CATALYTIC DEHYDROGENATION OF HYDRAZINE BORANE OVER Cu@Ni/MoO_3 CORE SHELL CATALYST FOR HYDROGEN STORAGE APPLICATION

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by

LEI YUNFENG

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LIST OF SYMBOLS

$	Us dollar
~	Approximately equal to
Φ	Work Function
Å	Ångström

LIST OF ABBREVIATIONS

AB	Ammonia borane
AC	Activated Carbon
Al Kα	Aluminum K alpha radiation
at%	Atomic Percent
BET	Brunauer–Emmett–Teller theory
BH_3	Borane group
BJH	Barrett–Joyner–Halenda method
B–N bond	Boron-Nitrogen bond
CeO_2	Cerium dioxide
CGH_2	Compressed Gaseous Hydrogen
CH_3OH	Methanol
CNT	Carbon Nanotube
COF	Covalent Organic Framework
Cu	Copper
Cu Kα	Copper K alpha radiation
Cu@Ni	Copper-nickel core-shell catalyst
Cu@Ni/MoO_3	MoO_3-supported copper–nickel core–shell catalyst
e^-	Electron
E_a	Activation Energy
Eb	Binding Energy
EDX	Energy-Dispersive X-ray spectroscopy
KE	Kinetic Energy
Eq.	Equation
EU	European Union
H*	Active hydrogen atom
H_2	Hydrogen gas
H_3BO_3	Boric acid
HB	Hydrazine borane
HDPE	High-Density Polyethylene
HRTEM	High-Resolution Transmission Electron Microscopy
hν	Photon Energy

JAXA	Japan Aerospace Exploration Agency
K	Kelvin
kg/m^3	kilograms per cubic meter
kJ/mol^3	Kilo Joule per mole
KOH	Potassium hydroxide
kWh/L	kilowatt-hour per liter
$LaNi_5$	Lanthanum Pentanickel
LH_2	Liquefied Hydrogen
$LiBH_4$	Lithium borohydride
LOHC	Liquid Organic Hydrogen Carrier
m^3	cubic meter
Mg Kα	Magnesium K alpha radiation
$Mg(BH_4)_2$	Magnesium borohydride
Mg_2Ni	Dimagnesium Nickel
MgH_2	Magnesium Hydride
MgO	Magnesium Oxide
mL	milliliter
MOF	Metal-Organic Framework
MOF-210	Metal-Organic Framework-210
mol	mole
MoO_3	Molybdenum trioxide
MPa	Megapascal
N_2	Nitrogen gas
N_2H_4	Hydrazine
$N_2H_4 \cdot 1/2H_2SO_4$	Hydrazine hemisulfate
$N_2H_4B(OCH_3)_3$	Hydrazine trimethoxyborane
$N_2H_4BH_3$	Hydrazine borane
$N_2H_5^+$	Hydrazinium ion
$N_2H_5B(OCH_3)_4$	Hydrazinium tetrakis(methoxy)borate
$NaBH_4$	Sodium borohydride
NEC	N-Ethyl carbazole
NH_3	Ammonia
NH_3BH_3	Ammonia borane
Ni	Nickel

$NiCl_2$	Nickel (II) Chloride
nm	Nanometer
NPs	Nanoparticles
OH^-	Hydroxide ion
P/P^0	Relative Pressure
Pd	Palladium
Pd/C	Palladium on Carbon
$PdCl_2$	Palladium (II) chloride
Pt	Platinum
Pt/Al_2O_3	Platinum on Aluminium oxide
R	Gas constant
Rh@MgO	Rhodium nanoparticles on Magnesium oxide support
$Rh_{0.7}Ru_{0.3}$-MoO_x/CNT	Rhodium-Ruthenium alloy supported on MoO_x and CNT
rpm	revolutions per minute
Ru NPs@nano-CeO_2	Ruthenium nanoparticles supported on nanocrystalline cerium oxide
Ru/Al_2O_3	Ruthenium on Aluminium oxide
SAED	Selected Area Electron Diffraction
SDD	Silicon Drift Detector
SMSI	Strong Metal-Support Interaction
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TiFe	Titanium Iron Intermetallic Compound
TOF	Turnover frequency
wt%	Weight percent
XRD	X-ray Diffraction

PENYAHHIDROGENAN BERMANGKIN BAGI HIDRAZINA BORANA MENGGUNAKAN PEMANGKIN BERSTRUKTUR KULIT TERAS Cu@Ni/MoO_3 UNTUK APLIKASI PENYIMPANAN HIDROGEN

ABSTRAK

Tenaga hidrogen merupakan sumber tenaga bersih yang berpotensi tinggi, namun penyimpanan hidrogen yang cekap masih menjadi cabaran utama. Hidrazina borana ($N_2H_4BH_3$, HB), dengan kandungan hidrogen yang tinggi iaitu 15.4 wt%, telah dikenal pasti sebagai calon bahan penyimpanan hidrogen kimia yang berpotensi. Walau bagaimanapun, tindak balas metanolisis konvensional lazimnya hanya menggunakan bahagian BH_3, sekali gus mengehadkan jumlah hidrogen yang dilepaskan. Dalam kajian ini, kami telah membangunkan pemangkin berkecekapan tinggi berstruktur kulit teras Cu@Ni/MoO_3 yang membolehkan pelepasan hidrogen sepenuhnya daripada kedua-dua bahagian BH_3 dan N_2H_4. Pada suhu 50 °C, sistem ini berjaya menghasilkan sebanyak 5.5 mol gas, iaitu nilai tertinggi yang pernah dilaporkan bagi tindak balas metanolisis HB di bawah keadaan sederhana. Kajian kinetik menunjukkan tenaga pengaktifan yang rendah, iaitu 36.5 ± 3.5 kJ/mol bagi langkah kedua penyahhidrogenan, yang membuktikan keberkesanan tindak balas ini pada suhu rendah. Pemangkin ini juga menunjukkan kestabilan dan kebolehulangan yang cemerlang dalam lima kitaran berturut-turut. Prestasi unggul ini disumbang oleh sinergi antara komponen: teras Cu mengubah suai struktur elektronik lapisan nikel (Ni), mempertingkat pengaktifan perantara, manakala Ni pula menggalakkan penguraian N_2H_4. Sokongan MoO_3 meningkatkan luas permukaan dan mewujudkan persekitaran kekurangan elektron, melemahkan ikatan B–N untuk memudahkan

pelepasan hidrogen. Tambahan pula, penambahan KOH menghalang pembentukan hasil sampingan dan meningkatkan selektiviti. Secara keseluruhannya, kajian ini mempersembahkan sistem pemangkin yang cekap dan menjimatkan kos untuk penjanaan hidrogen, serta menawarkan pandangan baharu ke dalam reka bentuk pemangkin bagi penyimpanan hidrogen kimia.

