

Review

Chemical material as a hydrogen energy carrier: A review

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Abstract: In light of climate change imperatives, there is a critical need for technological advancements and research endeavors towards clean energy alternatives to replace conventional fossil fuels. Additionally, the development of high-capacity energy storage solutions for global transportability becomes paramount. Hydrogen emerges as a promising environmentally sustainable energy carrier, devoid of carbon dioxide emissions and possessing a high energy density per unit mass. Its versatile applicability spans various sectors, including industry, power generation, and transportation. However, the commercialization of hydrogen necessitates further technological innovations. Notably, high-pressure compression for hydrogen storage presents safety challenges and inherent limitations in storage capacity, resulting in about 30%–50% loss of hydrogen production. Consequently, substantial research endeavors are underway in the domain of material-based chemical hydrogen storage that causes reactions to occur at temperatures below 200 °C. This approach enables the utilization of existing infrastructure, such as fossil fuels and natural gas, while offering comparatively elevated hydrogen storage capacities. This study aims to introduce recent investigations concerning the synthesis and decomposition mechanisms of chemical hydrogen storage materials, including methanol, ammonia, and Liquid Organic Hydrogen Carrier (LOHC).

Keywords: hydrogen storage; chemical hydride; catalysis; hydrogenation

1. Introduction

Conventional fossil fuels, while meeting global energy demand, generate carbon dioxide, a major contributor to global warming, making their limited resources and the quest for securing clean energy sources globally imperative [1–8]. Initially, research and industrial focus on environmentally friendly energy were primarily directed towards power production using renewable sources such as solar and wind energy. However, reliance on these sources can lead to unstable power production due to their susceptibility to environmental factors [9–18]. Furthermore, the storage of generated power is limited to short-term storage (~week) through Energy Storage Systems (ESS), necessitating alternative solutions for long-term (~season) and stable power supply. In this context, hydrogen has garnered attention as an environmentally friendly substance with a closed reaction cycle capable of producing water upon reaction, thereby facilitating the regeneration of hydrogen [19–28]. With significant chemical energy (142 MJ) and a high energy storage density per unit weight (three times that of gasoline), hydrogen serves not only as a fuel but also enables long-term storage (~year), making it viable for energy transportation. In view of the transportation sector, it is important to achieve sustainable goals by using hydrogen fuel. It also should consider the real data, which is collected from hydrogen commercial products, to evaluate direct and indirect effects [29]. However, hydrogen possesses a low volumetric storage density, posing a significant challenge in safely storing and

transporting large quantities, which is crucial for transitioning to a hydrogen-based society that efficiently utilizes renewable energy [30–39]. While hydrogen utilization technology for fuel, such as fuel cells, has reached a commercially viable stage with secured infrastructure, efficient large-scale hydrogen storage technology necessitates extensive research and development efforts for commercialization [40–45].

Various methods exist for hydrogen storage and transportation. Notably, storing gaseous hydrogen at high pressure (350–700 bar) in storage tanks and transporting it via tube trailers is a prominent approach, as is liquefying gaseous hydrogen ($-253\text{ }^{\circ}\text{C}$) and storing it in dedicated storage tanks. These methods require specialized infrastructure due to the high energy density of hydrogen, and liquefaction, in particular, incurs significant energy consumption [46–59]. As alternatives, research is underway on physically adsorbing hydrogen onto porous materials such as Metal Organic Frameworks (MOFs) and carbon nanotubes for storage and transportation, as well as chemically binding hydrogen to metals to enable solid-state storage and desorption, as seen in metal hydrides. Furthermore, compounds formed by combining hydrogen with carbon, nitrogen, or boron atoms, such as methanol, ammonia, and Liquid Organic Hydrogen Carriers (LOHCs), offer a chemical hydrogen storage system with high storage density and ease of storage compared to molecular hydrogen storage. **Figure 1** illustrates these various chemical hydrogen carriers [60–81]. Utilizing such liquid compound-based hydrogen facilitates easy application due to its compatibility with existing fossil fuel or natural gas infrastructure, thus saving additional infrastructure construction costs and enhancing its commercial viability. The dehydrogenation reactions required to get hydrogen from chemical hydrogen carriers commonly employ catalysts such as Fe, Ni, Pt, and Ru to promote exothermic reactions. Therefore, the development of catalysts enabling higher hydrogen production rates and efficiency at lower temperatures, along with high-purity hydrogen extraction, is imperative [82–96]. The hydrogen produced requires refinement, with coupling to existing commercial hydrogen production methods such as Steam Methane Reforming (SMR) with separation and purification facilities allowing for cost savings in hydrogen production by separating carbon monoxide and carbon dioxide [97–111].

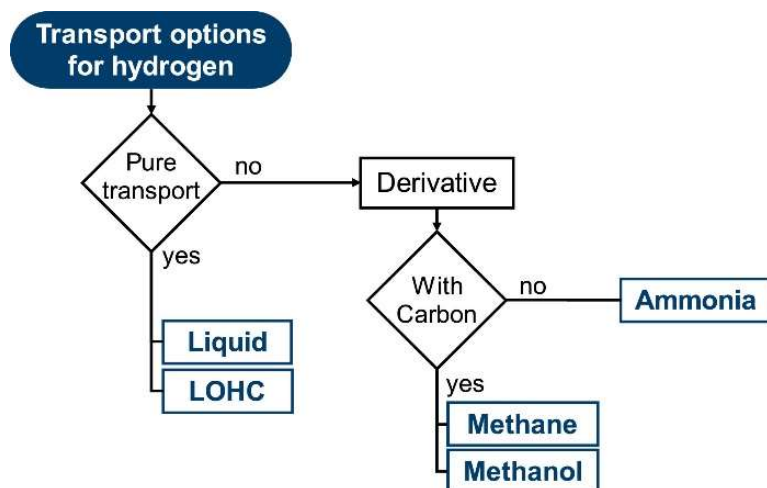


Figure 1. Considered intercontinental transport options for hydrogen as a renewable energy carrier [81].

This study aims to provide a comprehensive overview of the synthesis methods and technological advancements for the efficient extraction of hydrogen from commercially researched and viable chemical hydrogen carriers such as methanol, ammonia, and LOHCs. It includes the various catalyst studies with hydrogen conversion rates. Additionally, it seeks to offer an economic analysis of these chemical hydrogen carriers, comparing them to shed light on factors to consider during the transition from fossil fuels to hydrogen applications. By doing so, it will contribute to elucidating the future direction of the chemical industry, which previously held a dominant position in petrochemistry, considering elements such as chemical hydrogen carriers.

2. Chemical hydrogen carriers

2.1. Methanol

Methanol, a versatile raw material widely used in various industries such as hydrogen fuel (road, maritime, etc.), industrial fuel (boilers, etc.), and as a feedstock in the petrochemical industry (plastics, etc.), forms a large-scale market, producing approximately 65 million tons globally [21,23–24]. Methanol, being the simplest compound producible from natural gas and renewable energy sources, exhibits a high hydrogen storage density of 12 wt%. Utilizing methanol as hydrogen storage offers several advantages: 1) Methanol reforming can be conducted at much lower temperatures (150–450 °C) compared to natural gas reforming; 2) It can leverage the infrastructure of fossil fuels such as gasoline, diesel, and kerosene for various applications (transportation, fuel, power generation, etc.); and 3) It is relatively stable as a liquid and easy to store under normal environmental conditions [25–27]. Researchers are actively exploring the utilization of methanol as a fuel synthesized from biomass and carbon-containing sources, including carbon dioxide, with the aim of enhancing its economic viability. **Figure 2** shows the carbon cycle utilization of methanol [30,39,83–84]. The synthesis reactions of methanol are presented in **Table 1** [26].

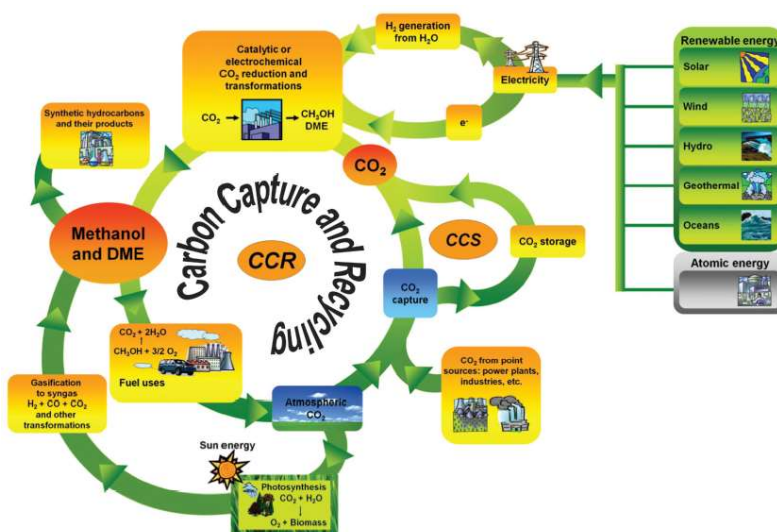


Figure 2. Anthropogenic carbon cycle within the Methanol Economy [25].

Table 1. Processes and Conditions for hydrogen production from Methanol [26].

Process	T(K)	Reaction	Advantage/Disadvantage
MSR (Methanol steam reforming)	423-623	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2$	Low Temperature High Methanol conversion Low CO content /Steam preheating Water waste management
MD (Methanol decomposition)	373-723	$\text{CH}_3\text{OH} \leftrightarrow \text{CO} + 2\text{H}_2$	/High CO content
POM (Partial oxidation)	300-723	$\text{CH}_3\text{OH} + 0.5\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2$	Reduction of heating cost /High CO content
ATRM (Autothermal reforming)	473-823	$\text{CH}_3\text{OH} + r\text{O}_2 + (1-2r)\text{H}_2\text{O} \leftrightarrow (3-2r)\text{CO}_2 + 2\text{H}_2$	Hydrogen-rich gas Reduction of heating cost /Need catalyst

Methanol can be synthesized by the reaction of carbon dioxide and hydrogen through endothermic reactions in Methanol Steam Reforming (MSR) processes to produce hydrogen. Among the introduced processes, MSR has the longest history and operates at relatively low temperatures (200–350 °C) without producing carbon monoxide. When carbon monoxide is present, it reacts with hydrogen to synthesize methanol, which is primarily employed in large-scale methanol production. Methanol Partial Oxidation (POM) methods, widely used in hydrogen production, offer the advantage of fast reaction rates and exothermic processes, enabling cost savings through heat application. However, POM entails complex oxidation, steam reforming, and decomposition reactions and tends to produce relatively impure hydrogen due to its high carbon monoxide content. A hybrid process combining MSR and POM, known as Autothermal Reforming (ATR), utilizes the heat generated in the exothermic POM reaction to drive the MSR reaction, simplifying the process. ATR offers advantages such as low energy requirements and rapid gas generation compared to other processes but needs optimized catalysts for obtaining appropriate products [84–91]. Catalysts used in the reforming reaction of methanol should possess excellent catalytic activity and stability to ensure large-scale hydrogen production and high conversion rates. Additionally, considering the generation of carbon monoxide during reforming, which can affect the purity of hydrogen, it is necessary to inhibit its formation by having high selectivity. Up to now, catalysts primarily based on Cu, Ni, and Pd have been utilized in methanol reforming reactions, and various research efforts are underway to enhance these catalyst properties. For instance, although Cu/ZnO/Al₂O₃, commonly used in commercial methanol synthesis, exhibits high activity, its stability decreases at high temperatures, leading to natural ignition, sintering, and deactivation. Consequently, various studies have been conducted to improve stability [94,95,104]. Cu-based catalysts typically involve a reaction between oxygen and hydrogen at two adsorption sites, as shown in **Figure 3** [89].

