KINETICS IMPROVEMENT OF LITHIUM ALUMINIUM HYDRIDE AND 9-ETHYLCARBAZOLE COMPLEX FOR HYDROGEN STORAGE

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by

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LIST OF ABBREVIATIONS AND SYMBOLS

8H-NCZ	8-Hydrogenated 9-ethylcarbazole
NCZ	9-ethylCarbazole
MCZ	9-Methylcarbazole
VCZ	9-Vinyl carbazole
E_a	Activation Energy
Al	Aluminium
Al_2O_3	Aluminum oxide
NH_3BH_3	Ammonia Borane
Ar	Argon gas
CaH_2	Calcium Hydride
CZ	Carbazole
CO_2	Carbon Dioxide
CMK-3	Carbon Mesostructured by KAIST-3 (ordered mesoporous carbon)
Pt–C	Carbon-modified Platinum Catalyst
Co_2O_3	Cobalt(III) oxide
°C	Degrees Celsius
P25-TiO_2	Degussa P25 Titanium Dioxide
DFT	Density Functional Theory
DBT	Dibenzyltoluene
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
ΔH	Enthalpy change
ΔH_d	Enthalpy of dehydrogenation
Fe_2O_3	Ferric oxide

Fig.	Figure
FTIR	Fourier Transform Infrared Spectroscopy
12H-NCZ	Fully hydrogenated 9-ethylcarbazole
H_{12}-BT	Fully hydrogenated benzyl toluene
H_{18}-DBT	Fully hydrogenated dibenzyltoluene
R	Gas Constant
β	Heating Rate
H_2	Hydrogen gas
Fe	Iron
K	Kelvin
kJ mol^{-1}	Kilojoules per mole
LOHC(s)	Liquid Organic Hydrogen Carrier(s)
Li_3AlH_6	Lithium aluminium hexahydride
$LiAlH_4$(LA)	Lithium Aluminum Hydride
$LiBH_4$	Lithium borohydride
LiH	Lithium hydride
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
Mg	Magnesium
$Mg(AlH_4)_2$	Magnesium aluminum hydride
$MgFe_2O_4$	Magnesium Ferrite
MgH_2	Magnesium hydride
MPa	Megapascal
$MAlH_4$	Metal Aluminum Hydride (where M = Na, Li, K)
Ru^0	Metallic ruthenium (zero oxidation state)
MOFs	Metal-Organic Frameworks
MCH	Methylcyclohexane
TiH_2^{nano}	Nanosized titanium hydride

Ni/Al_2O_3	Nickel supported on Aluminum Oxide
Nb	Niobium
NCMK-3	Nitrogen-doped CMK-3
Pd	Palladium
Pd/Al_2O_3	Palladium on Alumina Catalyst
H_0-BT	Partially hydrogenated benzyl toluene
H_0-DBT	Partially hydrogenated dibenzyltoluene
ppm	Parts per million (used in NMR chemical shifts)
T_{max}	Peak Temperature
T_p	Peak Temperature (Reaction Rate Peak Temperature)
%	Percentage
Pt	Platinum
psi	Pounds per square inch
A	Pre-exponential Factor
^1H NMR	Proton Nuclear Magnetic Resonance spectroscopy
G/D ratio	Ratio of centrifugal diameter to jar diameter
rpm	Revolutions per minute
Ru	Ruthenium
Ru^{3+}	Ruthenium ion with +3 oxidation state
Ru/Al_2O_3	Ruthenium supported on Aluminum Oxide
$RuCl_3 \cdot xH_2O$	Ruthenium(III) chloride hydrate
$Ru–Ni/TiO_2$	Ruthenium-Nickel bimetallic catalyst supported on Titanium Dioxide
NEC	Same as NCZ
$ScCl_3$	Scandium trichloride
$NaAlH_4$	Sodium aluminium hydride
TPD-MS	Temperature Programmed Desorption-Mass Spectroscopy

TPD	Temperature-programmed desorption
THF	Tetrahydrofuran
TGA	Thermogravimetric Analysis
Ti	Titanium
TiC	Titanium carbide
TiO_2	Titanium dioxide
$TiSiO_4$	Titanium Silicate
TOL	Toluene
sp^2/sp^3	Types of carbon hybridization: sp^2 (trigonal planar), sp^3 (tetrahedral)
bar	Unit of pressure (1 bar = 100 kPa)
USD	United States Dollar
V	Vanadium
cm^{-1}	Wavenumber (used in IR spectroscopy to denote frequency)
wt%	Weight percent
XRD	X-ray diffraction
YH_3	Yttrium hydride
ZrC	Zirconium carbide

PENAMBAHBAIKAN KINETIK KOMPLEKS LITIUM ALUMINIUM HIDRIDA DAN 9-ETILKARBAZOL UNTUK PENYIMPANAN HIDROGEN

ABSTRAK

Penyimpanan hidrogen kekal sebagai halangan utama dalam merealisasikan ekonomi hidrogen yang lestari. Litium aluminium hidrida ($LiAlH_4$) dan 9-etil karbazol (NCZ) merupakan dua bahan penyimpanan hidrogen yang berpotensi kerana mempunyai kapasiti teori penyimpanan hidrogen yang tinggi. Namun begitu, aplikasi praktikal kedua-dua bahan ini terhad oleh kebolehulangan $LiAlH_4$ yang rendah serta kinetik penghidrogenan dan penyahhidrogenan NCZ yang perlahan. Dalam kajian ini, satu sistem komposit baharu yang terdiri daripada $LiAlH_4$ dan NCZ dengan nisbah molar 1:1 (dinamakan sebagai LA–NCZ) telah disintesis dan dikaji secara sistematik. Komposit ini menunjukkan peningkatan sinergistik dalam prestasi penyimpanan hidrogen: NCZ menurunkan suhu penyahhidrogenan $LiAlH_4$ dengan ketara, membolehkan penyahhidrogenan dengan cepat dalam julat suhu sempit antara 150–160 °C. Kalorimetri pengimbasan berbeza (DSC) menunjukkan puncak penyahhidrogenan pada suhu yang lebih rendah berbanding dengan $LiAlH_4$ tulen, manakala analisis Kissinger menunjukkan pengurangan tenaga pengaktifan yang ketara iaitu 36 kJ/mol dan 83 kJ/mol masing-masing untuk langkah pertama dan kedua. Menariknya, hasil penyahhidrogenan $LiAlH_4$ (LiH dan Al) selanjutnya meningkatkan kadar dan selektiviti penghidrogenan NCZ, dengan pencapaian pengambilan hidrogen sebanyak 5.6 wt% pada 90 °C dan tekanan 70 bar H_2 dengan menggunakan 5 wt% pemangkin Ru, menghampiri nilai teori bagi penghidrogenan lengkap NCZ. Sebagai perbandingan, NCZ tulen dengan pemangkin Ru tunggal hanya menyerap 5.2 wt% H_2 selepas 12 jam. Analisis resonans magnet nucleus ^1H (^1H NMR) bagi produk