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ABSTRACT

Hydrogen energy is a promising clean energy source, and efficient hydrogen storage remains a critical challenge. Hydrazine borane ($N_2H_4BH_3$, HB), with a high hydrogen content of 15.4 wt%, has attracted attention as a potential chemical hydrogen storage material. However, conventional methanolysis reactions typically utilize only the BH_3 moiety, limiting hydrogen release. In this study, we developed a highly efficient MoO_3-supported copper–nickel core–shell catalyst (Cu@Ni/MoO_3) to enable complete hydrogen release from both the BH_3 and N_2H_4 moieties. At 50 °C, the system achieved a yield of 5.5 moles of gas, the highest reported for HB methanolysis under mild conditions. Kinetic studies showed a low activation energy of 36.5 ± 3.5 kJ/mol for the second dehydrogenation step, indicating rapid hydrogen evolution at relatively low temperatures. The catalyst also exhibited excellent stability and recyclability over five cycles. Its performance is attributed to the synergy between components: the Cu core tunes the electronic structure of the Ni shell, enhancing intermediate activation, while Ni promotes N_2H_4 decomposition. The MoO_3 support increases surface area and creates an electron-deficient environment, weakening the B–N bond to facilitate hydrogen release. Additionally, the addition of KOH suppresses by-product formation and improves selectivity. Overall, this study presents an efficient and cost-effective catalytic system for

hydrogen generation, offering new insights into catalyst design for chemical hydrogen storage.

CHAPTER 1

INTRODUCTION

1.1 Research Background and Significance

With the transformation of the global energy structure and the promotion of the National Energy Policy goal, hydrogen energy, as a clean, efficient and renewable secondary energy, is becoming an important part of the energy strategy of countries around the world. It is not difficult to see from Figure 1.1 that the current hydrogen supply chain is very complete [1], with various transportation methods including sea, land and air. However, it is all carried out by directly transporting gaseous or liquid hydrogen. This will bring considerable safety hazards. Therefore, at present, in terms of the application of hydrogen energy, there are already good solutions for transportation. However, the problem lies in how to safely store hydrogen for safe transportation, which is an urgent issue to be addressed [2,3].

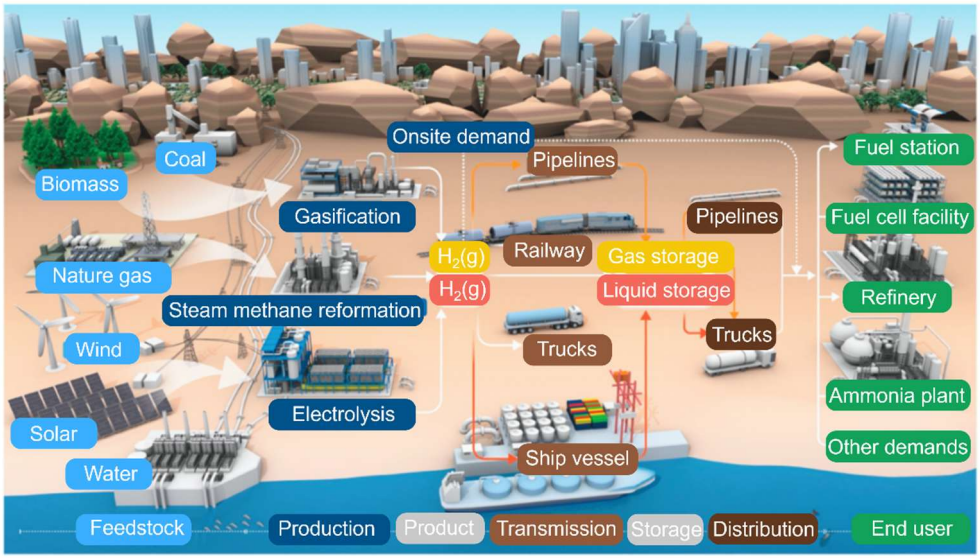

Figure 1.1 Overview of a hydrogen supply chain superstructure. Hydrogen can be produced and utilized onsite, stored, and distributed locally (via pipeline as gas or trucks as liquid or gas), or transported long distances (via pipelines as gas, railways, and trucks as liquid or gas, or via shipping vessels as liquid) [4].

In the hydrogen energy industry chain, safe and efficient hydrogen storage technology is one of the key bottlenecks restricting its large-scale application [5,6]. Among many hydrogen storage methods, solid chemical hydrogen storage materials have attracted much attention due to their advantages of high hydrogen storage density and good safety [7–9], among which high hydrogen capacity boron-containing materials show unique development potential [10,11].

Boron based hydrogen storage materials (such as borohydrides, hydrazine borane and their derivatives, etc.) have significant theoretical advantages for hydrogen storage: hydrazine borane ($N_2H_4BH_3$, HB), for example, has a mass hydrogen storage density of 15.4 wt%, far exceeding the capacity limits of traditional high pressure gaseous hydrogen storage and low temperature liquid hydrogen storage [12–14].

Thermolysis, as the most fundamental form of dehydrogenation reaction for hydrazine borane, refers to the process induced solely by external heating without solvents or additives, leading to molecular structure reconstruction and hydrogen release. Literature reports indicate that this process typically initiates significant hydrogen evolution above 150 °C, involving the cleavage and reorganization of B–H and N–H bonds to generate hydrogen molecules and various nitrogen- and boron-containing polymeric by-products [15]. Although this method offers operational simplicity by eliminating the need for solvents or exogenous catalysts, its high dehydrogenation temperature and the occurrence of complex side reactions severely limit its feasibility for room-temperature hydrogen storage applications. Furthermore, the solid residues generated during thermolysis are difficult to handle, reducing the overall hydrogen release efficiency. Consequently, the thermal

decomposition approach is currently primarily employed to investigate the thermal stability and degradation pathways of hydrazine borane, as well as its potential as a high-temperature hydrogen storage system.

