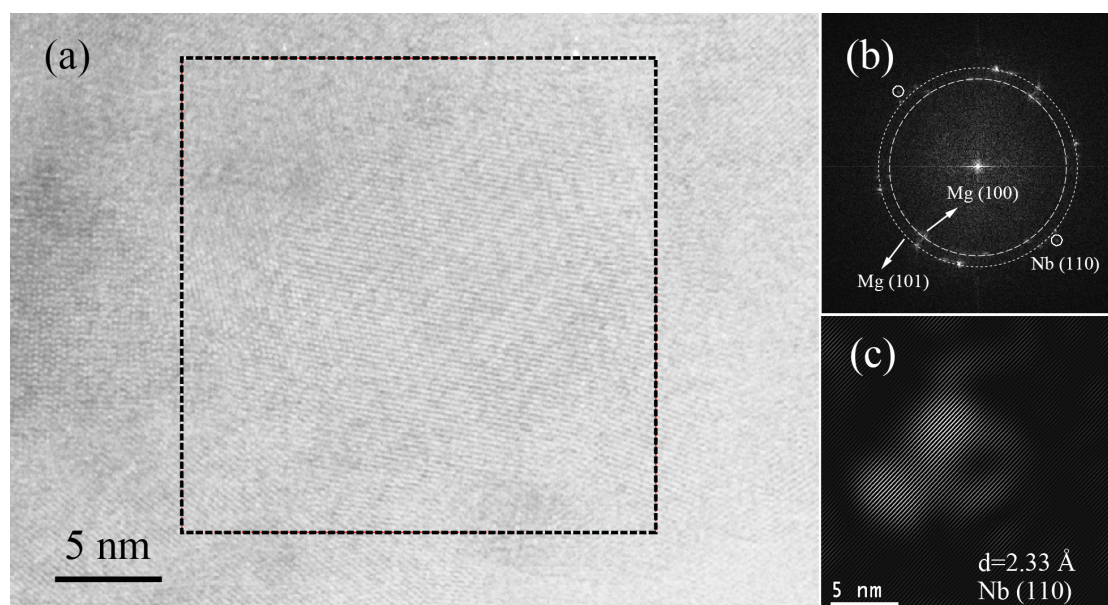
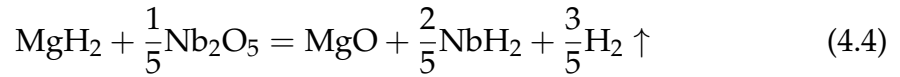


Figure 4.15: (a) High-resolution image, (b) FFT, and (c) IFFT images of the MgH_2 and 1 mol% Nb_2O_5 composite after dehydrogenation. The FFT area is marked by the square in (a).

of Nb (110) were found in the FFT image shown in Figure 4.15b. In the IFFT image shown in Figure 4.15c, the size of Nb was estimated to be around 10 nm. All these observations indicate that the catalyst highly dispersed in the sample, with the size around 10–20 nm. The results well validated the Nb-gateway model in the $\text{MgH}_2\text{-Nb}_2\text{O}_5$ system. Tiny crystals of Nb act as the gateway through which hydrogen transports from MgH_2 to the outside.

4.3.5 NbO-Catalyst and the mechanism

While strong interaction between MgH_2 and Nb_2O_5 , as well as Nb, was confirmed, the unexpected stability of NbO is obscure. If considering on the thermodynamics, $\Delta G^\ominus$ and $\Delta S^\ominus$ for the possible reactions between MgH_2 and Nb-contained catalysts can be calculated as follows:



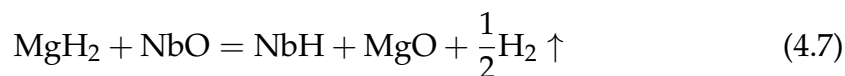
$$\Delta G^\ominus = -212\text{kJ} \cdot \text{mol}^{-1}; \Delta S^\ominus = 60\text{J} \cdot \text{mol}^{-1}$$



$$\Delta G^\ominus = -6.1\text{kJ} \cdot \text{mol}^{-1}; \Delta S^\ominus = 22\text{J} \cdot \text{mol}^{-1}$$



$$\Delta G^\ominus = -187\text{kJ} \cdot \text{mol}^{-1}; \Delta S^\ominus = -18\text{J} \cdot \text{mol}^{-1}$$



$$\Delta G^\ominus = -207\text{kJ} \cdot \text{mol}^{-1}; \quad \Delta S^\ominus = 59\text{J} \cdot \text{mol}^{-1}$$

According to the equilibrium thermodynamics, all the reactions should happen based on the free energy criterion. However, since ball-milling creates a non-equilibrium system, entropy should be considered mainly. Therefore reaction 4.6 cannot happen according to the entropy criterion. Whereas reaction Equation 4.7 seems able to occur, but depending on the reaction path. If it starts with Equation 4.6 and then follows the decomposition of NbH_2 , then the former will create an energy barrier, which could be too high to reach under mechanical milling. Similar consideration can also be made on reaction 4.4 and 4.5, because the reaction path is quite important in the solid-solid reactions. To clarify the issue, more investigation, with approaches more close to the pure chemistry, should be made in future. Nevertheless, these approaches are either out of the topic of this work or beyond our knowledge as a material researcher. Study on NbO will be done in the future work, using the approaches such as calculations to figure out this issue.

However, if considering from the viewpoint of material science, possible explanation on the issue could be addressed as follows. Since it was pointed out that Nb_2O_5 could be well pulverized while NbO could not, all due to that the former is brittle and the latter is ductile. When the size of the material is decreased, some properties, even including thermodynamics, could change unexpectedly. During ball-milling process of Nb_2O_5 with MgH_2 , the oxide may be gradually reduced following the sequence of $\text{Nb}_2\text{O}_5 \rightarrow \text{NbO}_2 \rightarrow \text{Nb}_2\text{O}_3 \rightarrow \text{NbO}$. And it could be predicted that the reduced fraction is tiny in size, leading to

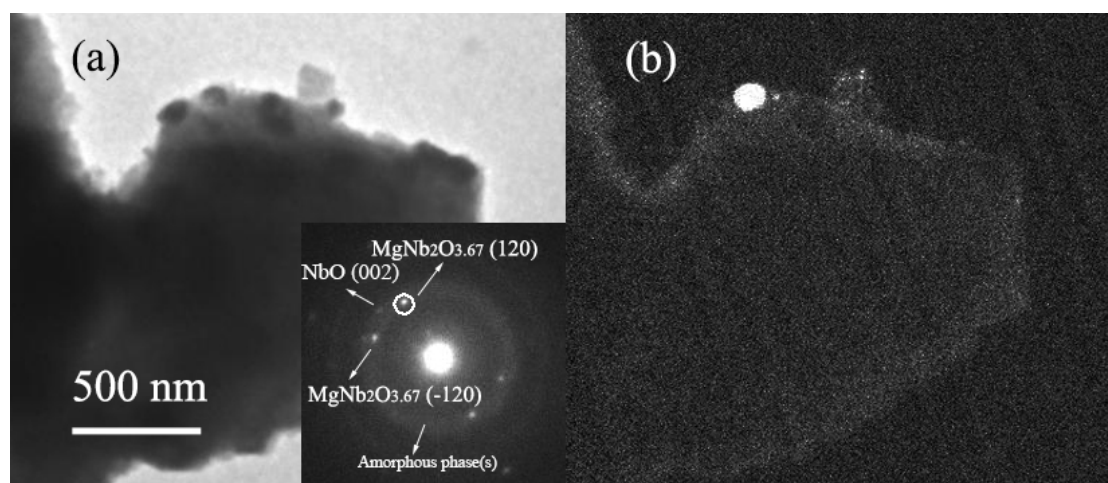


Figure 4.16: Typical TEM micrograph of the NbO-doped composite. (a): Bright field image. (b): Corresponding dark field image taken from the circled area.

good reaction kinetics. In contrast, NbO could not be cracked effectively into small pieces, which give a limitation on the reaction kinetics. Actually, small changes on the composition was confirmed in TEM observation. In the inset of Figure 4.16, single-crystal pattern of NbO, as well as $\text{MgNb}_2\text{O}_{3.67}$, has been indexed. In addition, a halo ring corresponding to an unknown amorphous phase(s), with the d -spacing range of 2.1–2.6 Å, could be seen in the diffraction pattern. It implied that some reactions between MgH_2 and NbO, with poor kinetics, did occur during the milling process, forming $\text{MgNb}_2\text{O}_{3.67}$ and the unknown amorphous phase(s). These changes support the explanation that the reaction is possible but in poor kinetics. Therefore, it is possible that the poor reactivity of NbO is relevant to the size effect.