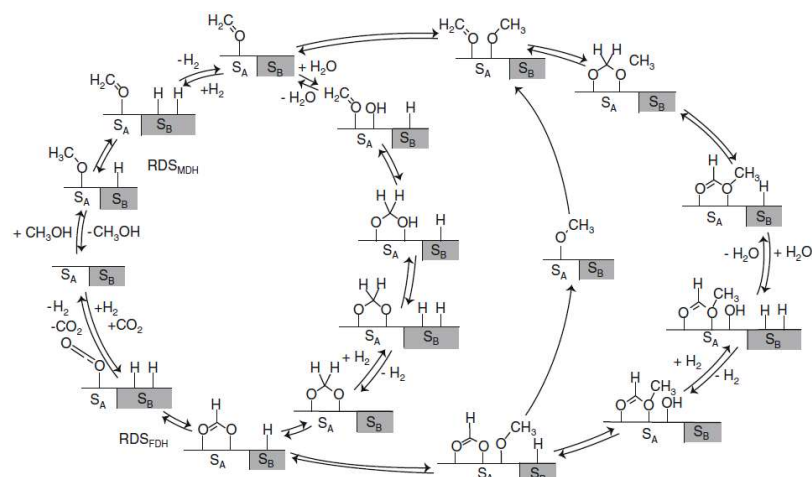


Figure 3. Catalysis cycle for MSR over Cu-based catalysts including two different kinds of reactive sites SA (adsorption and desorption of oxygenates) and SB (adsorption and desorption of hydrogen) [89].

Cu-based catalysts, commonly supported on materials such as Cu/ZnO or Cu/TiO₂ using Al-based supports, undergo research involving the addition of elements to improve methanol conversion rates and stability. Additives such as Mg and Ni enhance catalyst particle nanostructuring, dispersion, and activity. Notably, the addition of optimized Mg to Cu/ZnO/Al-5Mg catalysts has shown a reduction in particle size from 7.8 nm to 3.5 nm and an improvement in methanol conversion rates from 56% to 68% [96–98].

Similarly, Ni-based catalysts, predominantly supported on Al-based supports, exhibit enhanced catalytic performance with various additives. Using Ti oxide-based materials instead of Al-based supports in Ni catalysts revealed superior properties such as excellent oxidation-reduction characteristics, high concentrations of chemisorbed oxygen, and a hierarchical porous structure. Through simulations of methanol steam reforming reactions on Ti oxide-based catalysts using the Vienna Ab initio Simulation Package (VASP), NiTiO₃ catalysts were found to enhance the adsorption energy and activation of methanol molecules on the Ni-Ti-Ox catalyst surface (**Figure 4**), exhibiting methanol conversion rates (873 K) and H₂ selectivity of 99.9%. This demonstrates superior catalytic characteristics compared to Ni-Al₂O₃ catalysts mixed with Al-based materials, which exhibit methanol conversion rates of 77% and H₂ selectivity of 91.2% [97,99–102].

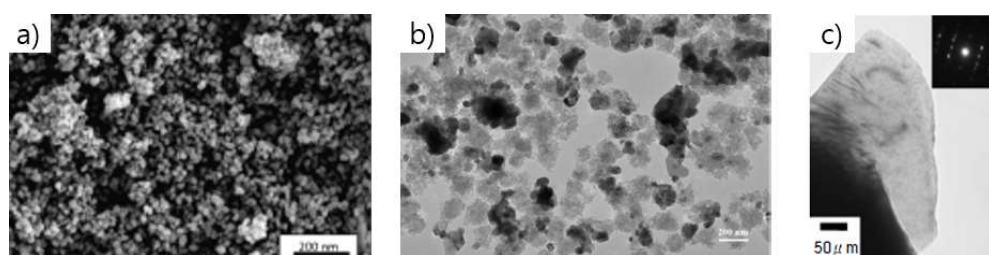


Figure 4. Scanning of particle size in the follow research: **(a)** Field emission scanning electron microscopy (FESEM) image; **(b)** Transmission electron microscopy (TEM) image; **(c)** Typical Dislocation free zone in fine particle [96–98].

Recent research in methanol reactions has witnessed active investigations into Pd-based catalysts, comparing the methanol reactions of Pd and PdZn catalysts using various supports. Comparisons of methanol production with Pd/TiO₂ and Pd/Al₂O₃ catalysts with and without Zn inclusion at constant pressure (20 bar) in the temperature range of 175~250 °C revealed increased methanol production and decreased methane selectivity when Zn was incorporated into the catalysts. This demonstrates the superior stability of PdZn alloys compared to other bimetallic alloys. Pd/Ga₂O₃ catalysts, regardless of the presence of Zn, exhibited high methanol selectivity when using Ga₂O₃ as a support material [95]. Methanol production using various Pd-based catalysts can be compared in **Figure 5**, and the various characteristics of catalysts used in methanol reactions are summarized in **Table 2**.

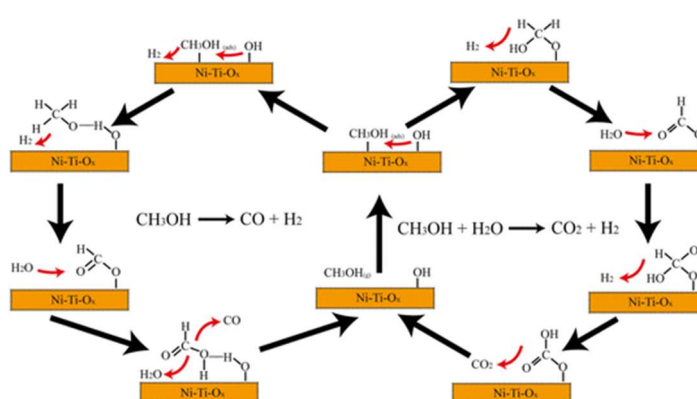


Figure 5. Reaction mechanism diagram of Ni–Ti–Ox catalyst [93].

Table 2. Comparison of catalytic performance of Methanol production [30–32,96–102].

Catalyst	T(K)	Electrochemical surface area (m ² /g)	Cycle(hour)	H ₂ selectivity (%)	Conversion (%)
NiPd-C	298	14.5	2	N/A	N/A
NiPd-MSN	298	19.53	2	N/A	N/A
Pd-NiO _x -P/C	298	5.76	3	N/A	N/A
Pd/C	298	2.56	3	N/A	N/A
Pd-NiO _x /C	298	4	3	N/A	N/A
Pd/ZrO ₂ -TiO ₂	523	N/A	5	66	22
MoC	573	N/A	12	N/A	30
Cu/ZnO/Al ₂ O ₃	523	N/A	1	82.3	98.8
Ni/Al ₂ O ₃	773	N/A	N/A	91.2	77
Ni-Cu/Al ₂ O ₃	773	N/A	24	99.1	86.3
10La-10Ni/Al ₂ O ₂	300	N/A	3	68	99
Cu-Ni/TiO ₂	573	N/A	10	92.7	92.6
Cu/TiO ₂	573	N/A	10	90	90.2
Pt/TiO ₂	573	N/A	10	94	95.5
Ru/TiO ₂	573	N/A	10	97.8	98.9

Furthermore, the cost of methanol production is heavily dependent not only on catalysts but also on the costs of hydrogen and carbon dioxide. Economic analysis conducted on the utilization of methanol produced from renewable sources (clean

methanol) as an energy carrier indicates that to ensure methanol production within the current market price range, hydrogen costs must be below 2.5 €/kg within ten years. Therefore, improvements in catalyst performance should be accompanied by reductions in raw material costs. The cost analysis of methanol is shown in **Figure 6** [81].

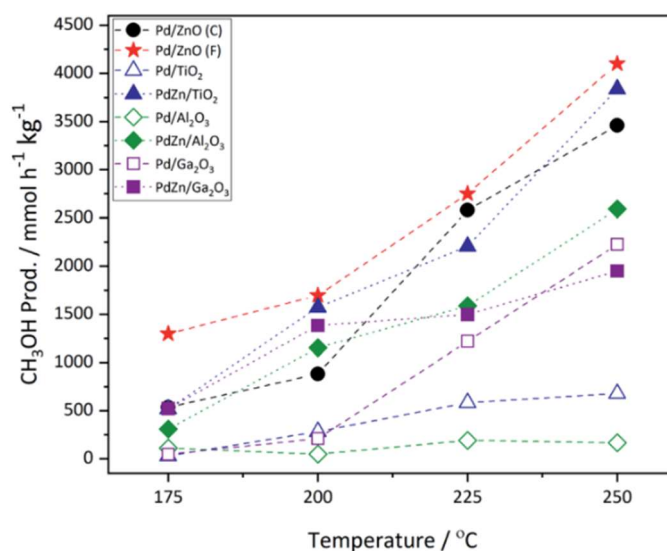


Figure 6. Methanol productivity as a function of CO₂ hydrogenation reaction temperature over Pd and PdZn supported catalyst [95].

2.2. Ammonia

Ammonia is one of the oldest and most widely produced compounds in the world, with sufficient infrastructure established for its production, transportation, and distribution. Currently, over 85% of the ammonia production in most plants (more than 200 million tons annually) is used as fertilizer, with the remainder primarily utilized in the chemical and processing industries. Ammonia (NH₃) is a stable binary hydride and the simplest hydride of nitrogen. From the perspective of hydrogen production, ammonia serves as an excellent hydrogen carrier, demonstrating a hydrogen storage capacity of 17.7 wt% at 20 °C and existing in a liquid state at around −30 °C, making it easy to store and transport. Consequently, there is active development of storage compounds and fuel cell technologies utilizing ammonia [103–122].

However, due to the substantial emission of carbon dioxide during the synthesis process and its inherent toxicity, technological development to address these issues is essential to utilizing ammonia as an environmentally friendly hydrogen energy carrier. The comparison of hydrogen storage capacities using ammonia is shown in **Figure 7** [104].

Currently, most of the ammonia is produced using the Haber-Bosch process, which utilizes catalysts based on Fe catalysts at high- temperatures (above 673 K) under high pressure (20–40 MPa). The synthesis and decomposition mechanisms of ammonia are shown in **Figure 8** [107].

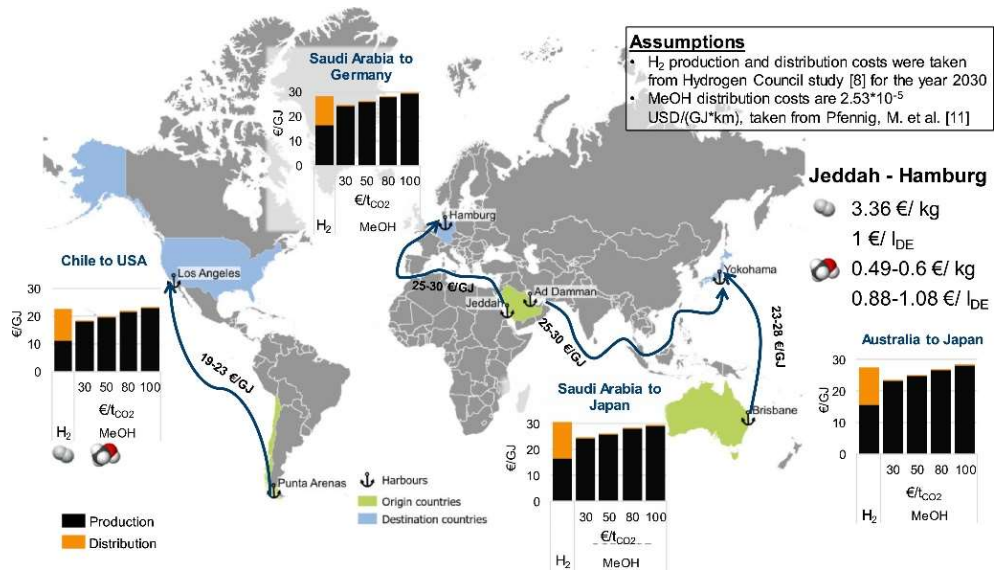


Figure 7. Hydrogen and methanol production and distribution costs for the four investigated origin/destination combinations [81].