The hydrolysis of hydrazine borane in aqueous media represents a mild and environmentally benign hydrogen generation approach. This reaction enables efficient dehydrogenation under moderate conditions (25 - 80 °C), though its kinetic process generally requires catalytic acceleration. Current research efforts are primarily focused on developing high-performance catalysts, particularly metal nanoparticles (e.g., Ru, Pt, Ni) and their oxide-supported variants, to facilitate the activation of B-H and N-H bonds. Notably, significant progress has been made in this field, with numerous efficient catalytic systems having been developed to achieve complete dehydrogenation of hydrazine borane.

Compared to thermolysis and hydrolysis, alcoholysis (particularly methanolysis) is regarded as one of the most promising dehydrogenation approaches for hydrazine borane. This process is typically carried out in alcoholic solvents (e.g., MeOH, EtOH) with the addition of catalysts that activate the B–H and N–H functional groups in hydrazine borane hydrogen release. Unlike water, methanol exhibits a lower freezing point, making methanolysis particularly advantageous for low-temperature applications. However, current studies reveal a critical limitation: hydrazine borane methanolysis primarily releases hydrogen from the BH_3 moiety, while the hydrogen atoms in the N_2H_4 unit remain largely unreleased as H_2 gas. This significantly reduces the overall hydrogen yield, posing a major challenge for the practical application of hydrazine borane methanolysis.

In addition, this kind of material is stable at room temperature and pressure, avoiding the safety risks caused by high pressure or cryogenic storage. However, its methanolysis practical application faces three core challenges: (1) Formation of by-products such as NH_3 and N_2H_4 which will reduce the selectivity and dehydrogenation amount of the reaction [16,17]. (2) Slow dehydrogenation kinetics restricts the rate of hydrogen release [18]. (3) The irreversibility of methanolysis dehydrogenation [19,20]. These intrinsic defects seriously restrict the engineering application of boron-based hydrogen storage materials.

Catalytic dehydrogenation technology may provide effective ways to solve some of the above problems. By introducing suitable catalyst, the energy barrier of dehydrogenation reaction can be significantly reduced [21], the reaction path can be regulated, and the by-product formation can be inhibited [22]. In recent years, as shown in Figure 1.2，with the development of new catalytic systems such as nano-catalysis [23,24], single-atom catalysis [25,26], as well as advanced characterization techniques and theoretical calculations, the understanding of catalytic dehydrogenation mechanism has been deepened. In particular, the discovery of interfacial effects in heterogeneous catalytic systems provides a new idea for the design of efficient catalysts. However, there are still some key scientific problems in the existing research, such as unclear catalyst active site, unclear structure-activity relationship, and insufficient long-term stability, which need systematic and in-depth research.

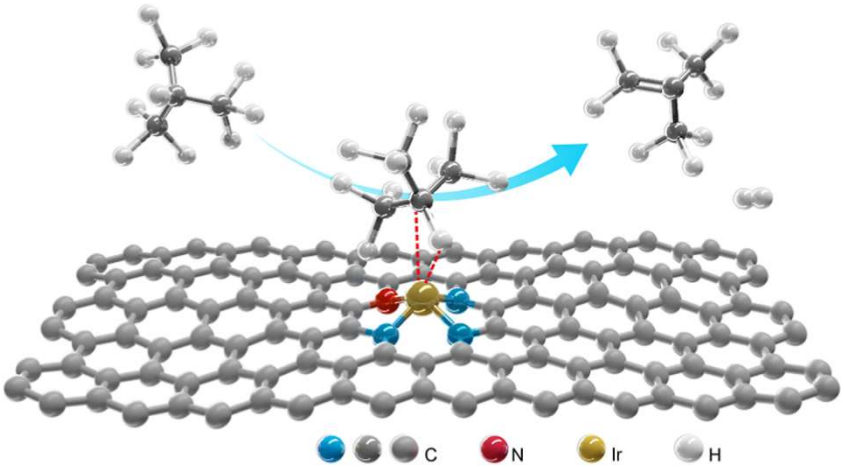

Figure 1.2 Carbon-enhanced and nitrogen-stabilized isolated single-atom catalysts [26].

The catalytic dehydrogenation of boron-containing materials with high hydrogen capacity holds significant importance in the field of hydrogen storage. Theoretically, investigating the catalytic activation mechanism, interfacial synergistic effects, and the structure–activity relationship can deepen the understanding of the catalytic modification mechanisms of solid-state hydrogen storage materials. Practically, the development of efficient and stable catalytic dehydrogenation systems can greatly enhance the hydrogen storage performance of boron-based materials, overcome current limitations in capacity, safety, and cost, and provide innovative solutions for hydrogen storage and transportation. This will facilitate technological breakthroughs in the hydrogen energy sector and promote the transformation of the energy structure and the development of emerging hydrogen energy industries.

1.2 Problem Statement

Despite significant progression in the hydrolysis of $N_2H_4BH_3$ for hydrogen production, the research on methanolysis of $N_2H_4BH_3$ remains a status quo with most

of the studies reported only successful extraction of hydrogen from the BH_3 moiety of $N_2H_4BH_3$ [19,20,27,28]. For instances, Karatas et al. [29] utilized Ru NPs@nano-CeO_2 as catalyst for methanolysis of $N_2H_4BH_3$ and reported the successful extraction of H only from BH_3 moiety, yielding $N_2H_5B(OCH_3)_4$ in the process (Eq. 1.1). Similar observation was also detected in our previous investigation [28].

$$N_2H_4BH_3 + 4CH_3OH \rightarrow N_2H_5B(OCH_3)_4 + 3H_2 \quad (1.1)$$

These studies demonstrated that the methanolysis dehydrogenation of the borane moiety in hydrazine borane is relatively facile. However, to date, there have been no reports of catalysts capable of decomposing the hydrazine moiety (N_2H_4) in methanol to release up to 5 equivalents of hydrogen gas, comparable to those achieved in hydrolysis reactions. This limitation significantly hinders the potential application of hydrazine borane for hydrogen storage especially under the extreme condition. In previous studies, Ni-based catalysts have demonstrated extraordinary performance in selective dehydrogenation of N_2H_4 [30]. Cu is known to have lower work function than Ni. Therefore, it is hypothesized a tuneable local electronic structure of Ni upon formation of CuNi bimetallic catalyst which may in turn alter the catalytic properties towards dehydrogenation of N_2H_4. To maximize the exposure of Ni for enhanced interaction with N_2H_4 moiety, a Cu@Ni core-shell structure dispersing on the MoO_3 support was designed.