On the other hand, since NbO was unexpectedly stable during the full cycle, it is possible that NbO itself as the main phase provided the catalytic effect, following some mechanism rather than the Nb-gateway model. In a recent study, NbO (111) was found to show effective catalytic activities [99], which lend support to such consideration. Besides, the existence of $\text{MgNb}_2\text{O}_{3.67}$ is

also worth considering. The dark field image in Figure 4.16b was taken from $\text{MgNb}_2\text{O}_{3.67}$ (120). By comparing it with the corresponding bright field image in Figure 4.16a, we can easily find out the single crystals of $\text{MgNb}_2\text{O}_{3.67}$, which show a dark contrast, with a size of ~ 200 nm. As it was stated previously, the Mg–Nb–O phase was considered to help with hydrogen diffusion. It was pointed out that MgO is almost impermeable for hydrogen [100]. The Mg–Nb–O phase was proved able to absorb hydrogen [101] and even improve desorption properties of MgH_2 as a catalyst [102]. Here the existence of $\text{MgNb}_2\text{O}_{3.67}$ may provide pathways for hydrogen diffusion through the MgO scale covered on the surface of MgH_2 , improving the desorption properties during dehydrogenation.

4.4 Summary

The state of the Nb-contained catalysts in MgH_2 composites was clarified in this chapter. Nb_2O_5 and Nb reacted with MgH_2 during the ball-milling process. NbH_2 and NbH, respectively, formed as the products of the reactions. During dehydrogenation, both NbH_2 and NbH decomposed into Nb and returned to the NbH state after rehydrogenation. It is suggested that both Nb_2O_5 -doped and Nb-doped samples dehydrogenated following the Nb-gateway model, in which Nb facilitates the hydrogen transportation from MgH_2 to the outside, and accelerates the recombination of hydrogen molecules during the process. On the other hand, reactions between NbO and MgH_2 were not confirmed. The promoted dehydrogenation may either be attributed to the catalytic effect of NbO itself or the existence of the $\text{MgNb}_2\text{O}_{3.67}$ phase. In addition, we found that the Nb_2O_5 -doped sample tended to be refined in size,

compared to the Nb-doped and NbO-doped ones, due to the hard and brittle features of Nb₂O₅. This size effect partially leads to a better dehydrogenation property in the sample. NbH₂ and Nb, with 10–20nm in size, were also observed in the composite doped by 1 mol% Nb₂O₅, validating the Nb-gateway model in the MgH₂-Nb₂O₅ system. All the results reveal that tiny Nb crystals highly dispersed in the composites act as the essential catalyst and improve the desorption properties following the Nb-gateway model.

Chapter 5

Mg→MgH₂ Transformation Process during Hydrogenation

5.1 Background and purpose

In the previous chapters, the catalytic effect of Nb₂O₅ was discussed. The Nb-gateway model was proposed, which explains the catalytic effect and provide the important guidance for further development on the system. The present chapter was put on understanding the Mg→MgH₂ transformation process during absorption, serving as another indicator for us to develop the material.

In this chapter, TEM was employed to observe the Mg/Nb₂O₅ evaporated composite before and after hydrogenation, in order to clarify the Mg→MgH₂ transformation process. Since it is difficult to make an in-situ observation, MgO was determined to associate the metal and hydride. We assume that MgO is the

oxidation product of Mg, while that of MgH₂ is Mg(OH)₂, which is amorphous and not easily identified via TEM. This assumption could be supported by the work of Friedrich et al., in which Mg was oxidized immediately when exposed to air, forming an oxide layer of 3-4 nm, while MgH₂ was less oxidized in the air, with only a small amount of amorphous hydroxide on the surface [103]. On the basis of that assumption, we were able to relate Mg and MgH₂ indirectly by separately investigating the relationships of Mg/MgO and MgH₂/MgO. Discussions on the transformation process was made according to the observations. A model demonstrating the atomic movement during the transformation process was proposed based on the observations.

5.2 Experimental procedures

A 150-A mesh copper TEM grid on which single crystals of Nb₂O₅ were dispersed was placed into a thermal-evaporator. Roughly 2 pieces of Mg turnings were placed in the tungsten boat, which was connected with a current-control system. The evaporator was evacuated for 1 h to ensure that a high vacuum of $\sim 1 \times 10^{-4}$ Pa was reached. Evaporation was carried out by slowly increasing the current to 30 A. After exposing the grid to the Mg vapor for 10 s, the deposition was stopped by a shutter immediately, and the current was powered off at the same time. In this way, Mg was randomly evaporated on the surface of Nb₂O₅. After evaporation, a custom designed container, with a lid that could be controlled by a lever out side the evaporation chamber, was used to prevent air exposure of the sample during transport from the evaporator into the glove box. Hydrogenation of the sample was carried out under a 5 bar H₂

atmosphere at 250 °C for 2 h. TEM observations were performed before and after hydrogenation using a 200 kV TEM and a 1250 kV HVEM.

5.3 Results and discussions

5.3.1 TEM observations on the as-prepared sample

The TEM image showing the typical microstructure of the sample before hydrogenation is presented in Figure 5.1. In the bright field image (panel a), small Mg particles, ~ 200 nm in size, are seen attaching on the surface of the single crystals of Nb_2O_5 . The inset image shows the diffraction pattern from the selected area, where Mg can be identified. By selection of the Mg(002) spot, the corresponding dark field image was captured, as shown in panel b. The particle with bright contrast shows the single crystal of Mg, with the size less than 180 nm.

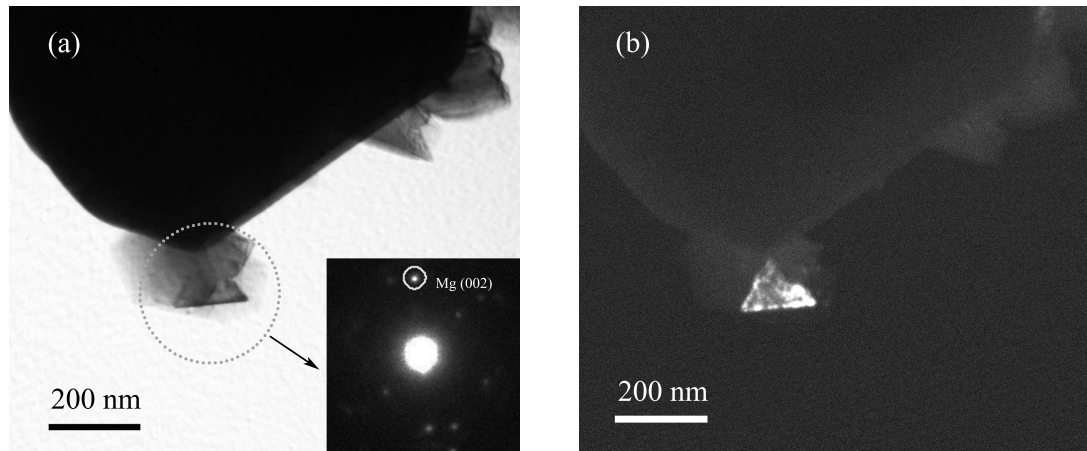


Figure 5.1: Typical TEM micrographs of the sample before hydrogenation. (a) Bright field image, with an inset image of the diffraction pattern from the selected area. (b) Dark field image from Mg (002).