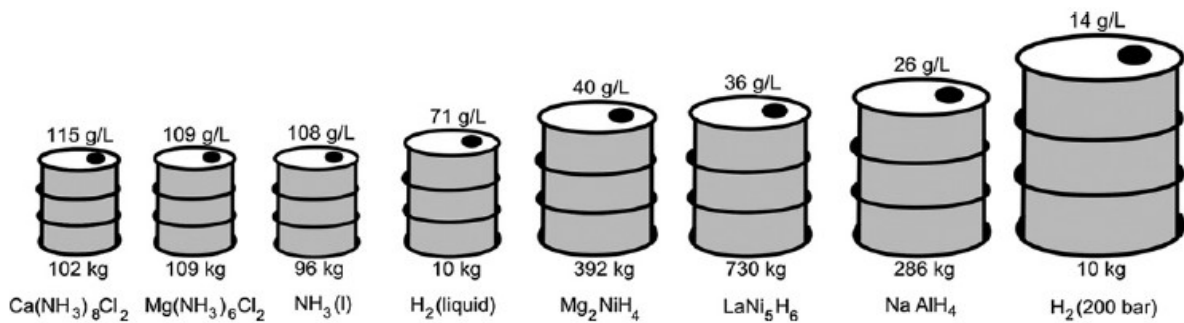


Figure 8. Mass and volume of 10 kg hydrogen stored reversibly by 8 different methods, based on the best obtained reversible densities without considering the space or weight of the container [104].

Ammonia synthesis is an exothermic reaction between nitrogen and hydrogen, requiring high temperatures and pressures to break the chemical bonds within nitrogen molecules. Due to the significant emission of carbon dioxide and the need to reduce energy consumption caused by the high temperatures and pressures required for ammonia synthesis, the development of new production processes is essential for using ammonia as an environmentally friendly hydrogen energy carrier. Research is actively underway to utilize catalysts to lower reaction temperatures and increase reaction rates to reduce energy consumption. Various ammonia synthesis processes are summarized in **Table 3** [106–109].

Table 3. Processes and Condition of Ammonia reaction based hydrogen Production [106–109].

Process	Condition	Reaction	Advantage/Disadvantage
Haber-Bosch method	573–773 K 200–350 atm	$N_2 + 3H_2 \leftrightarrow 2NH_3$	High conversion rate/High CO ₂ content High temperature and pressure
Photocatalysis method	300–500 K 1 atm	$N_2 + 3H_2O \leftrightarrow 2NH_3 + 1.5O_2$	Low temperature and pressure/Need catalyst technology
Electrocatalysis method	773 K 1 atm	1) $3H_2 \leftrightarrow 6H^+ + 6e^-$ 2) $N_2 + 6H^+ + 6e^- \leftrightarrow 2N_2H$ 3) $N_2 + 3H_2 \leftrightarrow 2NH_3$	Low energy consumption/Low efficiency Low production rate of ammonia

Ammonia catalysts typically use carbon-based supports and employ a variety of materials such as Pt, Rh, Co, Cs, Fe, and Ru as catalysts. Researches have been conducted on various carbon-supported catalysts, including carbon nanotubes, graphene, and carbonaceous materials doped with boron or nitrogen. Studies have shown that when using supported catalysts, a uniform dispersion of catalytic particles can be achieved, leading to improved catalyst activity and durability. Indeed, when boron-doped carbon materials were used as catalysts for synthesizing ammonia, a decrease in activation energy was observed, as depicted in **Figure 9** [108].

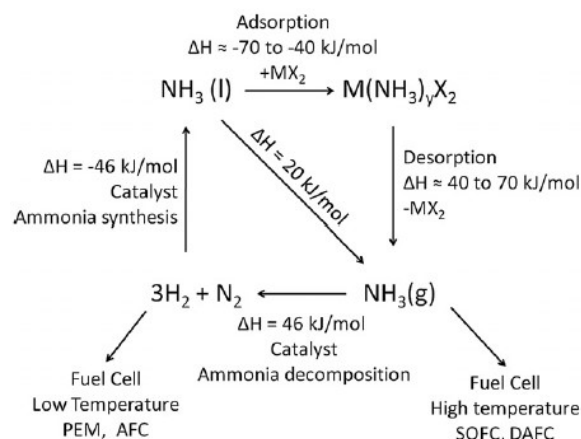


Figure 9. The life-cycle of hydrogen stored as ammonia in metal ammines, $\text{M}(\text{NH}_3)_y\text{X}_2$ [107].

Research on nanostructuring previously used Fe-based catalysts has demonstrated improvements in efficiency and long-term stability during operation. Moreover, introducing Cs into Fe catalysts has been shown to increase the rate of ammonia production, as depicted in **Figure 10** [110].

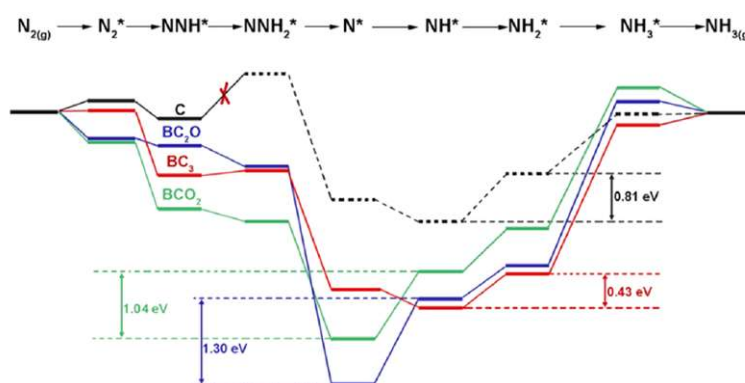


Figure 10. Free-energy diagrams of Boron-doped carbon samples for electrochemical Nitrogen Reduction Reaction (NRR) [108].

In addition to carbon-based supports, research on catalysts using various supports is also underway. One such study aimed to enhance stability using a catalyst supported on MgO for Cs/Ru alloy, comparing the catalytic activity over 680 h of operation. It was observed that while the catalyst exhibited consistent activity at an initial temperature of 325 °C for 150 h, the activity decreased at higher temperatures, maintaining only 42% of its initial activity after 680 h. Therefore, the development of

long-term active catalysts for ammonia production as energy carriers is crucial. Structural changes in the catalyst over time are shown in **Figure 11** [111].

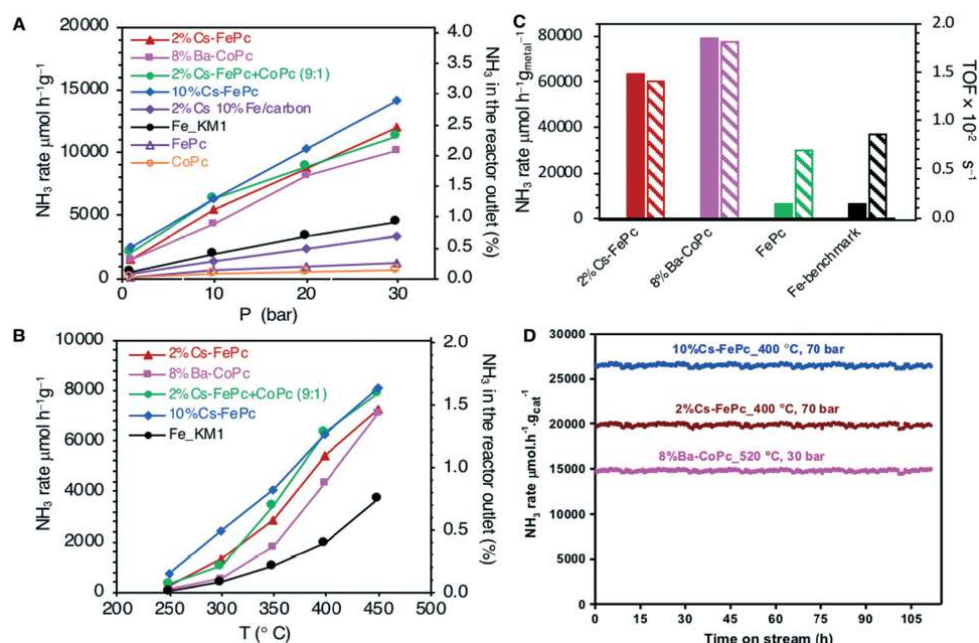


Figure 11. Structural changes in the catalyst over time for the ammonia synthesis reaction. (A) Pressure effect at 400 °C; (B) Temperature effect at 1 MPa; (C) Specific at 400 °C and 3 MPa; (D) Time dependence of the catalytic activities for stability testing in the range of 400–520 °C and 3–7 MPa [110].

Research has also been conducted on Ni-based catalysts, such as Ni₂Mg₃Al₂-HT, which demonstrated the highest NH₃ conversion rate and H₂ productivity at 500 °C. The ammonia conversion rate is shown in **Figure 12**. The structural characteristics of the catalyst significantly influence its activity, with parameters such as particle size, dispersion, crystalline structure, surface area, acidity, and thermal stability playing important roles. Optimization of structural characteristics enhances catalyst activity; for example, smaller particle size, higher dispersion, and acidity lead to increased catalytic activity, while higher thermal stability extends catalyst lifespan [112].

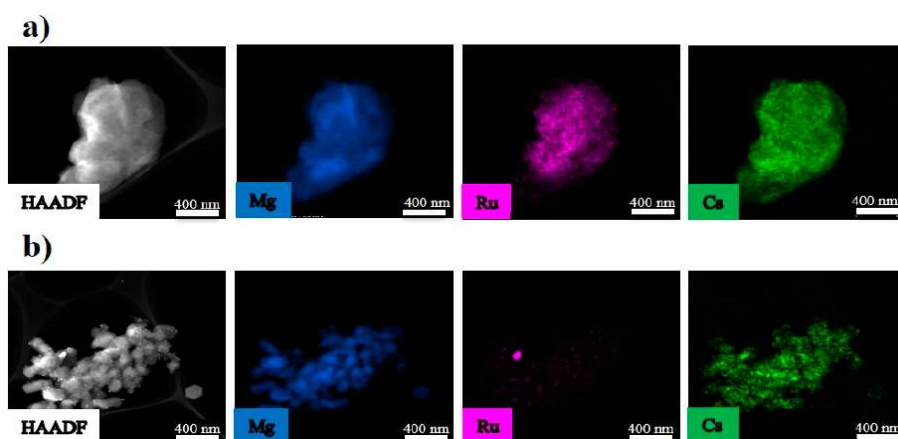


Figure 12. HAADF-STEM images with elemental mapping for Mg, Ru, and Cs: (a) as-synthesized catalyst; (b) after a time on stream of 680 h [111].

Research focusing on the durability of catalysts has proposed the use of pellet-shaped catalysts instead of powdered forms. By synthesizing highly durable Ru/La-Al₂O₃ pellet catalysts and designing catalyst reactors accordingly, a high catalyst activity and stability of 83.6% for reforming efficiency were achieved (**Figure 13**). It was confirmed that there was almost no CO₂ emission during the reaction process, introducing an environmentally friendly ammonia synthesis process [113].

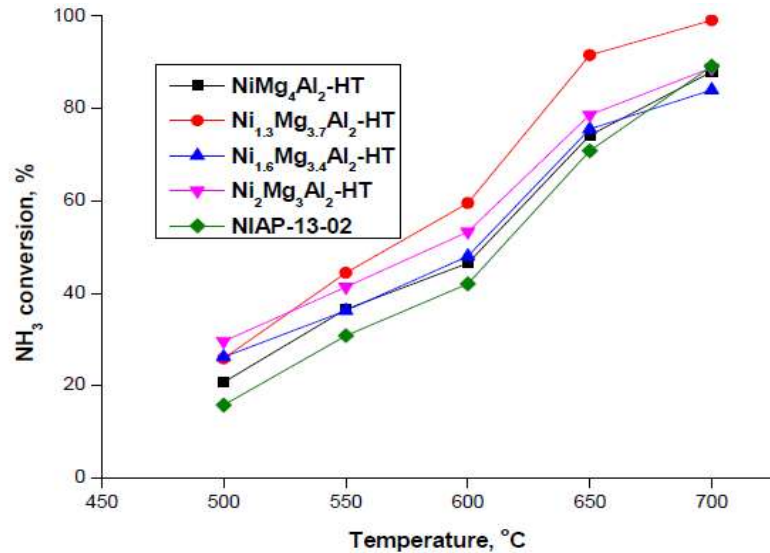


Figure 13. The influence of the reaction temperature on NH₃ conversion over Ni_xMg_yAl₂-HT catalysts [112].