terhidrogen mengesahkan selektiviti yang tinggi iaitu 97% 12H–NCZ dan hanya 3% 8H–NCZ, berbanding dengan 71% 12H–NCZ dan 29% 8H–NCZ dalam sistem kawalan tanpa LiH dan Al, menonjolkan kesan penggalak yang kuat daripada LiH dan Al. Analisis difraktometer belaun sinar-X (XRD) menunjukkan fasa LiH dan Al masih kekal selepas penghidrogenan, manakala spektrum spektroskopi inframerah transformasi fourier (FTIR) mempamerkan jalur ciri 12H–NCZ serta getaran oktahedron Li_3AlH_6 dalam julat 400–800 cm^{-1}. Analisis resonans magnet nukleus sudut ajaib berputar (NMR MAS) ^{27}Al keadaan pepejal turut mengesahkan pembentukan semula separa Li_3AlH_6 dengan isyarat pada –34.5 ppm, menunjukkan bahawa penyimpanan hidrogen yang boleh berulang mungkin berlaku dalam keadaan yang sederhana. Penemuan ini menekankan potensi strategi penggandingan kimia untuk mengatasi had intrinsik bahan individu, serta menyediakan panduan yang bernilai dalam reka bentuk sistem penyimpanan hidrogen generasi baharu.

KINETICS IMPROVEMENT OF LITHIUM ALUMINIUM HYDRIDE AND 9-ETHYLCARBAZOLE COMPLEX FOR HYDROGEN STORAGE

ABSTRACT

Hydrogen storage remains a critical bottleneck in the realization of a sustainable hydrogen economy. Lithium aluminum hydride ($LiAlH_4$) and 9-ethylcarbazole (NCZ) are two promising hydrogen storage materials due to their high theoretical hydrogen capacities. However, their practical applications are limited by the poor reversibility of $LiAlH_4$ and the sluggish (de)hydrogenation kinetics of NCZ. In this work, a novel composite system composed of $LiAlH_4$ and NCZ in a 1:1 molar ratio (denoted as LA–NCZ) was synthesized and investigated. The composite exhibited a synergistic enhancement in hydrogen storage behavior: NCZ significantly reduced the dehydrogenation temperature of $LiAlH_4$, enabling rapid dehydrogenation in a narrow temperature window between 150 °C and 160 °C. Differential scanning calorimetry (DSC) revealed dehydrogenation peaks at lower temperatures compared to pristine $LiAlH_4$, and Kissinger analysis yielded significantly reduced apparent activation energies of 36.76 ± 1.33 kJ/mol and 83.11 ± 2.87 kJ/mol for the first and second steps, respectively. Interestingly, the dehydrogenation products of $LiAlH_4$ (LiH and Al) further promoted the hydrogenation rate and selectivity of NCZ, achieving a hydrogen uptake of 5.6 wt% under 90 °C and 70 bar H_2 with 5 wt% Ru catalyst, close to the theoretical value of fully hydrogenated NCZ. In contrast, pristine NCZ with sole Ru catalyst absorbed only 5.2 wt% H_2 after 12 h. ^1H nuclear magnetic resonance (^1H NMR) spectra of the hydrogenated products confirmed a high selectivity of 97% 12H–NCZ and only 3% 8H–NCZ, compared to 71% 12H–NCZ and 29% 8H–NCZ in the control system without LiH and Al, highlighting the strong promoting effect of LiH

and Al. X-ray diffraction (XRD) analysis of the hydrogenated samples revealed remains of LiH and Al phases, while Fourier transformed infra-red (FTIR) spectra exhibited the characteristic bands of 12H–NCZ and octahedral Li_3AlH_6 vibrations in the 400–800 cm^{-1} region. Solid-state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) analysis further confirmed the partial regeneration of Li_3AlH_6, with a resonance at –34.5 ppm, indicating that reversible hydrogen storage can occur under moderate conditions. These findings underscore the potential of chemical coupling strategies in overcoming intrinsic material limitations and provide valuable guidance for the rational design of next-generation hydrogen storage systems.

CHAPTER 1

INTRODUCTION

1.1 Global Energy Landscape and the Prospects of Hydrogen Energy

As the global energy consumption structure shifts, we are facing the challenge of transitioning from reliance on fossil fuels to clean energy [1]. The combustion of fossil fuels has caused significant negative impacts on the environment and human health, including greenhouse gas emissions and acid rain. To address these challenges, the global energy transition is accelerating, particularly through the rapid development and use of renewable energy. In this process, hydrogen energy, as a potential clean energy carrier, shows significant potential in promoting the expansion of clean and renewable energy. Although the integration of hydrogen into the power system has not been fully studied, its key technologies in energy storage, re-electrification, and energy conversion have attracted widespread attention [2].

Hydrogen, as a sustainable energy carrier, has a high specific energy density, with energy output per unit mass three times that of gasoline, giving hydrogen significant advantages in energy storage and transportation [2]. The versatility of hydrogen also lies in its ability to be extracted from a variety of substances, including water, oil, natural gas, biomass fuels, and sewage sludge. Specifically, hydrogen production through water electrolysis not only synergizes with the use of renewable energy but also aligns with sustainable development goals. The abundance of water on Earth ensures that hydrogen can be produced in a sustainable way.

The global demand for hydrogen is currently 115 million tons per year, and it is expected to grow nearly sixfold by 2050, reaching 700 million tons, mainly due to increasing demand in the transportation sector and power generation. The share of hydrogen in final energy consumption is expected to reach 24%, highlighting its importance in the global energy structure. To achieve this goal, investments of up to one trillion USD are expected to be required in hydrogen production, transportation, and storage [3]. The construction of hydrogen infrastructure, including production, transportation, and storage systems, will be crucial to the widespread application of hydrogen energy.