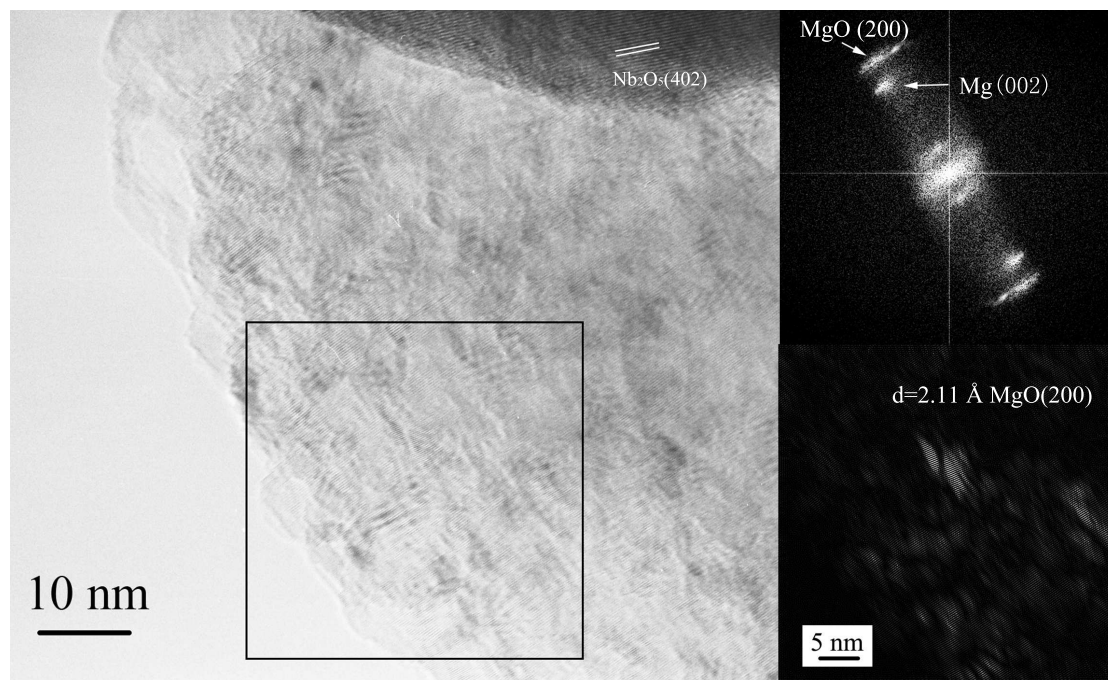


Figure 5.2: (a) Typical high-resolution image with the FFT area marked by the square. (b) FFT and (c) IFFT images of the sample before hydrogenation.

The typical high-resolution image of the sample before hydrogenation is shown in Figure 5.2. The FFT image (panel b) from the analyzed area clearly shows two pairs of spots, identified separately as Mg(002) and MgO(200), revealing that the evaporated Mg was partially oxidized during the process. Even though protection was taken at every step, slight oxidation is almost inevitable because of the high sensitivity of Mg to oxygen. On the other hand, the spots of Mg(002) and MgO(200) are collinear, revealing that their orientations should be parallel. This could indicate that during the oxidation of Mg, oxides may form along the direction of $\text{MgO}(200) \parallel \text{Mg}(002)$. The diffraction pattern of MgO in the FFT image is more like a pair of short arcs on the circle, rather than the single-crystal spots. It is likely that small MgO crystals formed and then partially cracked at a critical size. As a result, the direction of oxide formation gradually bent and deviated from the original direction, so that we were able to see the short arcs in the FFT image. When we made the IFFT by selecting

the arcs of MgO , it could be seen that MgO existed as the tiny crystals with a size smaller than 5 nm (see panel c). As an side, the lattice plane of $\text{Nb}_2\text{O}_5(402)$ could also be seen in the area with dark contrast. The orientation dependence was not found between evaporated Mg and the Nb_2O_5 substrate, suggesting that the evaporation of Mg was completely random.

5.3.2 TEM observations on the hydrogenated sample

In order to investigate the orientation of hydride formation, the hydrogenated sample was then observed by HVEM. Figure 5.3a shows the high-resolution image of the interface between evaporated Mg and the Nb_2O_5 substrate. FFT was performed on the selected area, shown in Figure 5.3b. The spot pairs in the FFT image could be separately identified as $\text{MgO}(200)$, $\text{MgH}_2(101)$ and $\text{Nb}_2\text{O}_5(110)$, meaning that the evaporated Mg was hydrogenated successfully under the given condition, though parts of it were oxidized. Moreover, three pairs of spots are on one straight line, similarly indicating that the orientation relationship of $\text{MgO}(200)$, $\text{MgH}_2(101)$ and $\text{Nb}_2\text{O}_5(110)$ is parallel. As we mentioned previously, Mg is more sensitive to oxygen compared to hydride. Here MgO , itself, was believed to be the oxidation product of Mg , rather than MgH_2 . Considering the orientation relationship of $\text{MgO}(200) \parallel \text{Mg}(002)$ during oxidation, as mentioned above, we proposed that hydride could form along the direction of $\text{MgH}_2(101) \parallel \text{Mg}(002)$ during hydrogenation. On the other hand, it is interesting that $\text{MgH}_2(101)$ is also parallel to $\text{Nb}_2\text{O}_5(110)$. It is possible that the phenomenon is related to some mechanisms of catalytic effect, though we could not confirm this in the present work. This point is still under investigation.

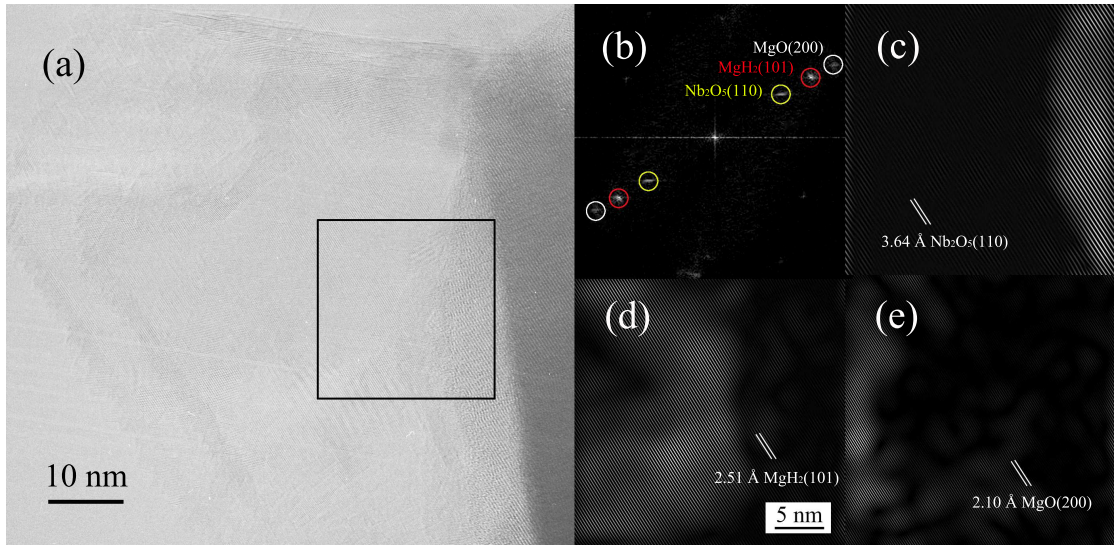


Figure 5.3: (a) High resolution image, (b) FFT and (c-e) IFFT images of the hydrogenated sample. FFT area is marked by the square in (a).