1.3 Research Objectives

In this research project, we aim to develop a viable hydrogen storage system for hydrogen on-demand application under extreme conditions. To achieve the aim, the research holds the following specific objectives:

1. To fabricate MoO_3-supported copper-nickel core-shell structure catalysts for methanolysis of hydrazine borane.

2. To optimize the catalyst formulation and reaction conditions, including the copper-to-nickel ratio, metal-to-support ratio, and the concentration of potassium hydroxide (KOH).

3. To investigate the dehydrogenation mechanism through comprehensive surface characterization techniques.

1.4 Structure of the Thesis

Chapter 1: This chapter introduces hydrogen energy as a clean and sustainable solution to global energy challenges. It highlights the importance of hydrogen storage and outlines the advantages of chemical hydrogen storage systems. The research objectives focus on enhancing the catalytic dehydrogenation of hydrazine borane (HB) through catalyst design.

Chapter 2: This chapter reviews the properties of hydrazine borane and recent developments in its catalytic dehydrogenation. It discusses transition metal catalysts, structural design strategies (e.g., core–shell structures), support effects, and base additives. These provide the theoretical basis for the catalyst system proposed in this work.

Chapter 3: This chapter outlines the materials and synthesis procedures used to prepare Cu@Ni/MoO_3 catalysts. It also describes the experimental setup for hydrazine borane methanolysis and the characterization techniques applied, including XRD, TEM, BET, FTIR, and gas evolution measurements.

Chapter 4: This chapter presents catalytic performance data and discusses hydrogen release under various conditions. Kinetic parameters and activation energy are analyzed, and the influence of catalyst structure is explored. A possible reaction mechanism and synergistic effects among components are proposed.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Hydrogen Storage Technology Development

The development of hydrogen storage technology has experienced the evolution process from physical hydrogen storage to chemical hydrogen storage [31]. Early physical hydrogen storage technology mainly includes high pressure gas storage [32] and low temperature liquid hydrogen storage [33]. Although these methods are mature, they have inherent defects such as high safety risk and high energy consumption. With deepening research, material-based hydrogen storage materials have become the focus of research because of their high safety and moderate hydrogen storage density. Material based hydrogen storage materials are mainly divided into physical adsorption and chemical absorption materials. Physical adsorption material involves storing molecular hydrogen in porous material such as activated carbon (AC), carbon nanotubes and metal organic framework (MOF). In contrast, chemical absorption materials involve storing atomic hydrogen chemically in materials such as metal hydrides, liquid organic hydrogen carriers, complex hydrides and chemical hydrides, which are mainly studied in this work. The following section, detail descriptions of each different hydrogen storage material were included. In recent years, chemical hydride hydrogen storage materials, especially boron-containing hydrogen storage materials such as borohydride and boron nitrogen compounds, have shown great potential due to their ultra-high theoretical hydrogen storage capacity. However, these materials still face technical bottlenecks such as high thermodynamic stability, emission of by-products and slow dehydrogenation kinetics in practical applications. Current research frontiers are

focused on optimizing material properties through nanostructure regulation, catalytic modification and interface engineering strategies. With the development of advanced characterization techniques and theoretical simulation methods, the understanding of structure-activity relationships of hydrogen storage materials has been deepened, which has laid an important foundation for the development of a new generation of high-performance hydrogen storage systems. It is particularly noteworthy that the breakthrough of catalytic dehydrogenation technology provides a new possibility for the practical application of boron-containing hydrogen storage materials, which has become one of the most promising research directions in the field of hydrogen storage.

Following the general overview of hydrogen storage technology development, the two primary storage approaches—physical hydrogen storage and chemical hydrogen storage—are discussed in more detail. These methods differ significantly in terms of storage mechanism, operating conditions, and material requirements. The next section focuses on physical hydrogen storage, including compressed gas and cryogenic liquid hydrogen, followed by an in-depth discussion of chemical hydrogen storage systems such as metal hydrides and chemical hydrogen carriers.

2.2 Physical Hydrogen Storage

2.2.1 High Pressure Gaseous Hydrogen Storage

High pressure gaseous hydrogen storage is one of the most widely used hydrogen storage methods [34,35]. Its core principle is to increase the volume energy density of hydrogen through physical compression. In the standard state (atmospheric

pressure, 25 ℃), the hydrogen density is only 0.0899 kg/m^3 , but by compression to 35-70 MPa high pressure environment, its volume hydrogen storage density can be significantly increased to 25-40 kg/m^3 (70 MPa conditions) [36]. The key to this technology is the use of lightweight, high-strength composite tanks. For example, Type IV hydrogen storage bottles [37] are usually composed of a lining (high-density polyethylene or aluminum alloy), a carbon fiber reinforced resin layer (compressive body) and an outer protective shell (impact and corrosion resistance), which can achieve a mass hydrogen storage density of 5-7 wt% (tank mass ratio) and a safe cycle life of more than 10,000 times [38].

The advantages of high-pressure gaseous hydrogen storage lie in the rapid charging and discharging capacity (filling within minutes) and the simple structure of the system (no cryogenic or chemical conversion equipment is required), making it the preferred solution for fuel cell vehicles. However, its technical bottlenecks focus on two aspects. The first is the material and cost: carbon fiber composites account for more than 60% [39] of the total cost of the tank, and the high pressure environment requires the material to resist hydrogen embrittlement (metal embrittlement caused by hydrogen atom penetration) [40]. The second is the energy density limit: even if the gas compressibility limit is increased to 70 MPa, the hydrogen storage amount is still difficult to meet the long-life demand (the hydrogen storage amount of passenger cars is usually less than 5 kg) [41].