In the context of the increasingly severe global energy crisis, the demand for renewable energy continues to grow, especially in terms of energy supply reliability and price volatility. The global reliance on fossil fuels not only leads to resource depletion risks but also causes profound negative impacts on the environment and climate. As climate change becomes an increasingly serious issue, governments worldwide are implementing a series of policies to promote the development and use of renewable energy [4]. The costs of wind and solar power have gradually decreased, and these renewable energy sources are becoming more widespread globally. However, despite the enormous potential of these renewable sources, they often face issues of intermittency and instability, especially when solar and wind power are inconsistent, leading to potential energy shortages. These challenges make it difficult for the existing power systems to be integrated with large-scale renewable energy.

Against this backdrop, hydrogen energy plays an increasingly important role as a clean energy carrier in the global energy transition. The advantages of hydrogen energy are not only reflected in its high energy density but also in its ability to be coupled with renewable energy, enhancing the stability and flexibility of renewable energy. For example, hydrogen can be produced using surplus solar or wind energy, and then used for power generation or to fuel electric vehicles when demand is higher, effectively balancing the fluctuation and intermittency of renewable energy [5]. Moreover, hydrogen can serve as an energy storage solution by converting electricity into hydrogen for storage, ensuring a reliable energy supply in the future. This flexible energy storage method allows hydrogen to play a crucial role not only in power systems but also in industrial, transportation, and building sectors. The diagram shown in Figure 1.1 illustrates the basic configuration of a green hydrogen energy system. This system consists of three main components: (1) the generation of green electricity from renewable energy sources, (2) the use of this electricity to produce green hydrogen via electrolysis, and (3) the storage of the hydrogen. The stored hydrogen can then be used either to generate electricity again or for various applications, such as replacing conventional hydrogen feedstocks in industries like refining, chemicals, steel, and even emerging sectors like transportation and building utilities.

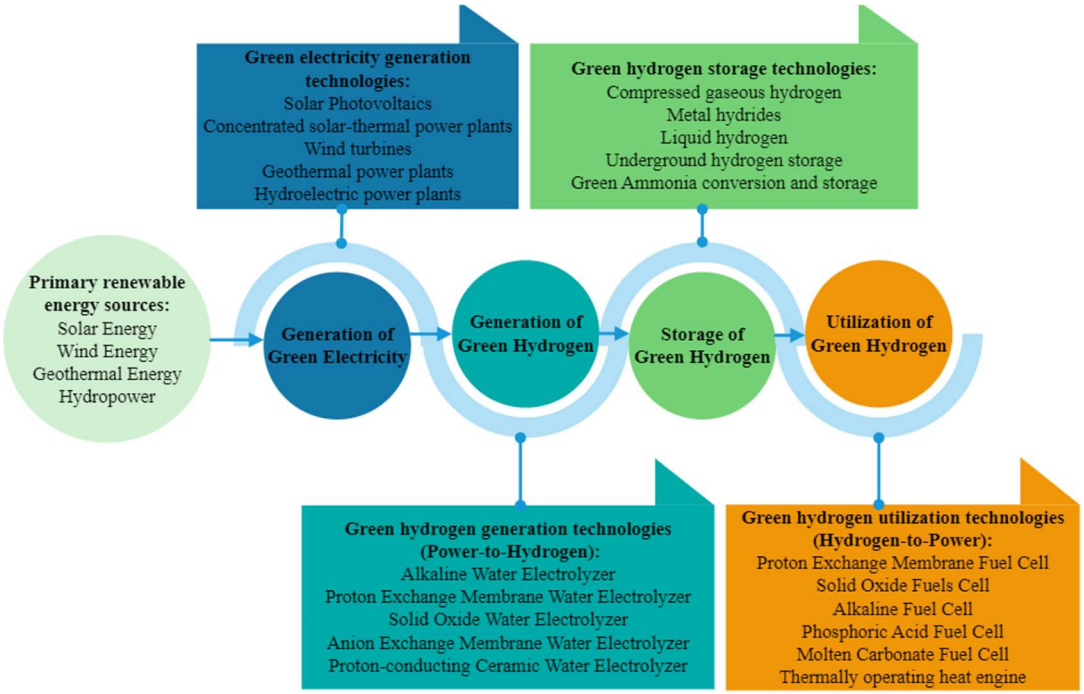

Figure 1.1 Schematic diagram of a green hydrogen energy system, consisting of renewable electricity generation, water electrolysis for hydrogen production, and hydrogen storage, with downstream applications in electricity regeneration and various industrial sectors [2].

However, the promotion and application of hydrogen energy is not without its challenges. First, the cost of hydrogen production, storage, and transportation is relatively high, especially for green hydrogen, which remains costly to produce. Currently, water electrolysis powered by renewable energy is the ideal method for producing green hydrogen, but this process requires significant amounts of electricity, and the capital and operating costs of the equipment are high, limiting its large-scale application [6]. While hydrogen production technologies continue to evolve, the economic viability of hydrogen still lags behind traditional energy sources. Therefore, reducing the cost of hydrogen production is the key to the development of the hydrogen industry. Achieving this will require technological innovation and significant

investment, particularly in improving the efficiency of water electrolysis, reducing raw material costs, and developing low-cost catalysts.

Secondly, hydrogen storage and transportation remain major challenges. Due to hydrogen's low volumetric density, storing it at normal temperature and pressure is not economically viable, requiring high-pressure storage, cryogenic liquefaction, or chemical storage technologies. Each storage method has its own advantages and disadvantages, such as high-pressure storage requiring significant energy for compression, and liquid hydrogen needing low-temperature conditions for liquefaction, which adds to costs and safety concerns [7]. However, as new hydrogen storage materials and technologies continue to develop, such as metal hydrides and chemical hydrogen storage, the issues surrounding hydrogen storage and transportation are gradually being addressed. Still, substantial research and investment are required to improve storage and transportation technologies to increase efficiency, lower costs, and ensure safety.