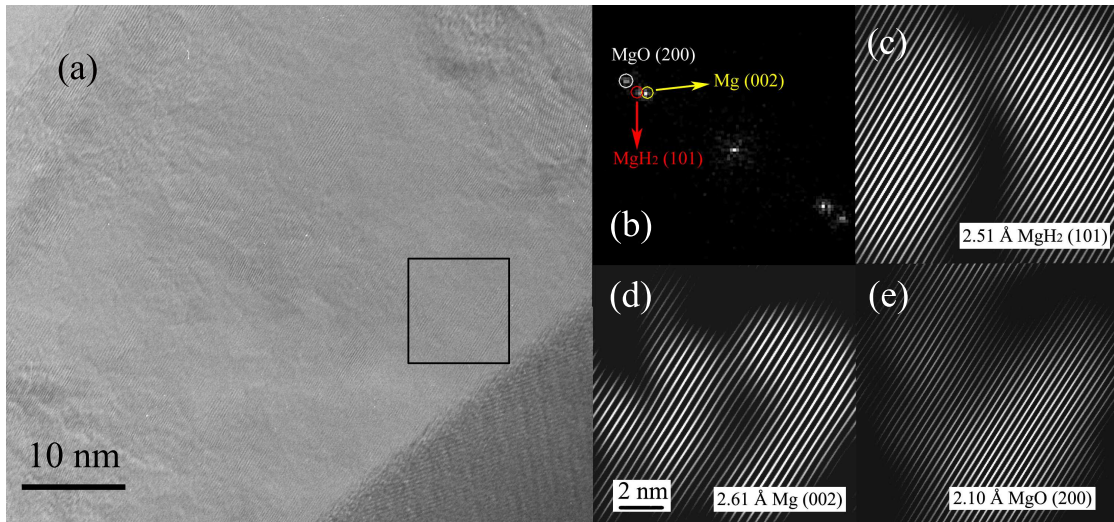


Figure 5.4: Another observation of the hydrogenated sample showing Mg-MgO-MgH₂ coexistence. (a) Lattice image. (b) FFT image from the selected area. (c-e) IFFT images showing MgH₂(101), Mg(002) and MgO(200), respectively. FFT area is marked by the square in (a).

Figure 5.4 shows another observation of the hydrogenated sample. Fortunately in the FFT image, we found that Mg, MgH₂, and MgO coexisted in the analyzed area (panel b). The collinearity of the spots corresponding to the three phases shows the parallel relationship of $\text{Mg}(002) \parallel \text{MgH}_2(101) \parallel \text{MgO}(200)$, verifying our assertion above. In addition, from the IFFT images in panels c-e, we can see that the position of MgH₂ almost coincides with Mg, while differing

from MgO. This suggests that Mg was partially oxidized, along the direction of $\text{MgO}(200) \parallel \text{Mg}(002)$, and then the unoxidized part was hydrogenated partially along the direction of $\text{MgH}_2(101) \parallel \text{Mg}(002)$, while MgO remained unchanged. As a result, the three-phase coexistence formed in the area.

5.3.3 $\text{Mg} \rightarrow \text{MgH}_2$ transformation process

According to the observations above, we were able to confirm that the transformation of Mg occurs along the particular direction of $\text{MgH}_2(101) \parallel \text{Mg}(002)$ or $\text{MgO}(200) \parallel \text{Mg}(002)$. Further extracting the information of these planes, the surface energy was noticed, since references suggested that the surface-formation energy for $\text{MgH}_2(101)$ as well as $\text{MgO}(200)$ was the lowest among those low-indexed planes [104]. Thus, the transformation process could be further inferred based on them. As is known to us that the surface reaction takes an important role in the hydrogenation and oxidation, the reaction may occur originally on the surface of the Mg matrix. By considering the beginning stage of the reaction, it is likely that a single layer of MgH_2 or MgO, with a small range of several atoms, forms first. In order to minimize the formation energy, these single layers may prefer the orientation that lowers the surface-formation energy. Therefore, single layers of $\text{MgH}_2(101)$ or $\text{MgO}(200)$ form on the surface of the Mg matrix, oriented along (002), at the beginning stage. Once these single layers have formed, they grow along these particular directions from the surface to the inside and enlarge the range of each layer at the same time. Finally, parts of Mg change to MgH_2 or MgO, resulting in the $\text{Mg}-\text{MgH}_2-\text{MgO}$ coexistence that we have observed above.

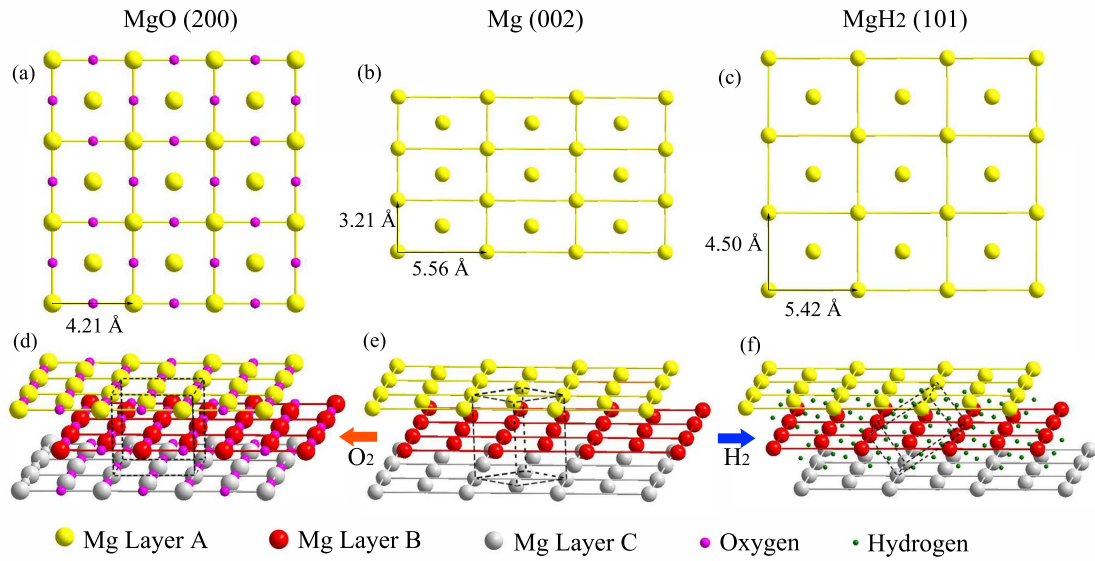


Figure 5.5: Atomic movement model of Mg transformation during oxidation or hydrogenation: (a), (b) and (c) show the critical plane of MgO, Mg and MgH₂, respectively; (d), (e) and (f) are the corresponding 3-dimensional structures.

The atomic movement model could be proposed according to the discussion above. We have drawn the critical plane of MgO, Mg, and MgH₂ in Figure 5.5a–c, as well as the three-dimension (3D) atomic skeleton containing three layers of each plane (marked as Mg layer A, B, and C, separately) in Figure 5.5d–f. The unit cell edge of each phase was delineated with the dashed line. During the transformation from Mg to MgH₂ or MgO, the Mg frame remains the same, except the slight adjustment of the atomic distances (see Figure 5.5, panels a–c). Because of the introduction of O or H, this frame expands in different degrees. From the 3D viewpoint (see Figure 5.5, panels d–f), the layers shift a little during the transformation. During hydrogenation, the second layer (Mg layer B) needs to shift along $[1\bar{1}00]$ by one-twelfth of the vector length and the third layer (Mg layer C) shifts along $[\bar{1}100]$ by one-half of the vector length. On the oxidation side, the formation of the second layer (Mg layer B) shifts along $[\bar{1}100]$ by one-sixth of the vector length while the

third layer (Mg layer C) is a complete repeat of layer A (because of the stacking method of the face-centered cubic structure). The complete transformation is the combination of both distance adjustment and layer shift. They occur simultaneously during the transformation, resulting in the formation of new structures.

5.4 Summary

The Mg→MgH₂ transformation of evaporated Mg-Nb₂O₅ composites during the hydrogenation was observed using TEM and HVEM. Mg crystals, ~180 nm in size, were evaporated thermally on single crystals of Nb₂O₅. The existence of MgH₂ was confirmed in the sample hydrogenated at 250 °C, under a 5 bar H₂ atmosphere, for 2 h. It was found that hydrogenation occurred along the preferred orientation relationship that MgH₂(101)||Mg(002), as well as MgO(200)||Mg(002) during the inevitable oxidation process. It was indicated that the transformation process of Mg during hydrogenation and oxidation occurs following the sequence that MgH₂(101) or MgO(200) single layers form on the surface of Mg(002) and then grow along these certain directions from the surface to the inside, as well as enlarge the range of each layer at the same time. A structural model, in which the Mg-Mg distance is adjusted according to the introduction of H or O, and correspondingly the Mg layers shift slightly, was proposed to demonstrate the transformation process.