Such reactors are capable of reforming processes for systems ranging from 10 kW to 10 MW for ammonia, showing significant potential for reducing CO₂ emissions. Ultimately, an investigation and analysis of the technical and economic feasibility of ammonia reforming for hydrogen production have been reported, showing the possibility of obtaining hydrogen at relatively similar prices to conventional production pathways (fossil fuels), as shown in **Figure 14** [112]. Various catalysts for ammonia synthesis are summarized in **Table 4** [114–123].

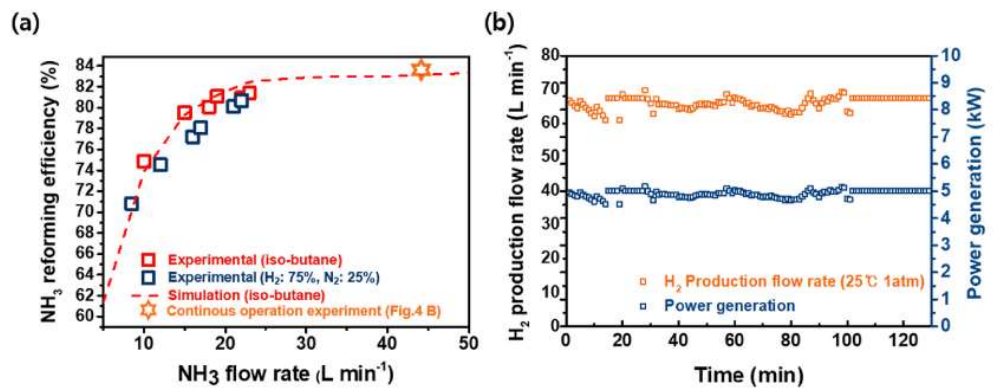


Figure 14. (a) NH₃ reformer efficiency over NH₃ flowrate using iso-butane and a product mixed gas of the system (H₂: 75%, N₂: 25%) as heat sources; (b) H₂ production flow and power generation (fuel cell equivalent) of the operated system continuously over 2 h [113].

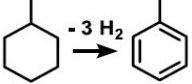
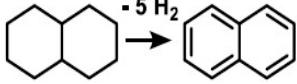
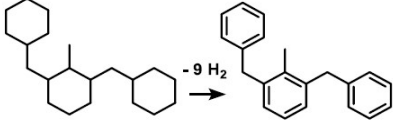
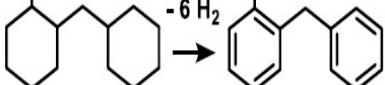
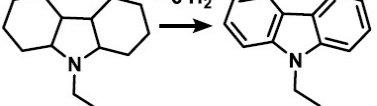
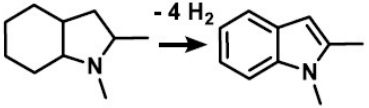
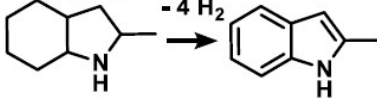
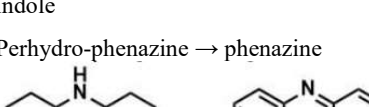
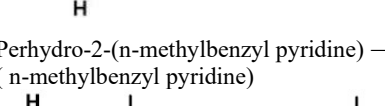
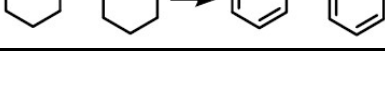
Table 4. Comparison of catalytic performance of reported Ammonia catalysts [114–123].

Catalyst	T(K)	Electrochemical Surface Area (m ² /g)	Cycle(hour)	Conversion (%)	H ₂ production rate(ml/min)
PtCO	473–573	74.48	30	N/A	N/A
Pt/C	823–973	74.7	30	N/A	N/A
Ir/C	353	85	24	N/A	N/A
Rh/C	353	67	24	N/A	N/A
Pt-NiO/C	298	7.2	500	N/A	N/A
NiMg ₄ Al ₂ -HT	773	N/A	5	20.7	16.6
Ni ₂ Mg ₃ Al ₂ -HT	773	N/A	5	29.6	23.8
Ni _{0.6} Mg _{0.3} Al _{0.6} O _n	773	N/A	5	42	14.1
Ru-Cs/MIL	673	N/A	10	98	25
Co/CNT	723	N/A	2	30	0.02
Cs ₂ O/Ru/Pr ₆ O ₁₁	623	N/A	75	45	10
Cs-Ru/graphene	723	N/A	4	85.8	N/A
Fe/CNT	873	N/A	4	51.3	N/A
CoFe ₅ /CNT	873	N/A	17	24	36
Ru/CNT	573	N/A	2	95.69	50

2.3. Liquid organic hydrogen carrier

In recent research and development fields, there has been attention drawn to the technology of synthesizing and storing hydrogen in the form of liquid organic molecules due to its relatively low cost and compatibility with existing fuel transportation infrastructure. Among various liquid compound-based hydrogen storage technologies, liquid organic compounds containing C-C double bonds have been extensively researched for their ability to store and transport large amounts of hydrogen at ambient pressure. These liquid organic compound-based hydrogen carriers are referred to as Liquid Organic Hydrogen Carriers (LOHC) [124]. LOHCs have several advantages: 1) They possess a high hydrogen storage capacity of approximately 7 wt%; 2) hydrogenation/dehydrogenation reactions occur reversibly under certain conditions; and 3) they are similar to gasoline and can utilize existing fossil fuel storage and transportation infrastructure without significant initial investment costs [123–127]. LOHCs allow for the repeated binding and release of hydrogen through chemical reactions without performance degradation. Therefore, optimization studies for LOHC-based hydrogen storage and transportation systems are actively conducted worldwide, and demonstration projects are underway to integrate LOHC systems with existing hydrogen infrastructure. However, continuous research and development efforts are needed due to the relatively low hydrogen density and availability compared to other hydrogen storage compounds (such as methanol and ammonia) [124,128–135]. Various LOHCs based on substances including benzene and toluene have been researched, and their characteristics are summarized in **Table 5** [126].

Table 5. Typical examples of potential LOHCs and their physicochemical properties [136].

LOHC System	H ₂ Capacity	Enthalpy (kJ/mol)	Melting Point (K)		Boiling Point (K)		Flash Point (K)	
	(wt.%)		H ₂ -Rich	H ₂ -Lean	H ₂ -Rich	H ₂ -Lean	H ₂ -Rich	H ₂ -Lean
Methylcyclohexane → Toluene 	6.2	68.3	147	178	378	384	270	279
Decalin → Naphthalene 	7.3	63.9	236	352	462	491	330	353
Perhydro-dibenzyl toluene → dibenzyl toluene Perhydro-benzyl 	6.2	65.4	N/A	239	N/A	671	N/A	463
toluene → benzyl toluene 	6.2	63.5	N/A	243	443	553	N/A	N/A
Dodecahydro-N-ethyl carbazole → N-ethyl carbazole 	5.8	50.6	188	343	N/A	439	N/A	459
1-methylperhydro indole → 1-methyl indole 	5.8	51.9	N/A	368	453	511	333	383
2-methylperhydro indole → 2-methyl indole 	5.8	N/A	N/A	333	451	545	331	414
1,2-perhydrodimethyl indole → 1,2 dimethyl indole 	5.23	N/A	<258	328	>533.5	533.5	>503	>503
Perhydro-phenazine → phenazine 	7.2	N/A	N/A	447-450	N/A	630.2	N/A	433.3
Perhydro-2-(n-methylbenzyl pyridine) → 2-(n-methylbenzyl pyridine) 	6.15	67.3	253.7	222.9	566	564	N/A	N/A

Various catalysts are being researched to enhance the hydrogen density of LOHCs and facilitate hydrogen adsorption-desorption reversible reactions. Metal-based catalysts such as Pt, Ru, Pd, and Ni are primarily used, and typically, inorganic

oxides such as Ti and Si are used as supports. Studies using Pt catalysts supported by γ -Al₂O₃ and TiO₂ have been conducted, revealing that γ -Al₂O₃ enhances the dispersion of highly nanosized Pt catalyst particles. Additionally, sulfurization improves hydrogen desorption reactions, with desorption rates of 97% and 87% reported for γ -Al₂O₃ and TiO₂ as support materials, respectively. Because the addition of sulfur seems to enhance the catalyst activity, leading to an extension of the fast dehydrogenation period. The structure and hydrogen desorption of these materials are shown in **Figures 15** and **16** [137].

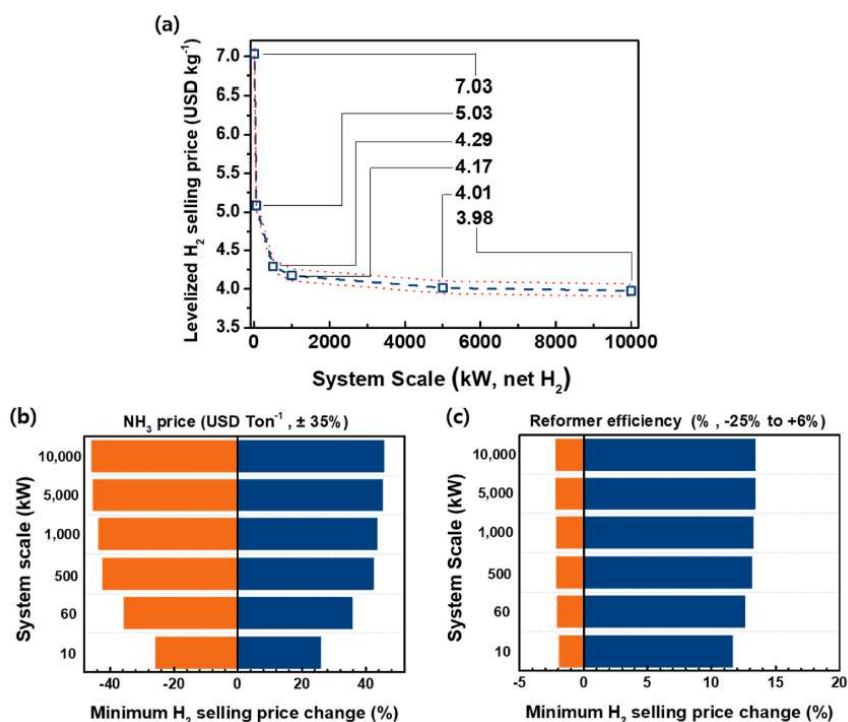


Figure 15. (a) The scale-up effect on minimum hydrogen selling price (MHSP). The error bars represent the average values of sensitivity parameter. Sensitivity analysis for 10 kW to 10 MW systems for parameters; (b) ammonia bulk price; and (c) reformer efficiency variation around a given data point [113].

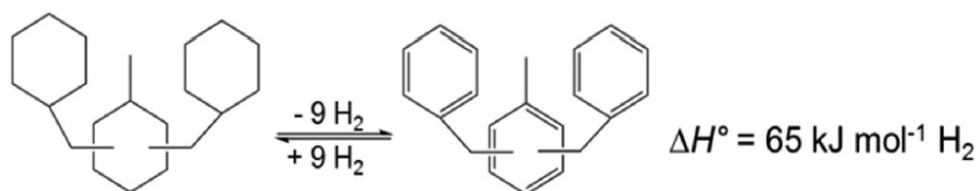


Figure 16. Reversible Dehydrogenation and Hydrogenation Scheme of the Perhydro Dibenzyltoluene/Dibenzyltoluene LOHC System [137].

Research on Pd catalysts supported by Al₂O₃ supports, specifically on Pd/a-Al₂O₃, investigated the coking of the catalyst due to hydrogen adsorption-desorption reactions with Methylcyclohexane (MCH)-based LOHCs. Under varying Ar flow conditions, two sizes of catalysts (6 nm and 15 nm) were compared, showing that smaller Pd nanoparticles (6 nm) decomposed after generating the Pd₆C phase and carbon deposition due to carbon separation, while larger Pd nano-particles (15 nm in diameter) coexisted

with two Pd carbide phases, Pd₆C and Pd_xC, upon exposure to MCH, followed by carbonaceous precipitation and carbide decomposition (**Figure 17**). Consequently, it indicates that catalysts may exist in various carbide forms with different carbon contents under LOHC dehydrogenation conditions, and structural changes in catalyst nanoparticles are highly reversible. Other types and characteristics of LOHCs and catalysts are summarized in **Table 6** [124,131–132,135–136,138–146].