Moreover, the construction of hydrogen infrastructure is a critical factor for the widespread application of hydrogen energy. The promotion of hydrogen energy requires significant investment in infrastructure, including hydrogen production stations, transportation pipelines, storage facilities, and refueling stations. However, the development of hydrogen infrastructure is still in its early stages, and there are large regional differences in infrastructure construction worldwide [8]. While some countries and regions are beginning to build hydrogen infrastructure, others face significant financial and technological challenges. To address this, governments and

the private sector must collaborate to promote the construction of hydrogen infrastructure globally and establish relevant policies and standards to ensure the safe, sustainable, and efficient use of hydrogen.

In conclusion, hydrogen energy, as a crucial form of clean energy, has immense potential and prospects for development. Although it faces challenges in terms of technology, economics, and infrastructure, the growing pursuit of sustainable development goals means that hydrogen energy is set to undergo rapid development. Through technological innovation, international collaboration, and policy support, hydrogen energy is expected to become a significant driving force in the global energy transition, contributing to a low-carbon and sustainable future.

1.2 Status and Challenges of Hydrogen Storage Technology

Hydrogen, as a clean and efficient energy carrier, has received significant attention due to its potential to address environmental and energy challenges. However, the practical application of hydrogen energy heavily depends on the development of efficient and reliable storage technologies. Hydrogen's extremely low molecular weight and density present substantial technical challenges, making its storage a critical bottleneck in hydrogen-based energy systems. As shown in Figure 1.2, the current main hydrogen storage methods can be broadly categorized into physical and chemical approaches. Each method has its own characteristics, advantages, and limitations [9,10].

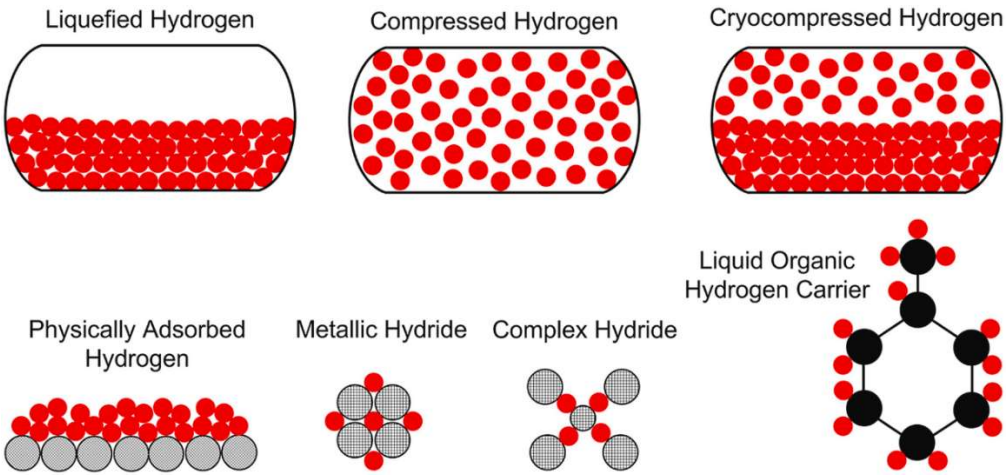

Figure 1.2 Principal methods of hydrogen storage [10].

Physical storage methods include compressed gaseous hydrogen storage and liquid hydrogen storage. Gas storage tanks are typically designed in a cylindrical shape and constructed from composite materials reinforced with fiber filaments, as illustrated in Figure 1.3 Physical storage is the most mature hydrogen storage technology. The current near-term technology for onboard automotive physical hydrogen storage is 350 and 700 bar (5,000 and 10,000 psi) nominal working-pressure compressed gas vessels—that is, "tanks" [11]. While technically advanced, compressed gas storage faces several limitations, including high costs associated with manufacturing lightweight yet high-strength storage tanks, as well as the risk of leakage and explosion under extreme conditions. These tanks typically use advanced composite materials such as carbon-fiber-reinforced polymers to ensure durability and safety. Despite these efforts, the overall energy density of compressed hydrogen remains low, which limits its suitability for applications requiring long storage durations or high capacities [12].

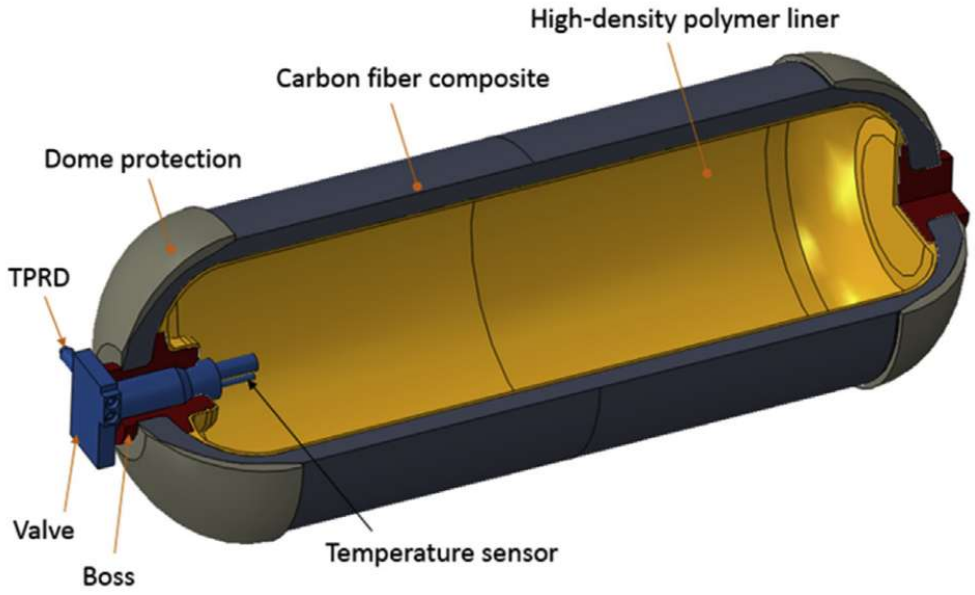

Figure 1.3 Schematic diagram of a pressurized hydrogen storage tank [13].

Liquid hydrogen storage represents another approach, relying on cryogenic technology to cool hydrogen to approximately 20 K (-253 °C) for liquefaction. This process significantly increases hydrogen's volumetric density, making it a promising option for large-scale and long-distance transportation. However, the energy cost of liquefaction is substantial, consuming about 30% of hydrogen's total energy content [14]. Additionally, maintaining the extreme low-temperature environment requires sophisticated thermal insulation systems to minimize boil-off losses, further complicating the design and operation of liquid hydrogen tanks. Although liquid hydrogen storage has been adopted in aerospace and niche industrial applications, its widespread use remains hindered by these challenges.