Current research focuses on lightweight tank design (such as nanocomposite coatings to inhibit hydrogen penetration) [42] and higher pressure system development (such as 90 MPa class hydrogen storage tank tests) [43]. In addition, by optimizing the hydrogen precooling temperature (40 °C to -60 °C), the compression

energy consumption can be reduced and the charging efficiency can be improved [44]. Although liquid hydrogen storage has more advantages in density, high-pressure gaseous hydrogen storage will still dominate in transportation, distributed energy storage and other fields with mature technical systems and low maintenance costs.

2.2.2 Low Temperature Liquefaction for Hydrogen Storage

Low temperature liquid phase hydrogen storage technology involves cooling the hydrogen at extremely low temperature (-253 °C boiling point under normal pressure) to liquefy it [45], thereby greatly improve the hydrogen storage volumetric density of hydrogen (about 70.8 kg/m^3). The core process includes hydrogen precooling, multistage compression expansion refrigeration and liquefaction storage. Challenges related to positive and secondary hydrogen conversion and heat release (incomplete conversion will lead to continuous evaporation of liquid hydrogen) must be overcome, and the proportion of secondary hydrogen is usually increased to more than 95% with the help of catalysts to reduce evaporation loss. The storage relies on multi-layer insulated vacuum dewar tank in combination of superinsulating materials (such as aluminized polyester film) and liquid nitrogen shielding layer, the daily evaporation rate is controlled in the range of 0.1% – 1%.

The significant advantages of this technology are its high energy density (about 1.95 times that of 70 MPa compressed gaseous hydrogen storage as shown in Table 2.1) and high purity hydrogen output (liquid hydrogen purity up to 99.99%) [46], which is especially suitable for scenarios with demanding hydrogen storage

requirements, such as space rocket propellant filling or large stationary energy storage systems [47,48].

Table 2.1 Comparison between various physical hydrogen storage technologies involving compressed H_2 and liquefied H_2 [1,45].

Storage method	**Temperature [°C]**	**Pressure [MPa]**	**Mass energy density [kg/m^3]**
Compressed gaseous hydrogen (CGH_2)	-40.15 – 26.85	15.00 – 80.00	25.0 at 35.00 MPa and 40.0 at 70.00 MPa
Liquefied hydrogen (LH_2)	-253.15 – -240.15	0.10 – 0.28	70.8

However, its limitations are also prominent: the first is the bottleneck of energy consumption: hydrogen liquefaction requires multi-level refrigeration, and energy consumption accounts for 30% – 40% of the hydrogen fuel's own energy [49], and the economy is far lower than that of high-pressure gaseous hydrogen storage. The second is evaporation loss: the inevitable heat leakage during long-term storage or transportation can lead to the vaporization of hydrogen, requiring the design of complex gas recovery systems. Then there is the material and cost: liquid hydrogen storage tanks need both ultra-low temperature tolerance and lightweight, commonly used austenitic stainless steel or aluminum alloy liner, but its manufacturing cost is high (about 3 – 5 times that of high-pressure storage tanks) [50].

In recent years, the research of low temperature liquid phase hydrogen storage technology focuses on the optimization of liquefaction process (such as helium refrigeration cycle instead of liquid nitrogen precooling) and the development of new thermal insulation materials (such as aerogel composite vacuum insulation

layer). In addition, demonstration projects of liquid hydrogen refueling stations and liquid hydrogen heavy trucks (such as Japan's JAXA Space Center [51] and the EU's "HySupply" program [52]) are promoting their expansion into the civilian sector. Despite the high technical threshold, low temperature liquid phase hydrogen storage is still one of the core paths to achieve large-scale and long-distance hydrogen transportation, and it may play a key role in trans-regional deployment of green hydrogen and industrial decarbonization in the future.

2.2.3 Physical Adsorption Storage

Physical adsorption hydrogen storage technology is a new hydrogen storage method based on the physical adsorption of hydrogen molecules on the surface of porous materials [53]. Its core principle is to enrich hydrogen molecules in the micropore structure of high specific surface area materials by van der Waals force. Common adsorbents include activated carbon (AC) [54], metal-organic framework materials (MOFs) [55], covalent organic framework materials (COFs) [56] and carbon nanotubes (CNTs) [57]. Taking MOFs as an example, its specific surface area can exceed 6240 m^2/g (such as MOF-210), and the mass hydrogen storage density can reach 17.6 wt% under low temperature (77 K, liquid nitrogen temperature zone) [58], which is significantly higher than that of traditional high-pressure gaseous hydrogen storage (5 – 7 wt%). However, the hydrogen storage performance of such materials at normal temperature is greatly reduced (usually less than 2 wt%) [59], and it is necessary to rely on temperature-pressure coordination to achieve an efficient adsorption/desorption cycle.

The advantages of this technology are mainly reflected in the mild storage conditions (avoiding extreme high pressure or low temperature) and fast absorption

and desorption dynamics (second response), which are suitable for scenarios with high safety requirements, such as portable hydrogen fuel cells or low temperature residual hydrogen recovery systems. However, this field still faces significant bottlenecks that cannot be ignored. For example, metal-organic frameworks (MOFs) often have a porosity exceeding 70%, resulting in low volumetric hydrogen storage density. The actual hydrogen storage capacity is typically less than 30 kg/m^3, which is only about 42% of that of liquid hydrogen. The second is insufficient material stability: after multiple cycles, the adsorbent is prone to structural collapse or impurity adsorption leading to performance decay (such as MOFs easy hydrolysis in a humid environment). The third is the cost and scaling up challenge: the synthetic process of high-performance adsorbents (such as COFs) is complex, and the mass production cost is as high as USD 1000 – 5000 per kg, which restricts the commercial application [59,60].