Chapter 6

Conclusions and Prospects

In this thesis, the catalytic effect of Nb_2O_5 , as well as the $\text{Mg} \rightarrow \text{MgH}_2$ transformation process was investigated in respect to the development of Mg/MgH_2 system for hydrogen storage. The desorption properties, mechanism of the catalytic effect, as well as the orientation relationship in the system were studied on the basis of a series of experiments. The results and conclusions were summarized as follows:

(1) The desorption properties of MgH_2 could be significantly improved by the addition of Nb_2O_5 during ball-milling. When the composite was milled for varied time from 0.02 h to 20 h, the desorption peak-temperatures started to decrease after 0.2 h and reached the lowest after 20 h. The activation energies were estimated to be 147, 138, 82, 70 and 63 kJ/molH_2 for the HM, 0.02 h, 0.2 h, 2 h and 20 h milled samples, respectively, thus decreasing in accordance with the improved desorption properties. Nb_2O_5 particles were refined gradually during ball-milling, as evidenced by XRD and TEM results. Thus the homogeneous distribution could lead to the improvement on the desorption properties. Moreover, in the XPS measurements, the reduced Nb compound(s)

with the valence of Nb less than +5 were confirmed to exist at least on the surface of the catalyst. The reduced compound(s), considering the importance of the surface reactions, should play an essential role on improving the desorption properties and decreasing the activation energy.

(2) In order to figure out the reduced Nb compound(s), the state of the catalyst was intensively studied. Not only Nb₂O₅ but also its reduced counterparts, NbO and Nb, were investigated and compared. XRD results on the as-milled, dehydrogenated, and rehydrogenated composites in which 50 wt% additives were added indicated the reactivity of MgH₂ towards the additives as follows:

a) Nb₂O₅ reacts with MgH₂ during ball-milling, forming NbH₂ and MgO. In dehydrogenation, the hydride decomposes into the metal state, Nb, and then returns to the NbH state after rehydrogenation.

b) Nb also reacts with MgH₂ similarly during ball-milling, except that the product is NbH rather than NbH₂. In the following dehydrogenation and rehydrogenation processes, its state changes as NbH→Nb→NbH.

c) No obvious reactions are there between NbO and MgH₂.

The same composition in the Nb₂O₅-doped and Nb-doped samples suggested that both samples dehydrogenated following the same mechanism, the Nb-gateway model, in which Nb facilitates the hydrogen transportation from MgH₂ to the outside, and accelerates the recombination of hydrogen molecules during the process. The different desorption properties in them were considered to be due to the difference in the size of the catalysts. SEM observations revealed that the Nb₂O₅-doped sample tended to be refined in size, because of the hard and brittle features of Nb₂O₅; TEM observations showed that NbH₂

and Nb highly dispersed in the Nb₂O₅-doped sample with 10–20 nm in size—both of them are in comparison with its counterpart, Nb, which is too ductile to be refined by ball-milling, as the Nb crystals with the size of ~100 nm were seen in TEM observations. As a side, the promoted dehydrogenation in the NbO-doped sample may either be attributed to the catalytic effect of NbO itself or the existence of the MgNb₂O_{3.67} phase; the latter was confirmed by the TEM observation. An unknown amorphous phase(s) was also seen under TEM, suggesting that NbO partially reacted with MgH₂ with poor kinetics. The exact mechanism in the sample needs further investigation.

(3) Mg→MgH₂ transformation process were investigated in terms of TEM observations. It was observed that the transformation occurred along the specific orientation relationship of MgH₂(101)||Mg(002), as well as MgO(200)||Mg(002) during the inevitable oxidation process. Considering the low surface-formation energies of MgH₂(101) and MgO(200), the transformation process could be inferred as follows: First, MgH₂(101) or MgO(200) single layers form on the surface of Mg(002); Then the new phases grow along these certain directions from the surface to the inside, as well as enlarge the range of each layer at the same time. A structural model was proposed to demonstrate the transformation process, in which in which the Mg–Mg distance is adjusted according to the introduction of H or O, and the Mg layers shift slightly, correspondingly.

The Mg/MgH₂ system could be a potential candidate for the hydrogen storage materials, as long as the poor kinetics is improved. According to the above-mentioned results in this thesis, further development on the system can be guided. First, a catalyst, which can be a nanocrystalline transition metal, is necessary to overcome the barrier in kinetics and thermodynamics. Following

the Nb₂O₅-pattern that generates highly active nanocrystalline Nb via a reaction, it can be expected that similar elements such like Ti, V, and Fe could also give good performance if they are effectively refined without contamination. Recently, a Nb cluster film was prepared and confirmed to have “unexpected” hydrogen absorption ability [105], serving as an indicator for the prospect of future work. Within the range of available technology, more and more metal clusters will be obtained and tested. Employing such clusters as the catalysts in Mg/MgH₂ will definitely improve the properties to a whole new level. Second, the microstructure of the additive could be specially designed so that it can give the nanocrystalline metal after necessary process. Experiences told us that a mesoporous Nb₂O₅ could give even better performance in improving kinetics (see works from Hanada et al. in Ref [73, 74, 76]) compared with a crystalline one that was used in the present work. Because of the metastable structure and weak crystallinity of the mesoporous Nb₂O₅, it probably generates Nb crystals with more refined size than the crystalline Nb₂O₅ can do, thus leading to the better kinetics in the system. It could be expected that the catalyst with a more unstable structure, such as microporous, may further improve the kinetics. Third, the preferred orientation relationship during Mg→MgH₂ transformation could be adopted for material design. The epitaxial ultra-thin film of Mg with (002)-preferred orientation may exhibit fast absorption kinetics because of such preference. A thin layer of Nb on such thin film can be expected to further facilitate the absorption and desorption.

At last, as a prospect, the author believes that the Mg/MgH₂ system can be used for hydrogen storage in one day, since our endeavor never ends. Hopefully this thesis could somewhat provide a reference for further development on the system, and attract more achievements in the awaiting future.

References

- [1] J. O. Bockris, *Energy, the Solar-Hydrogen Alternative*, Architectural Press, London, **1976**.
- [2] http://en.wikipedia.org/wiki/Energy_density.
- [3] A. Züttel, A. Borgschulte, L. Schlapbach (Eds.), *Hydrogen as a Future Energy Carrier*, WILEY-VCH, **2008**.
- [4] M. Felderhoff, C. Weidenthaler, R. von Helmolt, U. Eberle, Hydrogen storage: the remaining scientific and technological challenges, *Phys. Chem. Chem. Phys.* **2007**, 9, 2643–2653.
- [5] SRA strategic research agenda of the european hydrogen and fuel cell technology platform, <https://www.hfpeurope.org/>.
- [6] A. Léon (Ed.), *Hydrogen technology, in Mobile and Portable Applications*, Springer-Verlag, Berlin, Heidelberg, **2008**.
- [7] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, Storage of hydrogen in single-walled carbon nanotubes, *Nature* **1997**, 386, 377–379.
- [8] M. Uhlemann, O. Gutfleisch, A. Leonhardt, A. Graff, C. Taschner, J. Fink, Hydrogen storage in different carbon nanostructures, *Appl. Phys. Lett.* **2002**, 80, 2985–2987.
- [9] H. Schimmel, G. Nijkamp, G. Kearley, A. Rivera, K. de Jong, F. Mulder, Hydrogen adsorption in carbon nanostructures compared, *Mater. Sci. Eng., B* **2004**, 108, 124–129.