Compared to physical storage, chemical storage offers a fundamentally different approach by leveraging chemical reactions to store hydrogen in solid or liquid materials. Physisorption and chemisorption are the two primary mechanisms

underlying chemical hydrogen storage [13]. Physisorption involves weak van der Waals interactions between hydrogen molecules and high-surface-area materials such as metal-organic frameworks (MOFs), zeolites, and carbon-based materials (e.g., carbon nanotubes, graphene) [15]. These materials can adsorb hydrogen at relatively low pressures and temperatures, making them suitable for applications requiring low energy input for hydrogen storage and release. However, the storage capacities of physisorption materials are often insufficient to meet the demands of practical applications, particularly in automotive and stationary energy systems [16].

In contrast, chemical adsorption relies on the formation of strong chemical bonds between hydrogen and storage materials, which provides significantly higher hydrogen capacity. Common materials include metal hydrides (such as magnesium hydride, MgH_2) and complex hydrides (such as lithium borohydride, $LiBH_4$) [17–21]. Figure 1.4 illustrates the mechanism of solid-state hydrogen storage using metal hydrides, with magnesium (Mg) as a representative example [22]. The hydrogen absorption process can be divided into four main steps: (Step 1) molecular hydrogen (H_2) is initially physically adsorbed onto the surface of metal particles via weak van der Waals interactions; (Step 2) the adsorbed H_2 molecules are then chemisorbed and dissociated into atomic hydrogen (H) on the surface; (Step 3) these hydrogen atoms penetrate into the metal lattice, diffusing from the surface toward the interior of the material; (Step 4) once a sufficient concentration of hydrogen atoms is reached, a phase transformation occurs, resulting in the formation of a stable metal hydride phase (e.g., MgH_2). Compared to physical adsorption materials, these materials have higher

volumetric energy densities, making them more suitable for applications requiring compact storage solutions. However, chemical adsorption materials also face several challenges, including high dehydrogenation temperatures, slow reaction kinetics, and poor reversibility under moderate conditions. These factors limit their scalability and practicality in real-world applications [23].

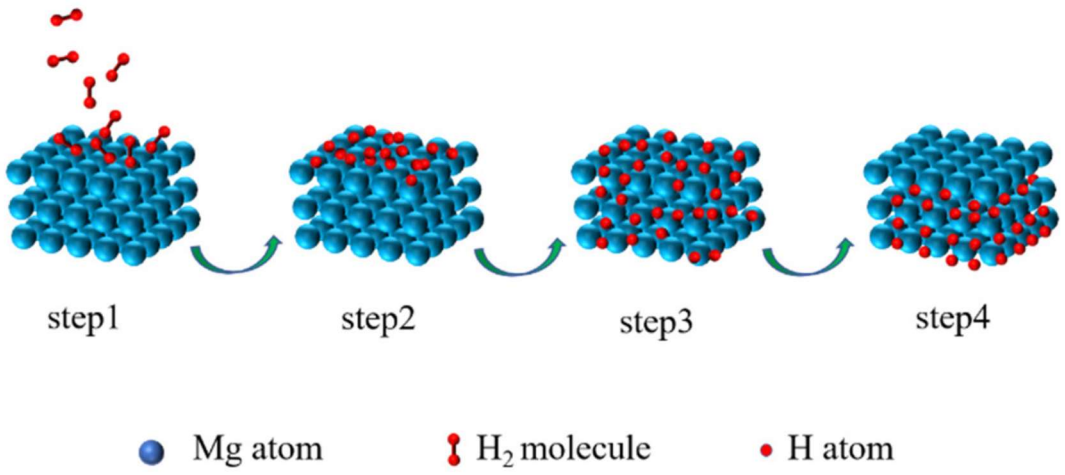

Figure 1.4 Schematic illustration of the hydrogen absorption mechanism in magnesium (Mg), including surface adsorption, H_2 dissociation, hydrogen diffusion into the metal lattice, and metal hydride (MgH_2) formation [22].

To overcome these limitations, recent research has focused on designing advanced materials with enhanced storage performance. Strategies include doping with catalysts to lower decomposition temperatures, nanostructuring to increase surface area and reaction kinetics, and integrating storage materials into hybrid systems to improve cycling stability were employed [15]. Solid state chemical hydrogen storage materials such as ammonia borane, alanates, borohydrides and liquid state hydrogen storage materials (also known as liquid organic hydrogen carrier) such as 9-ethylcarbazole, dibenzyltoluene and toluene are being explored for their potential to achieve high-capacity and low-cost hydrogen storage.

Despite the challenges associated with each storage method, ongoing advancements in hydrogen storage technologies are critical to enabling the widespread adoption of hydrogen energy systems. By addressing the bottlenecks in energy density, safety, and economic feasibility, these innovations could transform hydrogen into a practical and sustainable energy carrier for diverse applications, ranging from transportation to stationary energy storage systems.

1.3 Problem Statement

Materials based hydrogen storage appear to be promising alternative to conventional hydrogen storage technology. Among them, alanate, more specifically $LiAlH_4$ has attracted considerable attention due to its high theoretical hydrogen storage capacity of up to 10.5 wt%. Nevertheless, its poor reversibility and sluggish desorption kinetics remain the major challenges, severely limiting its practical application in hydrogen storage systems.

While most improvements in hydrogen storage have predominantly relied on the addition of metal-based catalysts and nanosizing approach to improve the dehydrogenation kinetics of $LiAlH_4$, only a few reports looked into improving the reversibility of $LiAlH_4$ via formation of complexes.

Bikiel and his colleagues [24] reported the use of ether as the ligand in the hydrogenation of LiH and Al to form $LiAlH_4$-ether complex. More recently, Cho [17] demonstrated that the confined $LiAlH_4$ within N-doped CMK-3 achieved rather high reversibility with an 80% yield at 100 MPa and 50 °C. Apparently, the inclusion of

either ether or N-doped CMK-3 altered the hydrogenation thermodynamic, making complete hydrogenation towards $LiAlH_4$ thermodynamically favorable via formation of a more thermodynamically stable $LiAlH_4$-ether or $LiAlH_4$-N-doped CMK-3 complexes.