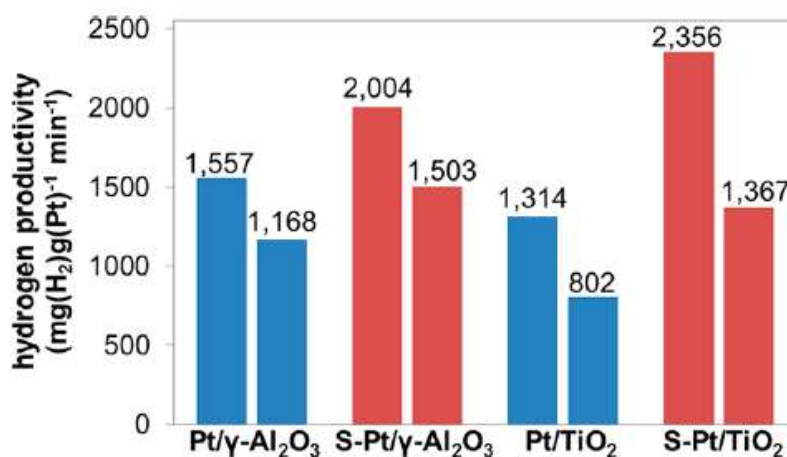


Figure 17. Hydrogen productivities normalized to metal dispersion (left column of each catalyst) in comparison to total Pt amount (right column of each catalyst) of the four catalysts [137].

Table 6. Comparison of catalytic performance of reported LOHC catalysts [124,131–132,135–136,138–146].

LOHCs	T (K)	Capacity (wt%)	Enthalpy (kJ/molH ₂)	Conversion (%)	Catalysts	Yield (%)
N-ethylcarbazole	543	5.8	50.6	90	Ru	85
					Ru/TiO ₂	95
					Ni	86.2
					Pd/SiO ₂ -TiO(OH) ₂	98.72
MCH-Toluene	593	6.2	68.3	95	Pd-Pt/SiO ₂	91.4
					Pd/SiO ₂	85.4
					Pt	90.8
Naphthalene	553	7.3	63.9	99	Pt	97.6
					Pd	73.15
Dibenzyl toluene	583	6.2	65.4	97	Ni/AlSiO	85
					Pt/Al ₂ O ₃	92
Benzene	453–593	5	686	N/A	Pd-Pt/ SiO ₂	90.8
					Pd/SiO ₂	84.1

Additionally, a comparative analysis of the technology and economic prospects of hydrogenation systems using high-density storage technologies and liquid organic hydrogen carriers (primarily ammonia or methanol) for large-scale hydrogen storage was conducted. Through analysis of the main system components of each technology, it was found that the cost of conventional liquid hydrogen storage is more than twice that of gaseous storage methods and more than four times that of storage methods using LOHCs. Although ammonia and methanol are considered suitable for large-scale hydrogen transportation as they can utilize existing fossil fuel infrastructure, they have the drawback of consuming energy and capital for synthesis and decomposition

compared to LOHCs. The comparison of energy consumption and equipment costs for storage is shown in **Figure 18** [134].

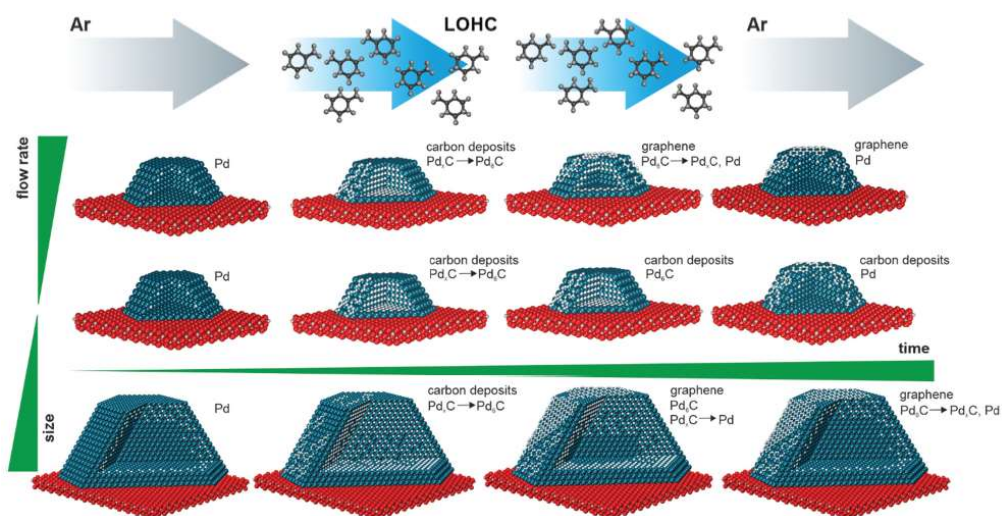


Figure 18. Schematic representation of the structural changes in the model Pd/Al₂O₃(0001) catalysts as a function of the flow rate of the reactant, size of supported Pd nanoparticles, and time of the catalyst on stream at 500 K [133].

LOHCs appear to be an economically producible technology for large-scale fixed hydrogen storage, but they must overcome the challenge of lower hydrogen storage density compared to other hydrogen carriers in **Figure 19**. The hydrogen storage densities of each material are compared in **Figure 20**. There is an urgent need for high-efficiency catalyst development, enhancement of durability for reversible reactions, and the development of synthesis processes from small to large-scale production for LOHCs.

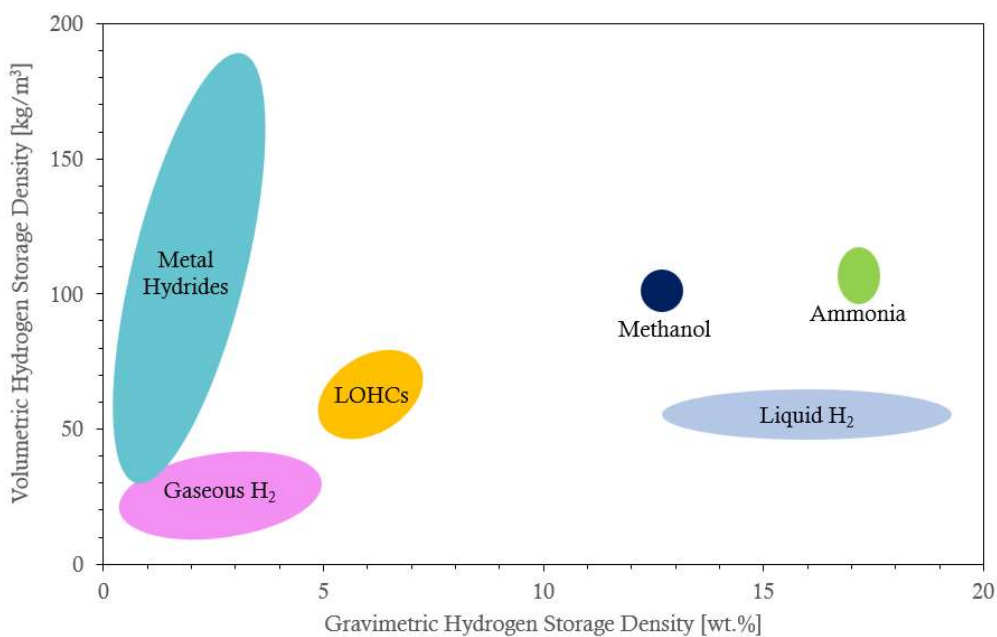


Figure 19. Hydrogen storage technologies and their energy densities [134].

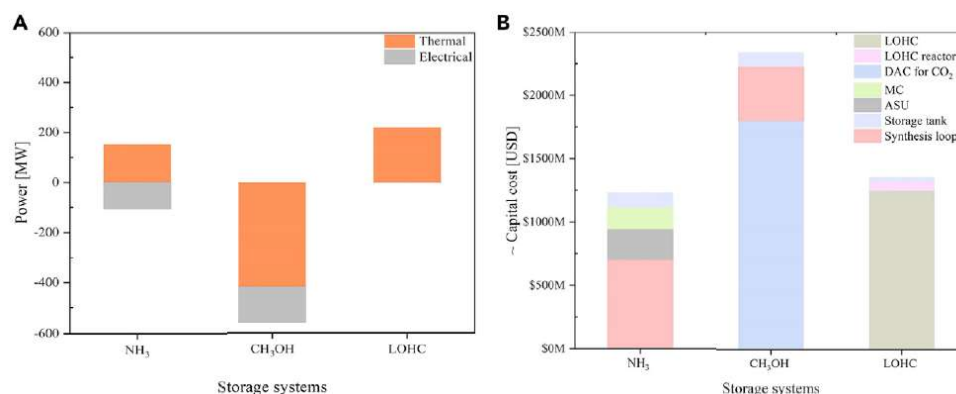


Figure 20. Estimation of power and capital cost for NH₃, CH₃OH, and LOHC hydrogenation plants [134].

3. Conclusions

The global shift from conventional fossil fuels to hydrogen as a clean energy alternative is gaining momentum, driven by growing environmental awareness and the imperative to reduce greenhouse gas emissions. However, the widespread adoption of hydrogen as a primary energy source faces significant challenges, particularly in the realm of storage and transportation infrastructure. Despite substantial research efforts directed towards developing viable storage solutions, such as porous carbon-based materials, metal-organic frameworks (MOFs), zeolites, and chemical hydrogen carriers, the scalability and efficiency of these options remain limited due to factors like low hydrogen capacity, high costs, and the lack of appropriate infrastructure.

As we strive to harness hydrogen's potential as a clean energy carrier, it becomes increasingly evident that technological innovation is essential to overcome these obstacles. Key considerations for hydrogen storage materials include their ability to maintain a liquid state during hydrogenation and dehydrogenation processes, operate at temperatures below 200 °C to minimize energy consumption, and ensure safety and environmental sustainability throughout their lifecycle. Chemical hydrogen carriers present a particularly promising avenue, offering lower energy losses, compatibility with existing infrastructure, and simpler handling compared to conventional storage methods. However, realizing their full potential hinges on advancing various technologies, including production, separation, catalyst development, and recovery, as well as refining dehydrogenation processes.

In essence, achieving a sustainable hydrogen economy requires a multifaceted approach that extends beyond mere technological advancements. It necessitates strategic collaborations between governments, industries, and research institutions to drive innovation, streamline regulatory frameworks, and invest in critical infrastructure. By continuously pushing the boundaries of scientific knowledge and engineering expertise, we can optimize catalysts and reaction systems, enabling the reversible, stable, and economically viable utilization of chemical hydrogen carriers for storage and transportation purposes. This holistic approach not only addresses the energy-intensive compression or liquefaction processes but also minimizes hydrogen loss, paving the way for a cleaner, greener future powered by hydrogen.