2.3 Chemical Hydrogen Storage

2.3.1 Metal Hydrides

Hydrogen gas can be stored reversibility in the form of atom via chemical reactions in metal hydrides. The core mechanism is that hydrogen reacts with certain metals or alloys (e.g. $LaNi_5$, Mg_2Ni, TiFe, Mg) at appropriate temperature and pressure to form metal hydrides (e.g. $LaNi_5H_6$, Mg_2NiH_4, $TiFeH_2$, MgH_2) and the controlled release of hydrogen is achieved by heating or depressurization [61]. The hydrogen gravimetric and volumetric density of such materials are in the range of 1.5 – 7.6 wt % and 50 – 110 kg/m^3 [62], respectively, which are significantly better than conventional hydrogen storage in the compressed form at 70 MPa (about 40 kg/m^3). The main advantages of storing hydrogen in metal hydrides include high volumetric

density and safety at ambient and pressure. For instances, TiFe hydride can stably store hydrogen at 25 °C and 2 MPa, which is suitable for submarine fuel cells (such as German U212A submarine) [63] and small stationary energy storage systems. However, the technical bottleneck centers on the kinetic performance and cyclic stability of hydrogenation and dehydrogenation. MgH_2, which has a high hydrogen storage capacity of 7.6 wt%, is another potential metal hydride for practical application. Although MgH_2 has high volumetric and gravimetric hydrogen storage capacity, its application is still subject to multiple limitations, such as high thermal stability and sluggish dehydrogenation kinetics. MgH_2 requires temperatures above 300 °C to dehydrogenate at an acceptable rate. Current studies partially alleviate these problems by using nanostructural design (MgH_2 particle size < 100 nm), catalytic doping (such as introduction of Nb_2O_5 or multiphase combination of Ti/Co/Mn to reduce activation energy) [64,65]. However, it is still facing challenges in achieving lower temperature dehydrogenation and yet maintaining high capacity and good cycle stability. To overcome the inherent bottleneck of this technology, it is urgent to make breakthroughs in material-system collaborative innovation.

2.3.2 Liquid Organic Hydrogen Carrier (LOHC)

Liquid organic hydrogen storage materials (LOHC) achieve hydrogen storage through reversible hydrogenation of unsaturated C=C double bonds (such as dibenzyltoluene, n-ethyl carbazole), offering higher hydrogen volumetric density of 50 kg/m^3 and safety advantage since it can be kept safely under ambient temperature and pressure [66]. Its core advantages include: (1) transportation convenience: the liquid carrier formed after hydrogenation can be transported by existing tank trucks or pipelines, without the need for high-pressure vessels or ultra-low temperature equipment, greatly reducing the cost of long-distance hydrogen transportation. (2)

Cycle stability: high quality LOHC can undergo thousands of absorption/dehydrogenation cycles without significant degradation (such as dibenzyltoluene cycle life). Since LOHC is in the form of liquid, the mass transport related barrier could be effectively avoided [67]. (3) Safety: the flash point of LOHC under normal pressure is higher than 150 °C. Thenceforth, the explosion risk is much lower than that of high-pressure gaseous hydrogen, making it ideal for large scale hydrogen storage application in densely populated areas.

Table 2.2 shows some catalysts developed for hydrogenation of N-ethyl carbazole (NEC). Numerous catalysts have already been reported to efficiently promote the dehydrogenation of N-ethylcarbazole (NEC).

Table 2.2 The hydrogenation performance of typical non-noble catalysts of NEC [71].

Catalysts	**T (°C)**	**P (MPa)**	**Time (h)**	**Conv[a] (%)**	**Yield[b] (%)**	**H_2 release (wt%)**	**Cycling performance**
5 wt% Ru/Al_2O_3	170	7	14.00	100	—	5.7	—
5.2 wt% Ru/Al_2O_3	160	6	6.00	100	98.00	5.6	100% in 3 cycles
1.0 wt% Ni/Al_2O_3–YH_3	150	7	1.5	100	100.00	5.8	100% in 3 cycles
Ni_{70}/AlSiO–1/1	150	7	1.5	100	—	5.8	—
5.0 wt% $Ni_{0.5}Ru_{0.5}$/pg-BC	130	6	1.17	100	99.06	—	97.9% in 10 cycles
$Ru_{0.3}Ni_{0.7}$/SBA15	130	6	1.33	100	98.00	—	99% in 3 cycles
Ru–Ni/P25	150	7	2.00	100	93.00	—	—
5.0 wt% Co@Ru/NGC	150	7	1.00	100	99.10	—	97.5% in 10 cycles
10 wt% $LaNi_5$	180	7	4.50	100	96.80	5.5	98.6% in 9 cycles
Co–B/Al_2O_3–YH_3	180	10	2.00	100	100.00	5.6	90% in 3 cycles

a Conversion of LOHCs (complete hydrogenation carriers).
b Yield of complete dehydrogenation products.

For instance, Ru/Al_2O_3, Ni/Al_2O_3 have demonstrated high catalytic activity under mild conditions. However, LOHC technology is still facing significant bottlenecks: (1) high energy consumption as high temperatures in the range of 250-300 ℃ is needed for endothermic dehydrogenation; (2) high catalyst costing as precious metal catalysts (such as Pt/Al_2O_3, Ru/Al_2O_3 and Pd/C) [68] are generally used to activate C-H bonds for dehydrogenation; (3) Slow reaction rate resulting from mass transfer and high activation barrier; (4) Hydrogen purity issue attributed by the formation of by-products during the high temperature dehydrogenation [69,70]. Current research focuses on developing non-precious metal catalysts.

2.3.3 Boron Containing Hydrogen Storage Materials

2.3.3(a) Metal Borohydride

Metal borohydrides have basic structures usually involve the chemical coordination of metal cations and borohydride anions, which form stable crystals or molecular structures through ionic or covalent bond interactions, such as lithium borohydrides ($LiBH_4$), sodium borohydrides ($NaBH_4$), and magnesium borohydrides ($Mg(BH_4)_2$). These compounds have high theoretical hydrogen storage capacity more than 10 wt% [72] and have therefore received a lot of attention in solid-state hydrogen storage research.