Although the inclusion of either ether or N-doped CMK-3 had promoted the reversibility of $LiAlH_4$, they did not contribute in hydrogen storage, thus, their presences as dead-weight sacrifice the hydrogen storage capacity of the materials. Inspired by previous studies, it is hypothesized that the N-heterocycles hydrogen storage material could provide a chemical environment similar to those of O-bearing organic ligand such as THF that have shown success in reversing the hydrogenation of Al and LiH via the formation of $LiAlH_4$-THF and $LiAlH_4$-dimethylether adduct. Furthermore, these N-heterocycles could contribute to hydrogen storage, thus, potentially reversing the hydrogenation of Al and LiH while retaining high hydrogen capacity of the material. Therefore, in this study, the reaction kinetics and thermodynamics of $LiAlH_4$ were tuned by forming composites of $LiAlH_4$ and carbazole derivatives.

1.4 Research Objectives

The present study focuses on improving the hydrogen storage properties of $LiAlH_4$ through complexation with 9-ethylcarbazole or 12H-9-ethylcarbazole. Accordingly, the following specific objectives are outlined:

1. To investigate the hydrogen storage performance of $LiAlH_4$ by forming composites with carbazole derivatives, especially 9-ethylcarbazole (NCZ).

2. To examine the dehydrogenation temperature and activation energy of $LiAlH_4$ to improve its reaction kinetics and make the process more energy-efficient.

3. To evaluate the reversibility and hydrogenation efficiency of the system via formation of $LiAlH_4$-12H-NCZ complex, enabling better cycling performance under milder conditions.

1.5 Scope of the Thesis

Chapter 1: Introduction presents the global energy context, emphasizing the role of hydrogen as a clean energy carrier. It highlights the challenges associated with hydrogen storage and identifies the specific limitations of $LiAlH_4$ and carbazole-based materials. The problem statement and research objectives are clearly defined.

Chapter 2: Literature Review reviews the current status of hydrogen storage technologies, with particular emphasis on complex hydrides and liquid organic hydrogen carriers (LOHCs). It also discusses general improvement strategies—such as catalyst doping, nanostructuring, and chemical complexation—followed by detailed reviews of $LiAlH_4$ and carbazole-based materials, including their hydrogen storage behavior and enhancement approaches.

Chapter 3: Experimental Method outlines the experimental procedures used in the study. It details the preparation of $LiAlH_4$–carbazole composites and the synthesis of 12H-ethylcarbazole, along with the catalyst preparation. It also describes

the characterization techniques employed, including XRD, FTIR, NMR, DSC, and volumetric hydrogenation/dehydrogenation measurements.

Chapter 4: Results and Discussion presents and analyzes the experimental findings. It investigates the influence of different carbazole derivatives on the dehydrogenation behavior of $LiAlH_4$, evaluates the optimized doping ratio, and examines the reaction kinetics. The hydrogenation performance, structural changes of the products, and a proposed reaction mechanism are also discussed in depth.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Hydrogen Storage Technologies

Hydrogen, as a clean and efficient energy carrier, has attracted extensive attention since the 1970s. Current hydrogen storage technologies primarily include compressed gas storage, liquid hydrogen storage, solid-state hydrogen storage, and liquid organic hydrogen carriers (LOHCs) [25]. Each method has its own advantages and limitations in terms of safety, energy density, cost, and operating conditions. Among these, solid-state hydrides and LOHCs have emerged as research hotspots due to their potential for high volumetric energy density, better safety profiles, and adaptability to various application scenarios. These systems offer promising pathways toward the development of practical, compact, and efficient hydrogen storage solutions, which are essential for advancing hydrogen-based energy technologies.

2.1.1 Complex Hydrides

Solid state hydrides, such as complex hydrides is composed of light elements such as lithium and sodium, offer significant advantages in hydrogen storage density and gravimetric capacity [26]. For example, alkali metal-based complex aluminum hydrides, $MAlH_4$ (where M = Na, Li, K), are promising hydrogen storage candidates under moderate pressure and temperature, with a theoretical hydrogen capacity of up to 10.4 wt%. Unlike conventional metal hydrides, $MAlH_4$ desorbs hydrogen via

chemical decomposition, beginning with melting, followed by the formation and decomposition of intermediate M_3AlH_6 in three steps [27]:

$$MAlH_4\ (s) \rightarrow MAlH_4\ (l) \qquad \text{(Equation 2.1)}$$

$$MAlH_4\ (l) \rightarrow \frac{1}{3}M_3AlH_6\ (s) + \frac{2}{3}Al\ (s) + H_2\ (g) \qquad \text{(Equation 2.2)}$$

$$\frac{1}{3}M_3AlH_6\ (s) \rightarrow MH\ (s) + \frac{1}{3}Al\ (s) + \frac{1}{2}H_2\ (g) \qquad \text{(Equation 2.3)}$$

While the high energy density of complex hydrides makes them promising candidates for hydrogen storage applications, challenges such as high thermodynamic stability and slow reaction kinetics persist. Researchers are addressing these issues through methods such as doping with nanocatalysts, destabilization via cation or anion substitution, and leveraging nanoscale confinement effects [13]. These advancements are driving the materials closer to practical applications.

In particular, among various complex hydrides, lithium aluminum hydride ($LiAlH_4$) has received significant research attention due to its relatively low decomposition temperatures and high hydrogen capacities. Despite their potential, the lack of reversibility and the requirement for multi-step dehydrogenation often complicate their practical use. Moreover, the sensitivity of these materials to air and moisture introduces handling difficulties, necessitating careful material design and system integration. A more detailed literature review related to the thermodynamic and kinetic improvements made on $LiAlH_4$ will be included in the section 2.3.

2.1.2 Liquid Organic Hydrogen Carriers (LOHCs)

Liquid organic hydrogen carriers (LOHCs) are a class of organic compounds capable of storing and releasing hydrogen through reversible hydrogenation and

dehydrogenation reactions. As they exist in liquid form under ambient conditions, LOHCs are easy to handle, store, and transport, and can be seamlessly integrated into the existing petrochemical infrastructure such as storage tanks and pipelines[28]. These characteristics make LOHCs one of the most promising technologies for large-scale hydrogen storage and distribution.