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References

1. Bellosta von Colbe J, Ares JR, Barale J, et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. *International Journal of Hydrogen Energy*. 2019; 44(15): 7780-7808. doi: 10.1016/j.ijhydene.2019.01.104
2. Bui M, Adjiman CS, Bardow A, et al. Carbon capture and storage (CCS): the way forward. *Energy & Environmental Science*. 2018; 11(5): 1062-1176. doi: 10.1039/c7ee02342a
3. Pérez-Fortes M, Schöneberger JC, Boulamanti A, et al. Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment. *Applied Energy*. 2016; 161: 718-732. doi: 10.1016/j.apenergy.2015.07.067
4. Klankermayer J, Wesselbaum S, Beydoun K, et al. Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry. *Angewandte Chemie International Edition*. 2016; 55(26): 7296-7343. doi: 10.1002/anie.201507458
5. Grinberg D, Elishav O, Bardow A, et al. Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis. *Angewandte Chemie International Edition*. 2016; 55(31): 8798-8805. doi: 10.1002/anie.201510618
6. Sang R, Wei Z, Hu Y, et al. Methyl formate as a hydrogen energy carrier. *Nature Catalysis*. 2023; 6(6): 543-550. doi: 10.1038/s41929-023-00959-8
7. Pfromm PH. Towards sustainable agriculture: Fossil-free ammonia. *Journal of Renewable and Sustainable Energy*. 2017; 9(3). doi: 10.1063/1.4985090
8. Philibert C. Producing ammonia and fertilizers: New opportunities from renewables. Available online: <https://cdi.mecon.gob.ar/bases/docelec/az3521.pdf> (accessed on 2 January 2024).
9. Hellman A, Honkala K, Dahl S, et al. Ammonia Synthesis: State of the Bellwether Reaction. In: Reedijk J, Poepelmeier K (editors). *Comprehensive Inorganic Chemistry II (Second Edition): From Elements to Applications*. Elsevier; 2013. pp. 459-474. doi: 10.1016/b978-0-08-097774-4.00725-7
10. Tunå P, Hulteberg C, Ahlgren S. Techno-economic assessment of nonfossil ammonia production. *Environmental Progress & Sustainable Energy*. 2013; 33(4): 1290-1297. doi: 10.1002/ep.11886
11. Noelker K, Ruether J. Low energy consumption ammonia production: baseline energy consumption, Options for energy optimization. Available online: https://ucpcdn.thyssenkrupp.com/_legacy/UCPthyssenkruppBAIS/assets.files/download_1/ammonia_2/low_energy_consumption_ammonia_production_2011_paper.pdf (accessed on 2 January 2024).
12. Cheddie D. Ammonia as a Hydrogen Source for Fuel Cells: A Review. In: Minic D (editor). *Hydrogen Energy - Challenges and Perspectives*. IntechOpen; 2012. doi: 10.5772/47759
13. Mukherjee S, Devaguptapu SV, Sviripa A, et al. Low-temperature ammonia decomposition catalysts for hydrogen generation. *Applied Catalysis B: Environmental*. 2018; 226: 162-181. doi: 10.1016/j.apcatb.2017.12.039
14. Giddey S, Badwal SPS, Munnings C, et al. Ammonia as a Renewable Energy Transportation Media. *ACS Sustainable Chemistry & Engineering*. 2017; 5(11): 10231-10239. doi: 10.1021/acssuschemeng.7b02219
15. Thomas G, Parks G. Potential Roles of Ammonia in a Hydrogen Economy: A Study of Issues Related to the Use Ammonia for On-Board Vehicular Hydrogen Storage. US Department of Energy; 2006.
16. David WIF, Makepeace JW, Callear SK, et al. Hydrogen Production from Ammonia Using Sodium Amide. *Journal of the American Chemical Society*. 2014; 136(38): 13082-13085. doi: 10.1021/ja5042836
17. Makepeace JW, Hunter HMA, Wood TJ, et al. Ammonia decomposition catalysis using lithium-calcium imide. *Faraday Discussions*. 2016; 188: 525-544. doi: 10.1039/c5fd00179j
18. Gianotti E, Taillades-Jacquín M, Rozière J, et al. High-Purity Hydrogen Generation via Dehydrogenation of Organic Carriers: A Review on the Catalytic Process. *ACS Catalysis*. 2018; 8(5): 4660-4680. doi: 10.1021/acscatal.7b04278
19. Felderhoff M, Weidenthaler C, von Helmolt R, et al. Hydrogen storage: the remaining scientific and technological challenges. *Physical Chemistry Chemical Physics*. 2007; 9(21): 2643. doi: 10.1039/b701563c
20. Nielsen TK, Besenbacher F, Jensen TR. Nanoconfined hydrides for energy storage. *Nanoscale*. 2011; 3(5): 2086. doi: 10.1039/c0nr00725k

21. Rihko-Struckmann LK, Peschel A, Hanke-Rauschenbach R, et al. Assessment of Methanol Synthesis Utilizing Exhaust CO₂ for Chemical Storage of Electrical Energy. *Industrial & Engineering Chemistry Research*. 2010; 49(21): 11073-11078. doi: 10.1021/ie100508w
22. Dowson G, Styring P. Conversion of Carbon Dioxide to Oxygenated Organics. In: Styring P, Quadrelli EA, Armstrong K (editors). *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Elsevier; 2015. pp. 141-159. doi: 10.1016/b978-0-444-62746-9.00009-8
23. Pontzen F, Liebner W, Gronemann V, et al. CO₂-based methanol and DME – Efficient technologies for industrial scale production. *Catalysis Today*. 2011; 171(1): 242-250. doi: 10.1016/j.cattod.2011.04.049
24. Palo DR, Dagle RA, Holladay JD. Methanol Steam Reforming for Hydrogen Production. *ChemInform*. 2007; 38(51). doi: 10.1002/chin.200751266
25. Goepfert A, Czaun M, Jones JP, et al. Recycling of carbon dioxide to methanol and derived products – closing the loop. *Chemical Society Reviews*. 2014; 43(23): 7995-8048. doi: 10.1039/c4cs00122b
26. Kappis K, Papavasiliou J, Avgouropoulos G. Methanol Reforming Processes for Fuel Cell Applications. *Energies*. 2021; 14(24): 8442. doi: 10.3390/en14248442
27. Andersson J, Krüger A, Grönkvist S. Methanol as a carrier of hydrogen and carbon in fossil-free production of direct reduced iron. *Energy Conversion and Management: X*. 2020; 7: 100051. doi: 10.1016/j.ecmx.2020.100051
28. Chatterjee S, Parsapur RK, Huang KW. Limitations of Ammonia as a Hydrogen Energy Carrier for the Transportation Sector. *ACS Energy Letters*. 2021; 6(12): 4390-4394. doi: 10.1021/acsenergylett.1c02189
29. Bilgili F, Magazzino C. The nexus between the transportation sector and sustainable development goals: Theoretical and practical implications. *Frontiers in Environmental Science*. 2022; 10. doi: 10.3389/fenvs.2022.1055537
30. Zhai L, Liu S, Xiang Z. Ammonia as a carbon-free hydrogen carrier for fuel cells: a perspective. *Industrial Chemistry & Materials*. 2023; 1(3): 332-342. doi: 10.1039/d3im00036b
31. Ma Y, Guan G, Phanthong P, et al. Steam reforming of methanol for hydrogen production over nanostructured wire-like molybdenum carbide catalyst. *International Journal of Hydrogen Energy*. 2014; 39(33): 18803-18811. doi: 10.1016/j.ijhydene.2014.09.062
32. Hou K, Hughes R. The kinetics of methane steam reforming over a Ni/ α -Al₂O₃ catalyst. *Chemical Engineering Journal*. 2001; 82(1-3): 311-328. doi: 10.1016/S1385-8947(00)00367-3
33. Jones SD, Hagelin-Weaver HE. Steam reforming of methanol over CeO₂- and ZrO₂-promoted Cu-ZnO catalysts supported on nanoparticle Al₂O₃. *Applied Catalysis B: Environmental*. 2009; 90(1-2): 195-204. doi: 10.1016/j.apcatb.2009.03.013
34. Smith C, Torrente-Murciano L. Guidance for targeted development of ammonia synthesis catalysts from a holistic process approach. *Chem Catalysis*. 2021; 1(6): 1163-1172. doi: 10.1016/j.checat.2021.09.015
35. Chang B, Li L, Shi D, et al. Metal-free boron carbonitride with tunable boron Lewis acid sites for enhanced nitrogen electroreduction to ammonia. *Applied Catalysis B: Environmental*. 2021; 283: 119622. doi: 10.1016/j.apcatb.2020.119622
36. Xie T. Performance analysis of ammonia decomposition endothermic membrane reactor heated by trough solar collector. *Energy Reports*. 2022; 8: 526-538.
37. Lim DK, Plymill AB, Paik H, et al. Solid Acid Electrochemical Cell for the Production of Hydrogen from Ammonia. *Joule*. 2020; 4(11): 2338-2347. doi: 10.1016/j.joule.2020.10.006
38. García A, Marín P, Ordóñez S. Hydrogenation of liquid organic hydrogen carriers: Process scale-up, economic analysis and optimization. *International Journal of Hydrogen Energy*. 2024; 52: 1113-1123. doi: 10.1016/j.ijhydene.2023.06.273
39. Andersson J, Grönkvist S. Large-scale storage of hydrogen. *International Journal of Hydrogen Energy*. 2019; 44(23): 11901-11919. doi: 10.1016/j.ijhydene.2019.03.063
40. Soloveichik G. Metal borohydrides as hydrogen storage materials. *Material Matters*. 2007; 2(11).
41. Liu J, Sun L, Yang J, et al. Ti–Mn hydrogen storage alloys: from properties to applications. *RSC Advances*. 2022; 12(55): 35744-35755. doi: 10.1039/d2ra07301c
42. Sahlberg M, Karlsson D, Zlotea C, et al. Superior hydrogen storage in high entropy alloys. *Scientific Reports*. 2016; 6(1). doi: 10.1038/srep36770
43. Schneemann A, White JL, Kang S, et al. Nanostructured Metal Hydrides for Hydrogen Storage. *Chemical Reviews*. 2018; 118(22): 10775-10839. doi: 10.1021/acs.chemrev.8b00313
44. Larpruenrudee P, Bennett NS, Gu Y, et al. Design optimization of a magnesium-based metal hydride hydrogen energy storage system. *Scientific Reports*. 2022; 12(1). doi: 10.1038/s41598-022-17120-3