- [10] M. Jordá-Beneyto, F. Suárez-García, D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, Hydrogen storage on chemically activated carbons and carbon nanomaterials at high pressures, *Carbon* **2007**, 45, 293–303.
- [11] B. Panella, M. Hirscher, S. Roth, Hydrogen adsorption in different carbon nanostructures, *Carbon* **2005**, 43, 2209–2214.
- [12] N. Hanada, *Hydrogen storage properties of well-catalyzed magnesium hydride by mechanical milling*, Ph.D. thesis, Hiroshima University, **2005**.
- [13] Targets for onboard hydrogen storage systems for light-duty vehicles, http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf.
- [14] L. Schlapbach, I. Anderson, J. Burger, *Hydrogen in Metal, in Electronic and Magnetic Properties of Metals and Ceramics Part 11*, vol. 3B, VCH, Weinheim, **1994**.
- [15] Y. Fukai, K. Tanaka, H. Uchida, *Hydrogen and Metals*, Uchida Rokakuho Publishing co., Ltd., **2002**.
- [16] J. Graetz, J. J. Reilly, Thermodynamics of the α , β and γ polymorphs of AlH_3 , *J. Alloys Compd.* **2006**, 424, 262–265.
- [17] G. Libowitz, *The Solid-State Chemistry of Binary Metal Hydrides*, W.A. Benjamin, New York, **1965**.
- [18] G. Liang, J. Huot, R. Schulz, Hydrogen storage properties of the mechanically alloyed LaNi_5 -based materials, *J. Alloys Compd.* **2001**, 320, 133–139.
- [19] J. J. Reilly, R. H. Wiswall, Formation and properties of iron titanium hydride, *Inorg. Chem.* **1974**, 13, 218–222.
- [20] M. Hirscher (Ed.), *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*, WILEY-VCH, **2010**.
- [21] H. Schlesinger, R. Sanderson, A. Burge, A volatile compound of aluminum, boron and hydrogen, *J. Am. Chem. Soc.* **1939**, 61, 536.
- [22] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, P. Maunon, C. Emmenegger, LiBH_4 a new hydrogen storage material, *J. Power Sources* **2003**, 118, 1–7.

- [23] J. Yang, A. Sudik, C. Wolverton, Destabilizing LiBH_4 with a metal ($\text{M}=\text{Mg}$, Al , Ti , V , Cr , or Sc) or metal hydride ($\text{MH}_2=\text{MgH}_2$, TiH_2 , or CaH_2), *J. Phys. Chem. C* **2007**, *111*, 19134–19140.
- [24] J. J. Vajo, S. L. Skeith, Reversible storage of hydrogen in destabilized LiBH_4 , *J. Phys. Chem. B* **2005**, *109*, 3719–3722.
- [25] J. B. A. A. P. Gray, The thermal decomposition of lithium aluminum hydride, *Inorg. Chem.* **1965**, *4*, 304–305.
- [26] B. Bogdanović, M. Schwickardi, Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials, *J. Alloys Compd.* **1997**, *253–254*, 1–9.
- [27] V. Balema, J. Wiench, K. Dennis, M. Pruski, V. Pecharsky, Titanium catalyzed solid-state transformations in LiAlH_4 during high-energy ball-milling, *J. Alloys Compd.* **2001**, *329*, 108–114.
- [28] J. Chen, N. Kuriyama, Q. Xu, H. T. Takeshita, T. Sakai, Reversible hydrogen storage via titanium-catalyzed LiAlH_4 and Li_3AlH_6 , *J. Phys. Chem. B* **2001**, *105*, 11214–11220.
- [29] P. Chen, Z. Xiong, J. Luo, J. Lin, K. L. Tan, Interaction of hydrogen with metal nitrides and imides, *Nature* **2002**, *420*, 302–304.
- [30] Y. H. Hu, E. Ruckenstein, Ultrafast reaction between LiH and NH_3 during H_2 storage in Li_3N , *J. Phys. Chem. A* **2003**, *107*, 9737–9739.
- [31] T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, Mechanism of novel reaction from LiNH_2 and LiH to Li_2NH and H_2 as a promising hydrogen storage system, *J. Phys. Chem. B* **2004**, *108*, 7887–7892.
- [32] T. Ichikawa, S. Isobe, N. Hanada, H. Fujiia, Lithium nitride for reversible hydrogen storage, *J. Alloys Compd.* **2004**, *365*, 271–276.
- [33] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, Destabilization and enhanced dehydriding reaction of LiNH_2 : An electronic structure viewpoint, *Appl. Phys. A* **2004**, *79*, 1765–1767.

- [34] Z. Xiong, G. Wu, J. Hu, P. Chen, Ternary imides for hydrogen storage, *Adv. Mater.* **2004**, *16*, 1522–1525.
- [35] W. I. F. David, M. O. Jones, D. H. Gregory, C. M. Jewell, S. R. Johnson, A. Walton, P. P. Edwards, A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction, *J. Am. Chem. Soc.* **2007**, *129*, 1594–1601.
- [36] M. Aoki, T. Noritake, G. Kitahara, Y. Nakamori, S. Towata, S. Orimo, Dehydrodring reaction of $\text{Mg}(\text{NH}_2)_2\text{--LiH}$ system under hydrogen pressure, *J. Alloys Compd.* **2007**, *428*, 307–311.
- [37] H. Leng, T. Ichikawa, S. Hino, H. Fujii, Investigation of reaction between LiNH_2 and H_2 , *J. Alloys Compd.* **2008**, *463*, 462–465.
- [38] M. Hu, R. Geanangel, W. Wendlandt, The thermal decomposition of ammonia borane, *Thermochim. Acta* **1978**, *23*, 249–255.
- [39] V. Sit, R. Geanangel, W. Wendlandt, The thermal dissociation of NH_3BH_3 , *Thermochim. Acta* **1987**, *113*, 379–382.
- [40] G. Wolf, J. Baumann, F. Baitalow, F. Hoffmann, Calorimetric process monitoring of thermal decomposition of B–N–H compounds, *Thermochim. Acta* **2000**, *343*, 19–25.
- [41] Z. Li, G. Zhu, G. Lu, S. Qiu, X. Yao, Ammonia borane confined by a metal-organic framework for chemical hydrogen storage: Enhancing kinetics and eliminating ammonia, *J. Am. Chem. Soc.* **2010**, *132*, 1490–1491.
- [42] S. F. Li, Z. W. Tang, Y. B. Tan, X. B. Yu, Polyacrylamide blending with ammonia borane: A polymer supported hydrogen storage composite, *J. Phys. Chem. C* **2012**, *116*, 1544–1549.
- [43] H. Diyabalanage, R. Shrestha, T. Semelsberger, B. Scott, M. Bowden, B. Davis, A. Burrell, Calcium amidotrihydroborate: A hydrogen storage material, *Angew. Chem. Int. Ed.* **2007**, *46*, 8995–8997.
- [44] Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards, W. I. F. David, High-capacity hydrogen storage in lithium and sodium amidoboranes, *Nat. Mater.* **2007**, *7*, 138–141.

- [45] Q. Zhang, C. Tang, C. Fang, F. Fang, D. Sun, L. Ouyang, M. Zhu, Synthesis, crystal structure, and thermal decomposition of strontium amidoborane, *J. Phys. Chem. C* **2010**, *114*, 1709–1714.
- [46] F. H. Ellinger, C. E. H. Jr., B. B. McInteer, D. Pavone, R. M. Potter, E. Staritzky, W. H. Zachariasen, The preparation and some properties of magnesium hydride, *J. Am. Chem. Soc.* **1955**, *77*, 2647–2648.
- [47] A. Zaluska, L. Zaluski, J. Ström-Olsen, Nanocrystalline magnesium for hydrogen storage, *J. Alloys Compd.* **1999**, *288*, 217–225.
- [48] J. Huot, G. Liang, S. Boily, A. V. Neste, R. Schulz, Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride, *J. Alloys Compd.* **1999**, *293–295*, 495–500.
- [49] N. Hanada, T. Ichikawa, S.-I. Orimo, H. Fujii, Correlation between hydrogen storage properties and structural characteristics in mechanically milled magnesium hydride MgH_2 , *J. Alloys Compd.* **2004**, *366*, 269–273.
- [50] P.-A. Huhn, M. Dornheim, T. Klassen, R. Bormann, Thermal stability of nanocrystalline magnesium for hydrogen storage, *J. Alloys Compd.* **2005**, *404–406*, 499–502.
- [51] R. A. Varin, T. Czujko, Z. Wronski, Particle size, grain size and $\gamma\text{-MgH}_2$ effects on the desorption properties of nanocrystalline commercial magnesium hydride processed by controlled mechanical milling, *Nanotechnology* **2006**, *17*, 3856–3865.
- [52] W. Li, C. Li, H. Ma, J. Chen, Magnesium nanowires: Enhanced kinetics for hydrogen absorption and desorption, *J. Am. Chem. Soc.* **2007**, *129*, 6710–6711.
- [53] J. Qu, B. Sun, J. Zheng, R. Yang, Y. Wang, X. Li, Hydrogen desorption properties of Mg thin films at room temperature, *J. Power Sources* **2010**, *195*, 1190–1194.
- [54] N. S. Norberg, T. S. Arthur, S. J. Fredrick, A. L. Prieto, Size-dependent hydrogen storage properties of Mg nanocrystals prepared from solution, *J. Am. Chem. Soc.* **2011**, *133*, 10679–10681.
- [55] K.-J. Jeon, H. R. Moon, A. M. Ruminski, B. Jiang, C. Kisielowski, R. Bardhan, J. J. Urban, Air-stable magnesium nanocomposites provide rapid and high-capacity