LOHC technology relies on reversible hydrogenation of aromatic compounds to store and release hydrogen efficiently. Early research focused on the toluene (TOL)/methylcyclohexane (MCH) system, which provides a hydrogen storage capacity of 6.1 wt% and achieves 99% dehydrogenation conversion at 320 °C under 1 bar. However, this system requires high hydrogenation and dehydrogenation temperatures and tends to produce by-products such as dealkylation or coke formation, complicating the reactions. Moreover, the low flashpoint of the TOL/MCH system and the need for complex condensation and purification steps for dehydrogenation products limit its further application. Despite these challenges, Japan's Chiyoda Corporation has successfully developed the technology and announced its large-scale application in hydrogen energy logistics . [29]

Due to these drawbacks, alternative LOHCs with improved thermal stability and hydrogen capacity have been investigated. To address the limitations of the TOL/MCH system, researchers have explored alternative LOHC systems, such as naphthalene/tetralin/decalin and benzyl toluene (H0-BT)/fully hydrogenated benzyl toluene (H12-BT) and dibenzyltoluene (H0-DBT)/fully hydrogenated dibenzyltoluene (H18-DBT) and 9-ethylcarbazole (NCZ)/12H-9-ethylcarbazole (12H-NCZ). The

NCZ/12H-NCZ system, in particular, has attracted significant interest due to its high hydrogen storage capacity (6.8 wt%), good reversibility, and relatively mild hydrogenation/dehydrogenation conditions. NCZ is a nitrogen-containing aromatic compound with excellent chemical stability and liquid-phase behavior, making it suitable for practical liquid organic hydrogen carrier (LOHC) applications. Its well-defined molecular structure and hydrogenation pathway also facilitate catalyst development and kinetic optimization, further enhancing its potential for efficient and recyclable hydrogen storage systems.

A more detailed literature review related to the thermodynamic and kinetic improvements made on carbazole based material will be included in the section 2.4.

2.2 General Strategies for Improving Hydrogen Storage Materials

Hydrogen storage materials, particularly solid hydrides and liquid organic hydrogen carriers (LOHCs), are key to advancing the hydrogen economy. Research attention has been focused on addressing key challenges related to both reaction thermodynamics and kinetics, such as high dehydrogenation temperatures, low rate of reaction and limited reversibility. Several strategies have emerged to improve the hydrogen storage properties of the potential hydrogen storage materials include catalyst doping, nanostructuring, and changing reaction pathway [13,28,30].

These strategies—doping, nanostructuring—are collectively contributing to the development of more efficient and scalable hydrogen storage solutions. By improving both the thermodynamics and kinetics of hydrogen storage materials, these

approaches bring us closer to realizing the practical use of hydrogen as a clean and sustainable energy carrier.

2.2.1 Catalyst Doping: Concepts and Examples

Doping is an effective strategy to enhance catalytic kinetics by modulating the electronic structure, introducing defects, and optimizing reaction pathways. It can alter the band structure and charge distribution of the catalyst, tune the d-band center, and improve electron conductivity, thereby regulating the adsorption behavior of reactants and facilitating the transformation of reaction intermediates. Additionally, doping can induce lattice defects such as oxygen or cation vacancies, leading to increased exposure of active sites and stabilization of highly active catalytic phases during reactions. In some cases, doping also enables alternative reaction mechanisms with lower energy barriers, improving both reaction efficiency and selectivity. In multicomponent systems, synergistic effects between dopants and host materials can further enhance catalytic performance. Overall, catalyst doping provides a versatile approach for constructing efficient and stable catalytic systems, with effectiveness largely determined by the compatibility between the dopant and the host material.

For solid hydrides like sodium alanate ($NaAlH_4$) and magnesium hydride (MgH_2), alloying and doping have been widely studied. One notable example is the doping of $NaAlH_4$ with titanium (Ti), which enhances the material's hydrogen desorption kinetics. Titanium-doped $NaAlH_4$ exhibits a significant reduction in the desorption temperature by approximately 50 °C, with the dehydrogenation process starting around 150 °C compared to 200 °C for undoped $NaAlH_4$. This improvement

is attributed to the catalytic effect of titanium, which lowers the activation energy for dehydrogenation [31].

Similarly, doping MgH_2 with elements such as vanadium (V) and niobium (Nb) has shown to reduce the dehydrogenation temperature from 400 °C to 300 °C. A study by Zhang and his colleagues [32] demonstrated that niobium-doped MgH_2 could release 6.1 wt% of hydrogen at 300 °C in just 1 hour, compared to 4.8 wt% for the pure material under the same conditions. These doping strategies effectively enhance the thermodynamics and kinetics of dehydrogenation, making these materials more practical for use in hydrogen storage systems.

New emerging hydrogen carriers, such as ammonia borane (NH_3BH_3 and ethanolamine, are being studied for their potential to provide higher hydrogen capacities and more favorable thermodynamics. Ammonia borane, for example, has a theoretical hydrogen content of 19.6 wt%, and recent work has focused on optimizing the catalyst systems to release hydrogen at lower temperatures [33]. Simon Gaspar and colleagues [34] developed an iron-based catalyst, [FeH(CO)(PNP)], which efficiently catalyzes the dehydrogenation of ammonia borane at 20 °C with a turnover number (TON) of up to 1800, producing linear polyaminoborane (PAB). The study revealed that free BH_3 leads to catalyst deactivation, but the addition of amines to scavenge BH_3 increased the TON to 3000, providing valuable insights for the design of low-cost hydrogen storage materials.

Solid-state hydrides and liquid organic hydrogen carrier (LOHC) technologies each possess unique advantages. The former exhibits high hydrogen

storage density and reversible dehydrogenation capabilities, while the latter offers excellent safety and convenience for storage and transportation under ambient conditions. The combination of these two systems holds great promise for developing future hydrogen storage technologies that are efficient, safe, and economically viable. A study conducted by Feng et al. [35] demonstrated that metal hydrides such as MgH_2 can serve as effective catalysts in the hydrogenation of dibenzothiophene (DBT), significantly enhancing both the reaction rate and selectivity. As illustrated in the mechanism shown in Figure 2.1, MgH_2 not only participates in hydrogen transfer during the hydrogenation process but also exhibits catalytic functionality to a certain extent. This finding opens up new possibilities for constructing low-cost, high-performance LOHC-based hydrogen storage systems. The results of this study have inspired further exploration into the use of a broader range of metal hydrides in LOHC hydrogenation reactions, particularly in the development of non-noble-metal and environmentally friendly hydrogen storage technologies.