45. Tarasov B, Arbuzov A, Mozhzhukhin S, et al. Metal Hydride Hydrogen Storage (Compression) Units Operating at Near-Atmospheric Pressure of the Feed H₂. *Inorganics*. 2023; 11(7): 290. doi: 10.3390/inorganics11070290
46. Kondo R, T. Hiroyuki T. Magnesium-Based Materials for Hydrogen Storage: Microstructural Properties. In: Gupta M (editor). *Magnesium - The Wonder Element for Engineering/Biomedical Applications*. IntechOpen; 2020. doi: 10.5772/intechopen.88679
47. Rabkin E, Skripnyuk V, Estrin Y. Ultrafine-Grained Magnesium Alloys for Hydrogen Storage Obtained by Severe Plastic Deformation. *Frontiers in Materials*. 2019; 6. doi: 10.3389/fmats.2019.00240
48. Yin F, Chang Y, Si T, et al. Structural and kinetic adjustments of Zr-based high-entropy alloys with Laves phases by substitution of Mg element. *Energy Advances*. 2023; 2(9): 1409-1418. doi: 10.1039/d3ya00243h
49. Li Z, Liu S, Pu Y, et al. Single-crystal ZrCo nanoparticle for advanced hydrogen and H-isotope storage. *Nature Communications*. 2023; 14(1): 7966. doi: 10.1038/s41467-023-43828-5
50. Lee YJ, Ha J, Choi SJ, et al. Decreasing Hydrogen Content within Zirconium Using Au and Pd Nanoparticles as Sacrificial Agents under Pressurized Water at High Temperature. *Materials*. 2023; 16(18): 6164. doi: 10.3390/ma16186164
51. Kamble A, Sharma P, Huot J. Effect of the Addition of 4 wt% Zr to BCC Solid Solution Ti₅₂V₁₂Cr₃₆ at Melting/Milling on Hydrogen Sorption Properties. *Frontiers in Materials*. 2022; 8. doi: 10.3389/fmats.2021.821126
52. Song J, Wang J, Hu X, et al. Activation and Disproportionation of Zr₂Fe Alloy as Hydrogen Storage Material. *Molecules*. 2019; 24(8): 1542. doi: 10.3390/molecules24081542
53. Hu WK, Gao XP, Kiros Y, et al. Zr-Based AB₂-Type Hydrogen Storage Alloys as Dual Catalysts of Gas-Diffusion Electrodes in an Alkaline Fuel Cell. *The Journal of Physical Chemistry B*. 2004; 108(26): 8756-8758. doi: 10.1021/jp0486548
54. Liang L, Wang F, Rong M, et al. Recent Advances on Preparation Method of Ti-Based Hydrogen Storage Alloy. *Journal of Materials Science and Chemical Engineering*. 2020; 8(12): 18-38. doi: 10.4236/msce.2020.812003
55. Loh SM, Grant DM, Walker GS, et al. Substitutional effect of Ti-based AB₂ hydrogen storage alloys: A density functional theory study. *International Journal of Hydrogen Energy*. 2023; 48(35): 13227-13235. doi: 10.1016/j.ijhydene.2022.12.083
56. Jangir M, Jain IP, Mirabile Gattia D. Effect of Ti-Based Additives on the Hydrogen Storage Properties of MgH₂: A Review. *Hydrogen*. 2023; 4(3): 523-541. doi: 10.3390/hydrogen4030034
57. Zhou C, Zhang J, Bowman RC, et al. Roles of Ti-Based Catalysts on Magnesium Hydride and Its Hydrogen Storage Properties. *Inorganics*. 2021; 9(5): 36. doi: 10.3390/inorganics9050036
58. Zholidayakova S, Gemma R, Uchida HH, et al. Mechanical Composition Control for Ti-Based Hydrogen Storage Alloys. *e-Journal of Surface Science and Nanotechnology*. 2018; 16(0): 298-301. doi: 10.1380/ejssnt.2018.298
59. Liu J, Xu J, Sleiman S, et al. Microstructure and hydrogen storage properties of Ti-V-Cr based BCC-type high entropy alloys. *International Journal of Hydrogen Energy*. 2021; 46(56): 28709-28718. doi: 10.1016/j.ijhydene.2021.06.137
60. Munekata Y, Washio K, Suda T, et al. Role of Annealing for Improving Hydrogen Storage Properties of Ti-Cr-V Alloy. *MRS Proceedings*. 2006; 971. doi: 10.1557/proc-0971-z07-21
61. Bellon Monsalve D, Ulate-Kolitsky E, Martínez-Amariz AD, et al. Effect of Zr₃Fe addition on hydrogen storage behaviour of Ti₂CrV alloys. *Heliyon*. 2023; 9(12): e22537. doi: 10.1016/j.heliyon.2023.e22537
62. Bouzidi A, Laversenne L, Nassif V, et al. Hydrogen Storage Properties of a New Ti-V-Cr-Zr-Nb High Entropy Alloy. *Hydrogen*. 2022; 3(2): 270-284. doi: 10.3390/hydrogen3020016
63. Yu X, Wu Z, Xia B, et al. Hydrogen storage in Ti-V-based body-centered-cubic phase alloys. *Journal of Materials Research*. 2003; 18(11): 2533-2536. doi: 10.1557/jmr.2003.0352
64. Mohammed Abdul J, Hearth Chown L, Kolawole Odusote J, et al. Hydrogen Storage Characteristics and Corrosion Behavior of Ti₂₄V₄₀Cr₃₄Fe₂ Alloy. *Batteries*. 2017; 3(4): 19. doi: 10.3390/batteries3020019
65. Li B, He L, Li J, et al. Ti-V-C-Based Alloy with a FCC Lattice Structure for Hydrogen Storage. *Molecules*. 2019; 24(3): 552. doi: 10.3390/molecules24030552
66. Yadav TP, Kumar A, Verma SK, et al. High-Entropy Alloys for Solid Hydrogen Storage: Potentials and Prospects. *Transactions of the Indian National Academy of Engineering*. 2022; 7(1): 147-156. doi: 10.1007/s41403-021-00316-w
67. Orłowski PA, Grochala W. Effect of Vanadium Catalysts on Hydrogen Evolution from NaBH₄. *Solids*. 2022; 3(2): 295-310. doi: 10.3390/solids3020021
68. Niaz S, Manzoor T, Pandith AH. Hydrogen storage: Materials, methods and perspectives. *Renewable and Sustainable Energy Reviews*. 2015; 50: 457-469. doi: 10.1016/j.rser.2015.05.011

69. Yadav M, Xu Q. Liquid-phase chemical hydrogen storage materials. *Energy & Environmental Science*. 2012; 5(12): 9698. doi: 10.1039/c2ee22937d
70. Kaur M, Pal K. Review on hydrogen storage materials and methods from an electrochemical viewpoint. *Journal of Energy Storage*. 2019; 23: 234-249. doi: 10.1016/j.est.2019.03.020
71. Ren J, Musyoka NM, Langmi HW, et al. Current research trends and perspectives on materials-based hydrogen storage solutions: A critical review. *International Journal of Hydrogen Energy*. 2017; 42(1): 289-311. doi: 10.1016/j.ijhydene.2016.11.195
72. Kumar S, Jain A, Ichikawa T, et al. Development of vanadium based hydrogen storage material: A review. *Renewable and Sustainable Energy Reviews*. 2017; 72: 791-800. doi: 10.1016/j.rser.2017.01.063
73. Marques F, Balcerzak M, Winkelmann F, et al. Review and outlook on high-entropy alloys for hydrogen storage. *Energy & Environmental Science*. 2021; 14(10): 5191-5227. doi: 10.1039/d1ee01543e
74. Rolo I, Costa VAF, Brito FP. Hydrogen-Based Energy Systems: Current Technology Development Status, Opportunities and Challenges. *Energies*. 2023; 17(1): 180. doi: 10.3390/en17010180
75. Badea IC, Şerban BA, Anasiei I, et al. The Energy Storage Technology Revolution to Achieve Climate Neutrality. *Energies*. 2023; 17(1): 140. doi: 10.3390/en17010140
76. Grigorova E, Markov P, Tsyntsarski B, et al. Hydrogen Storage Properties of Ball Milled MgH₂ with Additives- Ni, V and Activated Carbons Obtained from Different By-Products. *Materials*. 2023; 16(20): 6823. doi: 10.3390/ma16206823
77. Ahad M, Bhuiyan M, Sakib A, et al. An Overview of Challenges for the Future of Hydrogen. *Materials*. 2023; 16(20): 6680. doi: 10.3390/ma16206680
78. Habib AKMA, Sakib AN, Mona ZT, et al. Hydrogen-Assisted Aging Applied to Storage and Sealing Materials: A Comprehensive Review. *Materials*. 2023; 16(20): 6689. doi: 10.3390/ma16206689
79. Román-Sedano AM, Campillo B, Villalobos JC, et al. Hydrogen Diffusion in Nickel Superalloys: Electrochemical Permeation Study and Computational AI Predictive Modeling. *Materials*. 2023; 16(20): 6622. doi: 10.3390/ma16206622
80. Paskevicius M, Jepsen LH, Schouwink P, et al. Metal borohydrides and derivatives – synthesis, structure and properties. *Chemical Society Reviews*. 2017; 46(5): 1565-1634. doi: 10.1039/c6cs00705h
81. Schorn F, Breuer JL, Samsun RC, et al. Methanol as a renewable energy carrier: An assessment of production and transportation costs for selected global locations. *Advances in Applied Energy*. 2021; 3: 100050. doi: 10.1016/j.adapen.2021.100050
82. Baxter J, Bian Z, Chen G, et al. Nanoscale design to enable the revolution in renewable energy. *Energy & Environmental Science*. 2009; 2(6): 559. doi: 10.1039/b821698c
83. Gondal IA. Offshore renewable energy resources and their potential in a green hydrogen supply chain through power-to-gas. *Sustainable Energy & Fuels*. 2019; 3(6): 1468-1489. doi: 10.1039/c8se00544c
84. Sartbaeva A, Kuznetsov VL, Wells SA, et al. Hydrogen nexus in a sustainable energy future. *Energy & Environmental Science*. 2008; 1(1): 79. doi: 10.1039/b810104n
85. Mazloomi K, Gomes C. Hydrogen as an energy carrier: Prospects and challenges. *Renewable and Sustainable Energy Reviews*. 2012; 16(5): 3024-3033. doi: 10.1016/j.rser.2012.02.028
86. Züttel A, Remhof A, Borgschulte A, et al. Hydrogen: the future energy carrier. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2010; 368(1923): 3329-3342. doi: 10.1098/rsta.2010.0113
87. Eppinger J, Huang K. Formic acid as a hydrogen energy carrier. *ACS Energy Letters*. 2017; 2(1): 188-195. doi: 10.1021/acsenenergylett.6b00574
88. Lai Q, Sun Y, Wang T, et al. How to Design Hydrogen Storage Materials? Fundamentals, Synthesis, and Storage Tanks. *Advanced Sustainable Systems*. 2019; 3(9). doi: 10.1002/adsu.201900043
89. Behrens M, Marc A. Methanol steam reforming. In: Guenzi L, Erdöhelyi A (editors). *Catalysis for Alternative Energy Generation*. Springer; 2012. pp. 175-235. doi:10.1007/978-1-4614-0344-9_5
90. Özcan O, Ayşe N. Thermodynamic analysis of methanol steam reforming to produce hydrogen for HT-PEMFC: an optimization study. *International Journal of Hydrogen Energy*. 2019; 44(27): 14117-14126. doi: 10.1016/j.ijhydene.2018.12.211
91. Richards N, Needels J, Erickson P. Autothermal-reformation enhancement using a stratified-catalyst technique. *International Journal of Hydrogen Energy*. 2017; 42(41): 25914-25923. doi: 10.1016/j.ijhydene.2017.08.050
92. Ahmed AA, Al Labadidi M, Hamada AT, et al. Design and Utilization of a Direct Methanol Fuel Cell. *Membranes*. 2022;

