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Review Article

Dibenzyltoluene- based liquid organic hydrogen carrier systems: Recent advances, challenges and future perspectives

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ABSTRACT

This review provides a comprehensive overview of dibenzyltoluene (DBT)-based liquid organic hydrogen carrier (LOHC) systems, a promising technology for the safe, efficient, and scalable storage and transportation of hydrogen. Owing to their high thermal and chemical stability, low toxicity, and compatibility with existing energy infrastructure, DBT and its fully hydrogenated form (H_{18}-DBT) are among the most advanced candidates for industrial LOHC applications. Despite these advantages, several technical challenges remain, including high dehydrogenation temperatures (>300 °C), catalyst deactivation (coke formation and sintering), and slow molecular diffusion within porous supports. Recent progress in catalyst design — particularly through the development of bimetallic catalysts (e.g., Pd–Ni) and nanostructured supports — has significantly improved reaction efficiency and cycle stability. In addition, the integration of thermo-electrochemical hybrid approaches and process intensification strategies offers further potential for enhancing system performance. This review critically assesses the current state of DBT-based LOHC systems, highlights ongoing advancements, and identifies future research directions needed to overcome existing limitations and enable the commercial-scale deployment of this technology within a sustainable hydrogen economy.

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INTRODUCTION

The rapid advancement of technology, transportation, industry and artificial intelligence have considerably increased energy demand across various sectors. Data from the International Energy Agency (IEA), show that 81% of global energy production still relies on fossil fuels [1]. However, the rapid depletion of fossil fuel reserves, the continuous rise in energy consumption, and fluctuations in energy supply pose significant challenges to energy security. Moreover, the increase in greenhouse gas emissions resulting from fossil fuel use contributes to environmental threats such as global warming and climate change. In particular, global policies to reduce carbon emissions (such as the Paris Agreement) and sustainable energy targets necessitate the development of alternative energy sources [2]. In this context, while the proliferation of renewable energy sources (solar, wind, etc.) is an important development, the discontinuous nature of these sources (the sun shines at certain hours, the wind is variable) has created the need for energy storage. With its high bulk energy density (120 MJ/kg), zero carbon emissions at the point of use and compatibility with fuel cells, hydrogen is considered a key component of the energy infrastructure of the future. However, the safe, economical and efficient storage and transportation of hydrogen poses a significant barrier to large-scale deployment [3].

Hydrogen storage is critical for the efficient and safe utilization of hydrogen as an energy carrier. In this context, many hydrogen storage systems have been developed, such as compressed hydrogen storage (CH_2), liquid hydrogen storage (LH_2), metal hydrides, chemical hydrides, liquid organic hydrogen carriers (LOHCs) and carbon material hydrogen storage (CMH2) [4]. Among these, LOHCs stand out as an innovative technology that enables the chemical storage and transportation of hydrogen under atmospheric conditions. Compared to conventional systems (compressed hydrogen storage, liquid hydrogen storage, etc.), LOHCs chemically bind hydrogen in liquid organic compounds under atmospheric conditions, making it safe and easily transportable. One of the major advantages of LOHC technology is that it is compatible with existing fossil fuel infrastructure because it can be stored in conventional fuel tanks, transported via pipelines and easily integrated into industrial processes. In addition, LOHCs are non-explosive and non-volatile liquids, making them much safer than transporting hydrogen in liquid and compressed gas form. However, hydrogenation and dehydrogenation processes that require high temperatures and catalysts for efficient operation of LOHC systems are still under investigation. Current research focuses on developing catalysts that can operate at lower temperatures, consume less energy and have long lifetimes.

LOHC systems operate by hydrogenation (H_2 storage) and dehydrogenation (H_2 release) reactions of suitable organic compounds. The compounds used in these systems are in the liquid phase and show stable behaviour at atmospheric pressure and ambient temperatures. Many LOHC candidates (toluene/methylcyclohexane, N-ethylcarbazole/perhydro-NEC, dibenzyltoluene/perhydrodibenzyltoluene) have been investigated in the literature. Among these compounds, Dibenzyltoluene (DBT) and its fully hydrogenated form Perhydrodibenzyltoluene (H_{18}-DBT) stand out on an industrial scale with their superior properties such as high thermal and chemical stability, low toxicity and wide liquid phase working range. Notable advantages of the DBT system include high boiling point (~390 °C), low vapor pressure, low environmental risk and long-term availability. Furthermore, its long-standing industrial use as a heat transfer fluid supports the scalability of this system. However, technical challenges such as high dehydrogenation temperatures (>300 °C), slow molecular diffusion, and catalyst deactivation limit the efficiency of the system. Therefore, it is critical to develop more efficient and low-temperature catalysts specific to the DBT system [6,7].

Highlights

- DBT-based LOHC technology is a leading candidate for hydrogen storage.
- High dehydrogenation temperatures challenge system sustainability.
- Recent advances in catalyst and system design improve cycle stability.