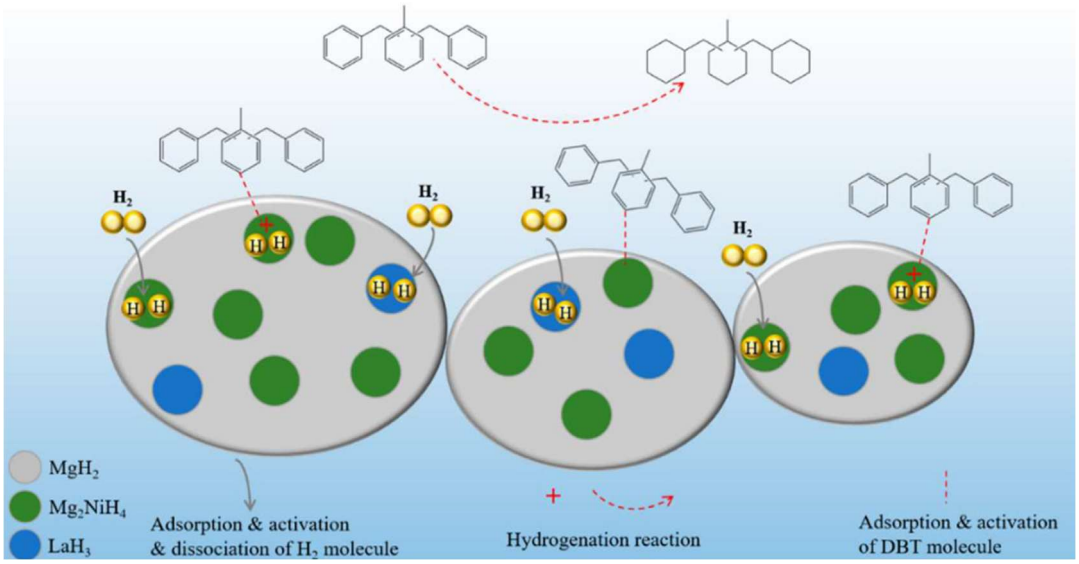

Figure 2.1 Scheme of the proposed reaction mechanism for the hydrogenation process of dibenzyltoluene catalyzed by Mg based metal hydrides [35].

2.2.2 Nanostructuring: Concepts and Applications

Nanostructuring refers to the process of manipulating the size, morphology, porosity, and interfacial properties of a material so that it is on the nanoscale (1–100 nm) in at least one dimension, thereby imparting unique physical, chemical, and mechanical properties. In the field of catalysis, nanostructuring is one of the core strategies to enhance reaction efficiency, with its advantages mainly stemming from high surface area, quantum confinement effects, and abundant active sites.

Nanostructuring is another powerful approach to optimizing hydrogen storage materials in improving the reaction thermodynamics and kinetics. For example, confining $NaAlH_4$ in mesoporous carbon frameworks has resulted in lower decomposition temperatures and faster kinetics [36]. A study by Bonatto Minella et al. [37] in 2013 reported that the carbon-loaded $NaAlH_4$ dehydrogenation temperature starts at 100 °C, with a faster dehydrogenation rate, the mesoporous carbon not only provides

a larger surface area but also stabilizes the intermediate phases during the dehydrogenation process, preventing the formation of less stable phases and improving the overall reversibility of the material.

Among various nanostructuring techniques, ball milling is one of the most widely recognized and commonly employed methods. Ball milling is a widely used technique in materials science, especially in the field of hydrogen storage, as it can significantly reduce the particle size of materials. The reduction in particle size is crucial for improving hydrogen absorption and desorption kinetics, as it increases the surface area of the material and shortens the diffusion path for hydrogen atoms [38]. The ball milling process not only reduces particle size but also generates new surfaces and introduces defects, which facilitate hydrogen diffusion, enhance material reactivity, and improve overall hydrogen storage performance.

In addition, Ball milling is widely used to improve catalyst dispersion and create nanostructures, enhancing dehydrogenation performance through better contact and increased active sites.

2.2.3 Complex Formation and Chemical Modification

In addition to catalyst doping and nanostructuring, changing reaction pathway has also proven to be a promising strategy in proving both reaction thermodynamics and kinetics. By combining different types of hydrides, such as calcium hydride (CaH_2) and lithium borohydride ($LiBH_4$), researchers have achieved better thermodynamic performance and improved hydrogen storage capacity. For example, CaH_2 /$LiBH_4$ composites have been shown to release 6.4 wt% hydrogen at 300 °C, a significant

improvement compared to the 5.5 wt% released by pure $LiBH_4$. This composite system also demonstrates improved reversibility, with over 90% of the hydrogen being recoverable after multiple cycles, which is a major step forward in the practical application of hydrides for hydrogen storage [39].

Liquid organic hydrogen carriers (LOHCs) have also shown significant promise in addressing the limitations of solid hydrides. LOHCs, such as toluene and methylcyclohexane, are particularly attractive for large-scale hydrogen storage and transport due to their liquid state at ambient conditions, making them easier to handle. One of the most studied LOHC systems is the toluene-methylcyclohexane (MCH) system, which has been extensively investigated for its ability to hydrogenate and dehydrogenate. A key advantage of this system is its relatively low dehydrogenation temperature. Recent studies have shown that using palladium-based (Pd) catalysts can lower the dehydrogenation temperature of MCH to 250 °C, a 50 °C reduction compared to traditional catalysts [40]. For instance, a study by Schuster et al. [41] demonstrated that the Pd/Al_2O_3 model catalyst effectively reduces the dehydrogenation temperature of methylcyclohexane (MCH) by maintaining high catalytic activity at 500 K, significantly lower than the typical MCH dehydrogenation temperature of around 623 K. The findings underscore the critical role of controlling H_2 partial pressure to suppress carbon deposition and enhance the stability of Pd-based catalysts during LOHC dehydrogenation. This is a significant improvement in the efficiency of the dehydrogenation process, especially considering the ease of handling and scalability of LOHC systems.