- 12(12): 1266. doi: 10.3390/membranes12121266
93. Cheng Z, Zhou W, Lan G, et al. High-performance Cu/ZnO/Al₂O₃ catalysts for methanol steam reforming with enhanced Cu-ZnO synergy effect via magnesium assisted strategy. *Journal of Energy Chemistry*. 2021; 63: 550-557. doi: 10.1016/j.jechem.2021.08.025
94. Jin Q, Meng X, Wu P, et al. Methanol steam reforming for hydrogen production over NiTiO₃ nanocatalyst with hierarchical porous structure. *RSC Advances*. 2023; 13(24): 16342-16351. doi: 10.1039/d3ra02891g
95. Lawes N, Gow IE, Smith LR, et al. Methanol synthesis from CO₂ and H₂ using supported Pd alloy catalysts. *Faraday Discussions*. 2023; 242: 193-211. doi: 10.1039/d2fd00119e
96. Mansor M, Timmiati SN, Wong WY, et al. NiPd Supported on Mesostructured Silica Nanoparticle as Efficient Anode Electrocatalyst for Methanol Electrooxidation in Alkaline Media. *Catalysts*. 2020; 10(11): 1235. doi: 10.3390/catal10111235
97. Kang Y, Wang W, Pu Y, et al. An effective Pd-NiO_x-P composite catalyst for glycerol electrooxidation: Co-existed phosphorus and nickel oxide to enhance performance of Pd. *Chemical Engineering Journal*. 2017; 308: 419-427. doi: 10.1016/j.cej.2016.09.087
98. De Rogatis L, Montini T, Cognigni A, et al. Methane partial oxidation on NiCu-based catalysts. *Catalysis Today*. 2009; 145(1-2): 176-185. doi: 10.1016/j.cattod.2008.04.019
99. Lu J, Li X, He S, et al. Hydrogen production via methanol steam reforming over Ni-based catalysts: Influences of Lanthanum (La) addition and supports. *International Journal of Hydrogen Energy*. 2017; 42(6): 3647-3657. doi: 10.1016/j.ijhydene.2016.08.165
100. Pérez-Hernández R, Avendaño AD, Rubio E, et al. Hydrogen Production by Methanol Steam Reforming Over Pd/ZrO₂-TiO₂ Catalysts. *Topics in Catalysis*. 2011; 54(8-9): 572-578. doi: 10.1007/s11244-011-9622-0
101. Abraham BG, Bhaskaran R, Chetty R. Electrodeposited Bimetallic (PtPd, PtRu, PtSn) Catalysts on Titanium Support for Methanol Oxidation in Direct Methanol Fuel Cells. *Journal of The Electrochemical Society*. 2020; 167(2): 024512. doi: 10.1149/1945-7111/ab6a7d
102. Tahay P, Khani Y, Jabari M, et al. Highly porous monolith/TiO₂ supported Cu, Cu-Ni, Ru, and Pt catalysts in methanol steam reforming process for H₂ generation. *Applied Catalysis A: General*. 2018; 554: 44-53. doi: 10.1016/j.apcata.2018.01.022
103. Wang T, Zhao Y, Setzler BP, et al. A high-performance 75 W direct ammonia fuel cell stack. *Cell Reports Physical Science*. 2022; 3(4): 100829. doi: 10.1016/j.xcrp.2022.100829
104. Pawelczyk E, Łukasik N, Wysocka I, et al. Recent Progress on Hydrogen Storage and Production Using Chemical Hydrogen Carriers. *Energies*. 2022; 15(14): 4964. doi: 10.3390/en15144964
105. Oh S, Oh MJ, Hong J, et al. A comprehensive investigation of direct ammonia-fueled thin-film solid-oxide fuel cells: Performance, limitation, and prospects. *iScience*. 2022; 25(9): 105009. doi: 10.1016/j.isci.2022.105009
106. Hasan MH, Mahlia TMI, Mofijur M, et al. A Comprehensive Review on the Recent Development of Ammonia as a Renewable Energy Carrier. *Energies*. 2021; 14(13): 3732. doi: 10.3390/en14133732
107. Klerke A, Christensen CH, Nørskov JK, et al. Ammonia for hydrogen storage: challenges and opportunities. *Journal of Materials Chemistry*. 2008; 18(20): 2304. doi: 10.1039/b720020j
108. Lu H, Fengshou Y, Raveendran S. Carbon-Based Catalysts for Selective Electrochemical Nitrogen-to-Ammonia Conversion. *ACS Sustainable Chemistry & Engineering*. 2021, 9(23): 7687-7703. Doi: doi.org/10.1021/acssuschemeng.1c00575
109. Jang JH, Park SY, Youn DH, et al. Recent Advances in Electrocatalysts for Ammonia Oxidation Reaction. *Catalysts*. 2023; 13(5): 803. doi: 10.3390/catal13050803
110. Morlanés N, Almaksoud W, Rai RK, et al. Development of catalysts for ammonia synthesis based on metal phthalocyanine materials. *Catalysis Science & Technology*. 2020; 10(3): 844-852. doi: 10.1039/c9cy02326g
111. Javaid R, Nanba T. Stability of Cs/Ru/MgO Catalyst for Ammonia Synthesis as a Hydrogen and Energy Carrier. *Energies*. 2022; 15(10): 3506. doi: 10.3390/en15103506
112. Fedorova ZA, Borisov VA, Pakharukova VP, et al. Layered Double Hydroxide-Derived Ni-Mg-Al Catalysts for Ammonia Decomposition Process: Synthesis and Characterization. *Catalysts*. 2023; 13(4): 678. doi: 10.3390/catal13040678
113. Cha J, Park Y, Brigljević B, et al. An efficient process for sustainable and scalable hydrogen production from green ammonia. *Renewable and Sustainable Energy Reviews*. 2021; 152: 111562. doi: 10.1016/j.rser.2021.111562
114. Anaya-Castro F de J, Beltrán-Gastélum M, Morales Soto O, et al. Ultra-Low Pt Loading in PtCo Catalysts for the Hydrogen Oxidation Reaction: What Role Do Co Nanoparticles Play? *Nanomaterials*. 2021; 11(11): 3156. doi: 10.3390/nano11113156

115. Li ZF, Wang Y, Botte GG. Revisiting the electrochemical oxidation of ammonia on carbon-supported metal nanoparticle catalysts. *Electrochimica Acta*. 2017; 228: 351-360. doi: 10.1016/j.electacta.2017.01.020
116. Kang Y, Wang W, Li J, et al. A Highly Efficient Pt-NiO/C Electrocatalyst for Ammonia Electro-Oxidation. *Journal of The Electrochemical Society*. 2017; 164(9): F958-F965. doi: 10.1149/2.1051709jes
117. Li J, Wang W, Chen W, et al. Sub-nm ruthenium cluster as an efficient and robust catalyst for decomposition and synthesis of ammonia: Break the “size shackles.” *Nano Research*. 2018; 11(9): 4774-4785. doi: 10.1007/s12274-018-2062-4
118. Zhang H, Alhamed YA, Al-Zahrani A, et al. Tuning catalytic performances of cobalt catalysts for clean hydrogen generation via variation of the type of carbon support and catalyst post-treatment temperature. *International Journal of Hydrogen Energy*. 2014; 39(31): 17573-17582. doi: 10.1016/j.ijhydene.2014.07.183
119. Nagaoka K, Eboshi T, Abe N, et al. Influence of basic dopants on the activity of Ru/Pr₆O₁₁ for hydrogen production by ammonia decomposition. *International Journal of Hydrogen Energy*. 2014; 39(35): 20731-20735. doi: 10.1016/j.ijhydene.2014.07.142
120. Li G, Nagasawa H, Kanezashi M, et al. Graphene nanosheets supporting Ru nanoparticles with controlled nanoarchitectures form a high-performance catalyst for CO_x-free hydrogen production from ammonia. *Journal of Materials Chemistry A*. 2014; 2(24): 9185-9192. doi: 10.1039/c4ta01193g
121. Duan X, Qian G, Zhou X, et al. Tuning the size and shape of Fe nanoparticles on carbon nanofibers for catalytic ammonia decomposition. *Applied Catalysis B: Environmental*. 2011; 101(3-4): 189-196. doi: 10.1016/j.apcatb.2010.09.017
122. Zhang J, Müller JO, Zheng W, et al. Individual Fe-Co Alloy Nanoparticles on Carbon Nanotubes: Structural and Catalytic Properties. *Nano Letters*. 2008; 8(9): 2738-2743. doi: 10.1021/nl8011984
123. Yin SF, Zhang QH, Xu BQ, et al. Investigation on the catalysis of CO_x-free hydrogen generation from ammonia. *Journal of Catalysis*. 2004; 224(2): 384-396. doi: 10.1016/j.jcat.2004.03.008
124. Eblagon KM, Rentsch D, Friedrichs O, et al. Hydrogenation of 9-ethylcarbazole as a prototype of a liquid hydrogen carrier. *International Journal of Hydrogen Energy*. 2010; 35(20): 11609-11621. doi: 10.1016/j.ijhydene.2010.03.068
125. Bourane A, Elanany M, Pham TV, et al. An overview of organic liquid phase hydrogen carriers. *International Journal of Hydrogen Energy*. 2016; 41(48): 23075-23091. doi: 10.1016/j.ijhydene.2016.07.167
126. Pujadó P, Moser M. *Catalytic reforming: Handbook of petroleum processing*. Dordrecht. Springer Netherlands; 2006. pp. 217-237. doi: 10.1007/1-4020-2820-2_5
127. Crabtree RH. Nitrogen-Containing Liquid Organic Hydrogen Carriers: Progress and Prospects. *ACS Sustainable Chemistry & Engineering*. 2017; 5(6): 4491-4498. doi: 10.1021/acssuschemeng.7b00983
128. Brückner N, Obesser K, Bösmann A, et al. Evaluation of Industrially Applied Heat-Transfer Fluids as Liquid Organic Hydrogen Carrier Systems. *ChemSusChem*. 2013; 7(1): 229-235. doi: 10.1002/cssc.201300426
129. Preuster P, Papp C, Wasserscheid P. Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy. *Accounts of Chemical Research*. 2016; 50(1): 74-85. doi: 10.1021/acs.accounts.6b00474
130. Rüde T, Bösmann A, Preuster P, et al. Resilience of Liquid Organic Hydrogen Carrier Based Energy-Storage Systems. *Energy Technology*. 2017; 6(3): 529-539. doi: 10.1002/ente.201700446
131. Acharya D, Ng D, Xie Z. Recent Advances in Catalysts and Membranes for MCH Dehydrogenation: A Mini Review. *Membranes*. 2021; 11(12): 955. doi: 10.3390/membranes11120955
132. Le TH, Tran N, Lee HJ. Development of Liquid Organic Hydrogen Carriers for Hydrogen Storage and Transport. *International Journal of Molecular Sciences*. 2024; 25(2): 1359. doi: 10.3390/ijms25021359
133. Schuster R, Bertram M, Runge H, et al. Metastability of palladium carbide nanoparticles during hydrogen release from liquid organic hydrogen carriers. *Physical Chemistry Chemical Physics*. 2021; 23(2): 1371-1380. doi: 10.1039/d0cp05606e
134. Abdin Z, Tang C, Liu Y, et al. Large-scale stationary hydrogen storage via liquid organic hydrogen carriers. *iScience*. 2021; 24(9): 102966. doi: 10.1016/j.isci.2021.102966
135. Sun F, An Y, Lei L, et al. Identification of the starting reaction position in the hydrogenation of (N-ethyl)carbazole over Raney-Ni. *Journal of Energy Chemistry*. 2015; 24(2): 219-224. doi: 10.1016/S2095-4956(15)60304-7
136. Rao P, Yoon M. Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress. *Energies*. 2020; 13(22): 6040. doi: 10.3390/en13226040
137. Chen X, Gierlich CH, Schötz S, et al. Hydrogen Production Based on Liquid Organic Hydrogen Carriers through Sulfur Doped Platinum Catalysts Supported on TiO₂. *ACS Sustainable Chemistry & Engineering*. 2021; 9(19): 6561-6573. doi: 10.1021/acssuschemeng.0c09048

138. Niermann M, Beckendorff A, Kaltschmitt M, et al. Liquid Organic Hydrogen Carrier (LOHC) – Assessment based on chemical and economic properties. *International Journal of Hydrogen Energy*. 2019; 44(13): 6631-6654. doi: 10.1016/j.ijhydene.2019.01.199
139. Niermann M, Drünert S, Kaltschmitt M, et al. Liquid organic hydrogen carriers (LOHCs) – techno-economic analysis of LOHCs in a defined process chain. *Energy & Environmental Science*. 2019; 12(1): 290-307. doi: 10.1039/c8ee02700e
140. Tang C, Feng Z, Bai X. In situ preparation of Pd nanoparticles on N-doped graphitized carbon derived from ZIF-67 by nitrogen glow-discharge plasma for the catalytic dehydrogenation of dodecahydro-N-ethylcarbazole. *Fuel*. 2021; 302: 121186. doi: 10.1016/j.fuel.2021.121186
141. Yang J, Fan Y, Li ZL, et al. Bimetallic Pd-M (M = Pt, Ni, Cu, Co) nanoparticles catalysts with strong electrostatic metal-support interaction for hydrogenation of toluene and benzene. *Molecular Catalysis*. 2020; 492: 110992. doi: 10.1016/j.mcat.2020.110992
142. Yang Y, Lin X, Tang J, et al. Supported mesoporous Pt catalysts with excellent performance for toluene hydrogenation under low reaction pressure. *Molecular Catalysis*. 2022; 524: 112341. doi: 10.1016/j.mcat.2022.112341
143. Zhu L, Shan S, Petkov V, et al. Ruthenium–nickel–nickel hydroxide nanoparticles for room temperature catalytic hydrogenation. *Journal of Materials Chemistry A*. 2017; 5(17): 7869-7875. doi: 10.1039/c7ta01437f
144. Zhang M, Song Q, He Z, et al. Tuning the mesopore-acid-metal balance in Pd/HY for efficient deep hydrogenation saturation of naphthalene. *International Journal of Hydrogen Energy*. 2022; 47(48): 20881-20893. doi: 10.1016/j.ijhydene.2022.04.191
145. Ding Y, Dong Y, Zhang H, et al. A highly adaptable Ni catalyst for Liquid Organic Hydrogen Carriers hydrogenation. *International Journal of Hydrogen Energy*. 2021; 46(53): 27026-27036. doi: 10.1016/j.ijhydene.2021.05.196
146. Jorschick H, Preuster P, Dürr S, et al. Hydrogen storage using a hot pressure swing reactor. *Energy & Environmental Science*. 2017; 10(7): 1652-1659. doi: 10.1039/c7ee00476a