This review offers a comprehensive examination of DBT-based LOHC systems, which have emerged as promising candidates owing to their high thermal and chemical stability, low toxicity, and compatibility with existing energy infrastructures. In particular, the study focuses on the structural properties of the catalysts developed for the DBT system, reaction performances, technical limitations encountered (e.g. high temperature requirements, sintering, coking) and current catalyst design strategies (bimetallic systems, mesoporous supports, thermo-electrochemical solutions). Thus, this review aims to technically assess the current status of DBT-based LOHC systems, analyze development trends and provide a guiding perspective for future research. The findings of this study are expected to contribute to the advancement of innovative technologies for the safe and sustainable storage and transportation of hydrogen.

FUNDAMENTALS OF LOHC TECHNOLOGY

LOHC systems operate by reversible hydrogenation (exothermic) and dehydrogenation (endothermic) reactions. Hydrogen-rich (H^{2+}) and hydrogen-poor (H^{2-}) states form a cyclic system in which hydrogen is stored and released using catalysts [8]. Hydrogenation is an exothermic reaction in which the organic compound is mixed with hydrogen in the reactor and this reaction is carried out under a certain temperature and pressure conditions under the influence of the catalyst. The products resulting from the hydrogenation reaction are called hydrogen carriers (Hx-LOHC) (Fig. 1). It is essentially a catalytic process using hydrogen to convert unsaturated bonds into saturated ones [9].

Hydrogenation typically occurs at 80-150°C and pressure 1-5 MPa, utilizing transition with the help of catalysts such as Pd, Pt or Ru [10,11]. In contrast, hydrogenation, dehydrogenation is an endothermic reaction in which, in the presence of a catalyst, hydrogen is extracted from Hx LOHCs in a dehydrogenation reactor [12]. Dehydrogenation takes place at 200-350°C and sub-atmospheric pressure (<1 MPa) with catalysts acting on hydrogen-rich LOHC compounds [13]. The process involves continuous absorption of heat from the outside due to the energy difference between the energy required for the dissociation of hydrogen atoms and the activation energy of C-H bonds. An efficient LOHC system should possess the following characteristics: i) high hydrogen storage capacity (>56kg/m3), ii) Long cycle stability with minimal degradation, iii) low melting point (<-30°C) and high boiling point (~300°C), iv) low energy demand for dehydrogenation, v) high hydrogen purity upon release, and vi) low toxicity and environmental compatibility during use and transport [9].

While early studies predominantly focused on simple aromatic compounds such as benzene and toluene, advancements in molecular design have led to the development of more structurally complex and efficient LOHC candidates, including DBT, N-ethylcarbazole (NEC), and naphthalene/decalin systems. Recent research indicates that the incorporation of heteroatoms—particularly nitrogen—into the molecular framework can reduce dehydrogenation enthalpy and enhance overall system performance [11]. As the field progressed, a diverse array of LOHC systems emerged, including toluene/methylcyclohexane (TOL/MCH), DBT/perhydro-DBT (DBT/H_{18}-DBT), CO_2/methanol, CO_2/formic acid, naphthalene/decalin, and NEV/dodecahydro-NEC [7, 14]. Among these, DBT-based systems have gained significant attention due to their high thermal stability, low vapor pressure, and proven industrial scalability as heat transfer fluids. Alongside DBT, the most extensively studied LOHC candidates in academic and industrial contexts are toluene/methylcyclohexane, NEC/dodecahydro-NEC, and naphthalene/decalin, as summarized in Table 1.

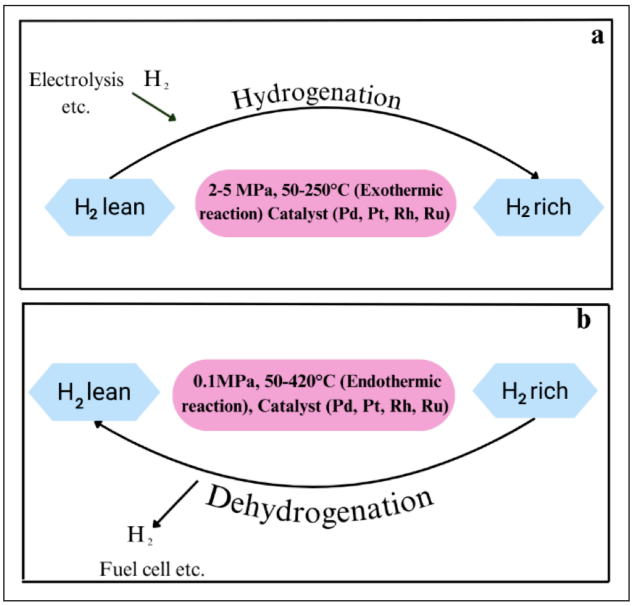

Figure 1. Schematic representation of the LOHC cycle hydrogenation **(a)** and dehydrogenation **(b)**.