- hydrogen storage without using heavy-metal catalysts, *Nat. Mater.* **2011**, *10*, 286–290.
- [56] A. Karty, J. Grunzweig-Genossar, P. S. Rudman, Hydriding and dehydriding kinetics of Mg in a Mg/Mg₂Cu eutectic alloy: Pressure sweep method, *J. Appl. Phys.* **1979**, *50*, 7200–10.
- [57] A. Stepanov, E. Ivanov, I. Konstanchuk, V. Boldyrev, Hydriding properties of mechanical alloys Mg–Ni, *J. Less-Common Met.* **1987**, *131*, 89–97.
- [58] I. Konstanchuk, E. Ivanov, M. Pezat, B. D. V. Boldyrev, P. Hagenmuller, The hydriding properties of a mechanical alloy with composition Mg-25%Fe, *J. Less-Common Met.* **1987**, *131*, 181–189.
- [59] M. Pezat, B. Darriet, P. Hagenmuller, A comparative study of magnesium-rich rare-earth-based alloys for hydrogen storage, *J. Less-Common Met.* **1980**, *74*, 427–434.
- [60] M. Terzieva, M. Khrussanova, P. Peshev, Hydriding and dehydriding characteristics of Mg–LaNi₅ composite materials prepared by mechanical alloying, *J. Alloys Compd.* **1998**, *267*, 235–239.
- [61] G. Liang, E. Wang, S. Fang, Hydrogen absorption and desorption characteristics of mechanically milled Mg–35wt.%FeTi_{1.2} powders, *J. Alloys Compd.* **1995**, *223*, 111–114.
- [62] G. Liang, J. Huot, S. Boily, A. V. Neste, R. Schulz, Hydrogen storage properties of the mechanically milled MgH₂–V nanocomposite, *J. Alloys Compd.* **1999**, *291*, 295–299.
- [63] G. Liang, J. Huot, S. Boily, A. V. Neste, R. Schulz, Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH₂–Tm (Tm=Ti, V, Mn, Fe and Ni) systems, *J. Alloys Compd.* **1999**, *292*, 247–252.
- [64] J. Huot, J. F. Pelletier, L. B. Lurio, M. Sutton, R. Schulz, Investigation of dehydrogenation mechanism of MgH₂–Nb nanocomposites, *J. Alloys Compd.* **2003**, *384*, 319–324.

- [65] J. F. Pelletier, J. Huot, M. Sutton, R. Schulz, A. R. Sandy, L. B. Lurio, S. G. J. Mochrie, Hydrogen desorption mechanism in MgH_2 -Nb nanocomposites, *Phys. Rev. B* **2001**, 63, 052103.
- [66] S. Li, P. Jena, R. Ahuja, Dehydrogenation mechanism in catalyst-activated MgH_2 , *Phys. Rev. B* **2006**, 74, 132106.
- [67] G. Barkhordarian, T. Klassen, R. Bormann, Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb_2O_5 as catalyst, *Scr. Mater.* **2003**, 49, 213–217.
- [68] W. Oelerich, T. Klassen, R. Bormann, Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials, *J. Alloys Compd.* **2001**, 315, 237–242.
- [69] W. Oelerich, T. Klassen, R. Bormann, Comparison of the catalytic effects of V, V_2O_5 , VN, and VC on the hydrogen sorption of nanocrystalline Mg, *J. Alloys Compd.* **2001**, 322, L5–L9.
- [70] G. Barkhordarian, T. Klassen, R. Bormann, Effect of Nb_2O_5 content on hydrogen reaction kinetics of Mg, *J. Alloys Compd.* **2004**, 364, 242–246.
- [71] G. Barkhordarian, T. Klassen, R. Bormann, Kinetic investigation of the effect of milling time on the hydrogen sorption reaction of magnesium catalyzed with different Nb_2O_5 contents, *J. Alloys Compd.* **2006**, 407, 249–255.
- [72] G. Barkhordarian, T. Klassen, R. Bormann, Catalytic mechanism of transition-metal compounds on Mg hydrogen sorption reaction, *J. Phys. Chem. B* **2006**, 110, 11020–11024.
- [73] N. Hanada, T. Ichikawa, H. Fujii, Catalytic effect of Ni nano-particle and Nb oxide on H-desorption properties in MgH_2 prepared by ball milling, *J. Alloys Compd.* **2005**, 404–406, 716–719.
- [74] N. Hanada, T. Ichikawa, S. Hino, H. Fujii, Remarkable improvement of hydrogen sorption kinetics in magnesium catalyzed with Nb_2O_5 , *J. Alloys Compd.* **2006**, 420, 46–49.
- [75] M. Porcu, A. Petford-Long, J. Sykes, TEM studies of Nb_2O_5 catalyst in ball-milled MgH_2 for hydrogen storage, *Journal of Alloys and Compounds*. **2008**, 453, 341–346.

- [76] N. Hanada, E. Hirotoishi, T. Ichikawa, E. Akiba, H. Fujii, SEM and TEM characterization of magnesium hydride catalyzed with Ni nano-particle or Nb₂O₅, *J. Alloys Compd.* **2008**, 450, 395–399.
- [77] B. Fromme, *d–d Excitations in Transition-Metal Oxides, A Spin-Polarized Electron Energy-Loss Spectroscopy (SPEELS) Study*, vol. 170 of *Springer Tracts in Modern Physics*, Springer, New York, **2001**.
- [78] Dean, A. John, *Lange's Handbook of Chemistry*, 12th ed., McGraw-Hill: New York, **1979**.
- [79] O. Friedrichs, D. Martínez-Martínez, G. Guilera, J. C. S. López, A. Fernández, In situ energy-dispersive XAS and XRD study of the superior hydrogen storage system MgH₂/Nb₂O₅, *J. Phys. Chem. C* **2007**, 111, 10700–10706.
- [80] N. Hanada, T. Ichikawa, S. Isobe, T. Nakagawa, K. Tokoyoda, T. Honma, H. Fujii, Y. Kojima, X-ray absorption spectroscopic study on valence state and local atomic structure of transition metal oxides doped in MgH₂, *J. Phys. Chem. C* **2009**, 113, 13450–13455.
- [81] O. Friedrichs, J. Sánchez-López, C. López-Cartes, T. Klassen, R. Bormann, A. Fernández, Nb₂O₅ “pathway effect” on hydrogen sorption in Mg, *J. Phys. Chem. B* **2006**, 110, 7845–7850.
- [82] O. Friedrichs, F. Aguey-Zinsou, J. A. Fernández, J. Sánchez-López, A. Justo, T. Klassen, R. Bormann, A. Fernández, MgH₂ with Nb₂O₅ as additive, for hydrogen storage: Chemical, structural and kinetic behavior with heating, *Acta Mater.* **2006**, 54, 105–110.
- [83] T. K. Nielsen, T. R. Jensen, MgH₂–Nb₂O₅ investigated by in situ synchrotron X-ray diffraction, *Int. J. Hydrogen Energy* **2012**, 37, 13409–13416.
- [84] B. Bokhonov, E. Ivanov, V. Boldyrev, A study of the electron-beam-induced decomposition of magnesium hydride single crystals, *Mater. Lett.* **1987**, 5, 218–221.
- [85] B. Paik, I. Jones, A. Walton, V. Mann, D. Book, I. Harris, MgH₂ → Mg phase transformation driven by a high-energy electron beam: An in situ transmission electron microscopy study, *Philos. Mag. Lett.* **2010**, 90, 1–7.