Metal borohydrides have good chemical stability and can safely store hydrogen at lower temperatures. However, there are some technical challenges in their practical application. For example, most metal borohydrides require higher temperatures for hydrogen release due to high thermal stability [73] and slow kinetics. In addition, the release of hydrogen is not reversible [74], restricting its application to only as a single use hydrogen storage material.

At present, researchers are using a variety of strategies to improve the hydrogen storage performance of metal borohydrides, including adding catalysts, preparing nanocomposite materials and constructing composite hydrogen storage systems. Through the synergistic effect of catalyst and nano-scale material modification, the hydrogen release temperature can be significantly reduced, and the reaction rate of hydrogen absorption and discharge can be accelerated. At the same time, the design of the new composite system is also aimed at improving the reversibility and cycle stability of hydrogen storage. Although there are still challenges in optimizing hydrogenation kinetics, reducing energy barriers and realizing economic regeneration, metal borohydrides, as materials with high hydrogen storage density, have broad development prospects in future hydrogen energy applications and clean energy technologies.

2.3.3(b) Boron-Nitrogen Containing Hydrides

Boron-nitrogen containing hydrogen storage materials mainly refer to the utilization of boron-nitrogen containing compounds (such as hydrazine borane ($N_2H_4BH_3$, HB), ammonia borane (NH_3BH_3, AB) and their derivatives for dehydrogenation. In addition, most of the boron-nitrogen containing compounds are of high hydrogen capacity and stable in air [75], showing great potential for portable hydrogen storage applications.

Among various hydrogen storage materials, hydrazine borane ($N_2H_4BH_3$, HB) stands out as a solid-state candidate due to its substantial hydrogen content (15.4 wt%) and stability under ambient conditions [76,77]. Generally, hydrogen stored in $N_2H_4BH_3$ can be extracted either via thermolysis, hydrolysis or alcoholysis. Thermolysis dehydrogenation requires high thermal input while hydrolysis and

alcoholysis dehydrogenation generally involve relatively mild conditions or even at ambient temperatures. As compared to hydrolysis which involves water, the alcohol used in the alcoholysis offers extra advantage in terms of application under extremely cold conditions owing to its low freezing temperatures. Among a series of alcohols, methanol stands out to be the most promising candidate due to its light weight. Thenceforth, methanolysis of hydrides has been a hot topic of research for hydrogen production on-demand.

Theoretical analyses indicate that hydrolysis of the BH_3 group, coupled with the complete decomposition of the N_2H_4 moiety, can theoretically produce up to 5 moles of hydrogen per mole of hydrazine borane (Eq. 2.1 – 2.3) [78]. The capability of hydrazine borane to generate considerable amount of usable hydrogen makes hydrazine borane an attractive material for hydrogen storage applications. However, achieving efficient and controlled hydrogen release requires addressing the challenges associated with incomplete and undesired decomposition [79]. In particular, the formation of ammonia as a by-product resulting from the decomposition of N_2H_4 moiety is a critical issue (Eq. 2.3), as it can affect the efficiency and stability of the hydrogen storage system [80].

$$N_2H_4BH_3 + 3H_2O \rightarrow N_2H_4 + H_3BO_3 + 3H_2 \quad (2.1)$$

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad (2.2)$$

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \quad (2.3)$$

Through catalysts innovation, several studies have demonstrated complete hydrolysis of BH_3 and selective decomposition of N_2H_4 to form N_2 and H_2 [16,17,81].

2.4 Catalytic Dehydrogenation

2.4.1 Principle of Catalysis

The essence of catalysis is to accelerate the chemical reaction rate by reducing the activation energy of the reaction. In borohydride hydrogen storage systems, transition metal catalysts (such as Ni, Pt, Pd) play a key role through their special electronic structure. The d-orbital electrons of these metals can interact with either B-H in borohydrides, weakening the bond through electron transfer mechanisms. In the case of the dehydrogenation of hydrazine borane catalyzed by Pt, the active hydrogen atom (H^*) is first dissociated from the metal surface and then migrates to the reactant surface through the hydrogen spillover effect, which significantly accelerates the B-H bond breaking process. This catalytic action can increase the dehydrogenation rate of hydrazine borane in folds.

Acid-base synergistic catalysis is another important catalytic method. In a borohydride hydrolysis reaction, the acidic site provides protons (H^+) to react with hydridic H^- in the BH_4^- to produce hydrogen, while the alkaline site increases reaction selectivity by inhibiting the formation of by-products. For example, in the $NaBH_4$ hydrolysis system, the synergistic effect of Lewis acid-base sites resulted in improved hydrogen conversion of over 99%. For hydrides such as ammonia borane, Lewis acid catalysts (such as $AlCl_3$) are able to polarize N-H bonds and promote

intramolecular hydrogen transfer reactions, resulting in a significant decrease in dehydrogenation temperature.

The nano-confined effect provides a new idea for the optimization of catalytic performance. Loading metal nanoparticles (such as Pd) on porous carriers such as carbon materials or MOFs can not only increase the number of active sites but also change the electronic structure through strong metal-carrier interaction. The results show that Pd graphene composite catalyst can reduce the dehydrogenation temperature of ammonia borane by 80 ℃. In addition, the introduction of organic ligands can further regulate the catalytic performance through steric hindrance and electronic effects. Large steric organic ligands can prevent catalyst poisoning, while electron-withdrawing groups can enhance the Lewis acidity of the metal center, thus improving catalytic activity and stability.

The synergistic application of these catalytic mechanisms provides an important way to develop efficient hydrogen storage materials. By precisely designing the composition and structure of the catalyst, the precise regulation of kinetics and thermodynamics of the hydrogen storage reaction can be achieved, laying the foundation for the development of future clean energy technologies. Further studies need to combine advanced characterization techniques and theoretical calculations to reveal the evolution of the active site and the reaction mechanism in the catalytic process.