- [86] C. Zhu, N. Sakaguchi, S. Hosokai, S. Watanabe, T. Akiyama, In situ transmission electron microscopy observation of the decomposition of MgH_2 nanofiber, *Int. J. Hydrogen Energy* **2011**, 36, 3600–3605.
- [87] T. Schober, The magnesium-hydrogen system: Transmission electron microscopy, *Metall. Mater. Trans. A* **1981**, 12, 951–957.
- [88] R. Kelekar, H. Giffard, S. T. Kelly, B. M. Clemens, Formation and dissociation of MgH_2 in epitaxial Mg thin films, *J. Appl. Phys.* **2007**, 101, 114311.
- [89] A. Léon, E. Knystautas, J. Huot, R. Schulz, Hydrogenation characteristics of air-exposed magnesium films, *J. Alloys Compd.* **2002**, 345, 158–166.
- [90] B. Cullity, S. Stock, *Elements of X-Ray Diffraction*, Prentice-Hall Inc., 3rd ed., **2001**.
- [91] H. E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* **1957**, 29, 1702–1706.
- [92] A. Khawam, D. R. Flanagan, Basics and applications of solid-state kinetics: A pharmaceutical perspective, *J. Pharm. Sci.* **2006**, 95, 472–498.
- [93] <http://www.microscopy.ethz.ch/se.htm>.
- [94] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy*, Springer, 2nd ed., **2009**.
- [95] H. Yao, S. Isobe, Y. Wang, N. Hashimoto, S. Ohnuki, Plastic bag method for active sample loading into transmission electron microscope, *J. Electron Microsc.* **2011**, 60, 375–378.
- [96] S. F. Ho, S. Contarini, J. W. Rabalais, Ion-beam-induced chemical changes in the oxyanions (Moyn-) and oxides (Mox) where M = chromium, molybdenum, tungsten, vanadium, niobium and tantalum, *J. Phys. Chem.* **1987**, 91, 4779–4788.
- [97] K.-F. Aguey-Zinsou, J. A. Fernandez, T. Klassen, R. Bormann, Using MgO to improve the (de)hydriding properties of magnesium, *Mater. Res. Bull.* **2006**, 41, 1118–1126.
- [98] A. R. Yavari, G. Vaughan, G. Heunen, Structural evolution and metastable phase detection in MgH_2 –5%NbH nanocomposite during in-situ H-desorption in a synchrotron beam, *J. Alloys Compd.* **2003**, 353, 246–251.

- [99] K. Takahashi, S. Isobe, S. Ohnuki, The catalytic effect of Nb, NbO and Nb₂O₅ with different surface planes on dehydrogenation in MgH₂: Density functional theory study, *J. Alloys Compd.* **2013**, <http://dx.doi.org/10.1016/j.jallcom.2013.02.044>.
- [100] R. Gonzalez, Y. Chen, K. L. Tsang, Diffusion of deuterium and hydrogen in doped and undoped MgO crystals, *Phys. Rev. B* **1982**, 26, 4637–4645.
- [101] M. Rahman, S. Livraghi, F. Dolci, M. Baricco, E. Giamello, Hydrogen sorption properties of ternary Mg–Nb–O phases synthesized by solid-state reaction phases synthesized by solid-state reaction, *Int. J. Hydrogen Energy* **2011**, 36, 7932–7936.
- [102] M. Rahman, A. Castellero, S. Enzo, S. Livraghi, E. Giamello, M. Baricco, Effect of Mg–Nb oxides addition on hydrogen sorption in MgH₂, *J. Alloys Compd.* **2011**, 509S, S438–S443.
- [103] O. Friedrichs, J. Sánchez-López, C. López-Cartes, M. Dornheim, T. Klassen, R. Bormann, A. Fernández, Chemical and microstructural study of the oxygen passivation behaviour of nanocrystalline Mg and MgH₂, *Appl. Surf. Sci.* **2006**, 252, 2334–2345.
- [104] P. Vajeeston, P. Ravindran, H. Fjellvåg, Theoretical investigations on low energy surfaces and nanowires of MgH₂, *Nanotechnology* **2008**, 19, 275704.
- [105] C. Romero, R. Trabol, J. Avila, P. Lievens, A. Cabrera, Unexpected large hydrogen adsorption by Nb cluster films under mild conditions of pressure and temperature, *Int. J. Hydrogen Energy* **2011**, 36, 13595–13602.

Accomplishments

Publications concerned to this work

- [1] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Nb-gateway for hydrogen desorption in Nb₂O₅ catalyzed MgH₂ nanocomposite, *J. Phys. Chem. C*, **2013**, 117(20), 10302–10307.
- [2] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Catalytic effect of Nb₂O₅ in MgH₂–Nb₂O₅ ball-milled composites, *Catalysts* **2012**, 2, 344–351.
- [3] **Tao Ma**, Shigehito Isobe, Keisuke Takahashi, Yongming Wang, Shuai Wang, Naoyuki Hashimoto, Somei Ohnuki, Phase transition of Mg during hydrogenation of Mg–Nb₂O₅ evaporated composites, *J. Phys. Chem. C* **2012**, 116(32), 17089–17093.
- [4] **Tao Ma**, Shigehito Isobe, Eri Morita, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Toru Kimura, Takayuki Ichikawa, Yoshitsugu Kojima, Correlation between kinetics and chemical bonding state of catalyst surface in catalyzed magnesium hydride, *Int. J. Hydrogen Energy* **2011**, 36(19), 12319–12323.

Other publications

- [1] Ankur Jain, Takayuki Ichikawa, Erika Kawasako, Hiroki Miyaoka, **Tao Ma**, Shigehito Isobe, Yoshitsugu Kojima, Destabilization of LiH by Li insertion into Ge, *J. Phys. Chem. C* **2013**, 117(11), 5650–5657.

Conferences

- [1] **Tao Ma**, Shigehito Isobe, Keisuke Takahashi, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Reactions between MgH_2 and Nb-catalysts, in *Spring Meeting of the Japan Institute of Metals*, Tokyo, Japan, **March 2013**. (Poster presentation)
- [2] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Catalytic effect and phase transition in MgH_2 – Nb_2O_5 system, in *International Symposium on Metal-Hydrogen Systems*, Kyoto, Japan, **October 2012**. (Oral presentation)
- [3] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Study on chemical bonding state and phase-transition process in MgH_2 – Nb_2O_5 system, in *7th Symposium on Hydrogen for Young Scientists*, Osaka, Japan, **October 2012**. (Poster presentation)
- [4] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Phase transition of magnesium during hydrogenation of Mg – Nb_2O_5 evaporated composites, in *Summer Branch of the Japan Institute of Metals*, Sapporo, Hokkaido, Japan, **July 2012**. (Poster presentation)
- [5] **Tao Ma**, Shigehito Isobe, Eri Morita, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, Kinetics of desorption and chemical bonding state on catalyst surface in MgH_2 , in *Autumn Meeting of the Japan Institute of Metals*, Okinawa, Japan, **November 2011**. (Oral presentation)

- [6] **Tao Ma**, Shigehito Isobe, Yongming Wang, Naoyuki Hashimoto, Somei Ohnuki, HVEM observation on the hydrogenation and oxidation process of Mg–Nb₂O₅ deposited composites: Investigation on the orientation relationship between Mg, MgH₂, MgO and Nb₂O₅, in *6th Symposium on Hydrogen for Young Scientists*, Seoul, Korea, **August 2011**. (Poster presentation)
- [7] **Tao Ma**, Yi Long, Hydrogen absorption of LaFe_{11.5}Si_{1.5} compound: evaluation for homogeneity, in *Autumn Meeting of the Japan Institute of Metals*, Sapporo, Hokkaido, Japan, **September 2010**. (Oral presentation)