2.4.2 Hydrolysis Catalyst

It is clear that Mehmet et al. successfully immobilized monodispersed Rh nanoparticles to MgO solid support to synthesize the Rh@MgO catalyst, which demonstrated excellent catalytic performance in the dehydrogenation of hydrazine

borane. According to the results shown in Figure 2.1, the Rh@MgO catalyst was unable to dehydrogenate the N_2H_4 component in the absence of NaOH, and only catalyzed the hydrolysis of the $–BH_3$ group. With increasing NaOH concentration, both the reaction rate and conversion were enhanced, reaching optimal performance at 5.0 M. However, further increases beyond this concentration led to a decline in catalytic activity, likely due to electrostatic interactions between hydroxide ions and the Rh metal surface, which poisoned the active sites. Based on this, a NaOH concentration of 5.0 M was selected as the optimal condition for subsequent experiments.

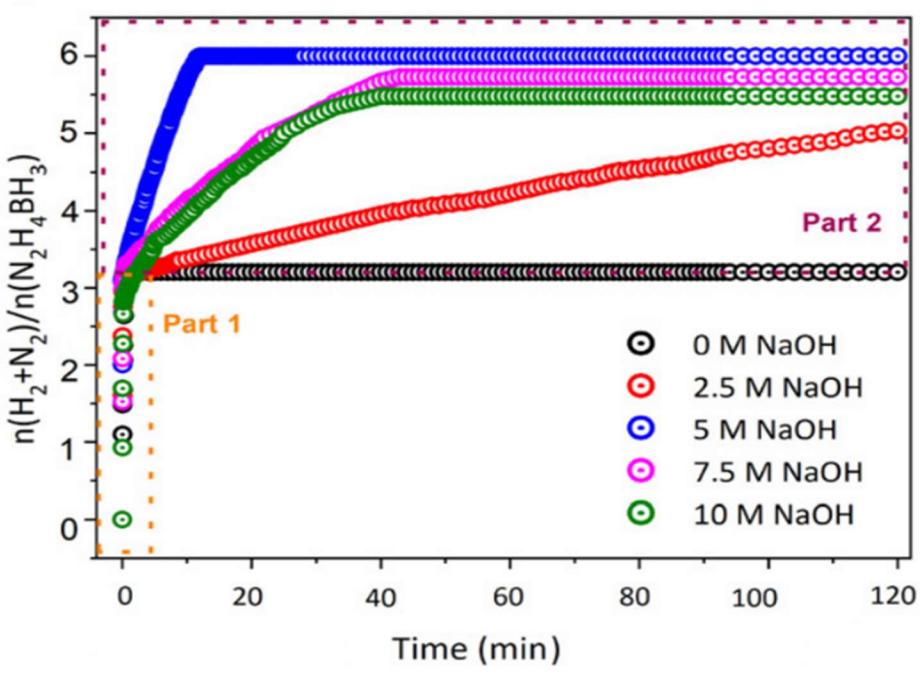

Figure 2.1 Mole ratio of generated gas (H_2+N_2)/HB versus time graph for the Rh@MgO-catalyzed hydrolysis of hydrazine borane at different NaOH concentration (For all, [HB] = 100 M, V_{water} = 10 mL, Rh@MgO = 100 mg, reaction temperature = 50 ℃) [17].

After optimizing the base concentration, the effect of different Rh loadings on catalytic efficiency was investigated. According to the results shown in Figure 2.2，under identical conditions, Rh@MgO catalysts with 1%, 2%, and 4% Rh were

evaluated. The results showed that the 1% Rh-loaded catalyst exhibited significantly lower efficiency, while the 2% and 4% Rh-loaded catalysts displayed comparable catalytic performance. Considering the high cost of the precious metal Rh and the principle of atom economy, the catalyst with 2 wt% Rh was selected for further studies.

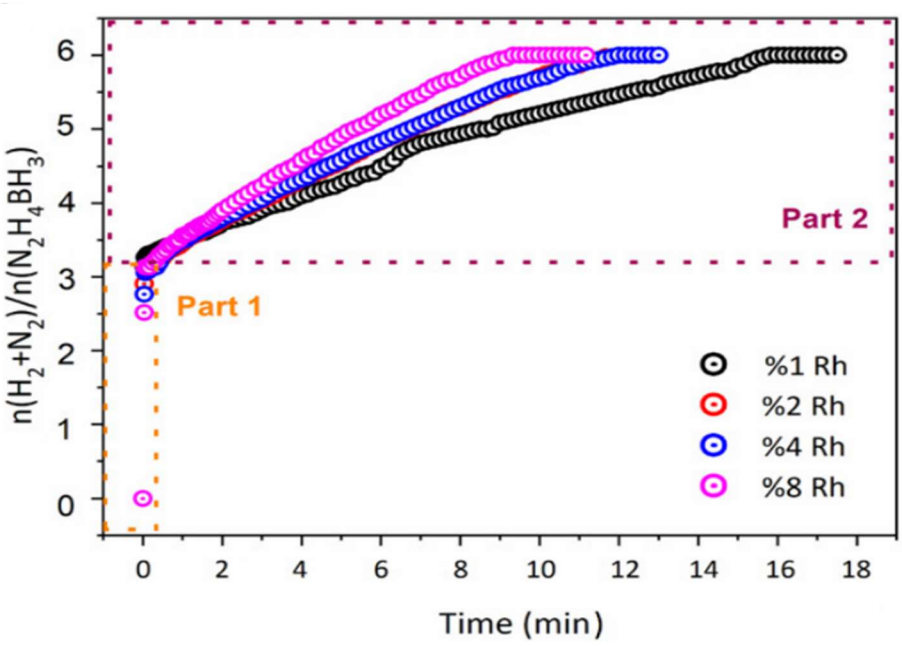

Figure 2.2 Mole ratio of generated gas (H_2+N_2)/HB versus time graph for the Rh@MgO-catalyzed hydrolysis of hydrazine borane depending on different Rh content. (For all, [HB] = 100 M, V_{water} = 10 mL, Rh@MgO = 100 mg, reaction temperature = 50 °C) [17].

As shown in Figure 2.3, even in the presence of an HCl trapping agent, the measured gas volume remained unchanged, indicating that no ammonia (NH_3) was produced during the reaction. This confirms that the catalytic system enables highly selective, ammonia-free hydrogen generation in an alkaline aqueous environment. Ultimately, the Rh@MgO catalyst containing 2 wt% Rh exhibited excellent catalytic performance, achieving complete conversion (100%).