DBT SYSTEMS

In the LOHC cycle, catalysts play a critical role for both yield and selectivity in the hydrogenation and dehydrogenation steps of the aromatic compound. An ideal LOHC catalyst is expected to i) ii) Provides high conversion efficiency at low temperatures, ii) Allows pure H_2 to be obtained during dehydrogenation, iii) Maintains its activity during long cycle life iv) Resistance to catalyst poisoning and sintering. The high energy consumption in LOHC technology, the difficulty of catalyst development in hydrogenation and dehydrogenation systems, and the decrease in hydrogen storage performance as the number of cycles increases limit industrial-scale commercialization [20,21]. Therefore, the design of catalysts that minimize energy requirements and offer high efficiency is critical. In addition, carbon-based supports and various carriers such as Al_2O_3 and zeolite are used to enhance the performance of the catalysts [11]. Since hydrogenation and dehydrogenation reactions are reversible in LOHC systems, catalysts with high hydrogenation activity generally exhibit high performance in the dehydrogenation step.

In recent years, several LOHC compounds including toluene and N-ethylcarbazole have been investigated. However, the low boiling points and toxic nature of compounds such as toluene and naphthalene present significant disadvantages. N-ethylcarbazole, for instance, has a melting point of 68 °C, which leads to solidification during the dehydrogenation process. Additionally, its high cost limits its feasibility for industrial-scale applications. To overcome these issues, DBT has emerged as a focal point in LOHC research. Dibenzyltoluene (H_0-DBT) is an organic compound classified among cycloalkanes and is extensively used as a heat transfer fluid in industrial applications. Upon hydrogenation, H_0-DBT is converted into its fully hydrogenated form, perhydrodibenzyltoluene (H_{18}-DBT). It is considered a non-toxic and non-flammable environmentally friendly compound.. DBT can store hydrogen up to 6.2 wt%, corresponding to an energy capacity of approximately 2.05 kWh/kg. The market price of DBT is around €4/kg, making it more expensive than

Table 1. Comparision of Liquid Organic Hydrogen Compounds

Systems	Hydrogen storage capacity (wt%)	Advantages	Challenges	References
Benzene-Cyclohexane	7.2	High hydrogen storage capacity, liquid at room temperature, well-studied system, high selectivity and conversion.	High toxicity and corrosiveness, high dehydrogenation temperature, low boiling and flash points	[15]
Toluene-Methylcyclohexane	6.2	High stability and low toxicity, liquid under atmospheric conditions, no CO_2 emissions during dehydrogenation, high flash point, low cost.	Requires high dehydrogenation temperature (300–400 °C), MCH is hazardous to the environment, MCH is in gas phase during dehydrogenation, necessitating hydrogen purification.	[7, 16]
Napthalene-Decalin	7.3	High boiling point minimizes evaporation losses.	Solid at room temperature, requires solvent, prone to side reactions, not suitable for transport and storage due to material properties, high melting point (~80 °C).	[6,7]
N-ethylcarbazole-Dode-N-ethylcarbazole	5.8	Hydrogen storage possible below 200 °C, high stability, low reaction temperatures.	Requires different catalysts for hydrogenation and dehydrogenation, solid at room temperature, H_{12}-NEC cracking during dehydrogenation, high cost.	[17]
Dibenzyltoluene-Perhydrodibenzyltoluene	6.2	Low melting point and high boiling point, long-standing use as heat transfer fluid demonstrates scalability.	High dehydrogenation temperature required, slow molecular diffusion of DBT in porous catalysts.	[18, 19]
CO2- Formic acid	4.4	Low dehydrogenation temperature, low energy consumption, low cost and abundant availability, low toxicity.	Lower hydrogen storage capacity (4.4 wt%) compared to other systems, CO_2 released during dehydrogenation must be captured and managed or reused.	[7]

toluene and benzene but more affordable than N-ethylcarbazole [22]. The benzyltoluene perhydrobenzyltoluene system is being used on an industrial scale for hydrogen storage as a liquid organic hydrogen carrier by Hydrogenious Technologies GmbH (Erlangen, Germany) [23].

Hydrogenation of DBT

Hydrogenation of DBT involves the addition of hydrogen molecules to its aromatic rings, converting it into its fully saturated form, perhydrodibenzyltoluene (H_{18}-DBT). The liquid state of DBT facilitates transportation and storage, while its hydrogen storage capacity is approximately 6.2 wt%. This exothermic reaction typically requires elevated hydrogen pressures (1–5 MPa) and moderate temperatures (150–200°C) to ensure high conversion and selectivity (Fig. 2). The hydrogenation reaction of the compound dibenzyltoluene (H0-DBT), i.e. its saturation with hydrogen (hydrogen charging), can be written as in Eq 1:

$$C_{21}H_{20}+8H_2 \rightarrow C_{21}H_{36} \quad (1)$$

The selection of suitable catalysts to carry out the hydrogenation reaction is important. The most widely used as catalysts are noble metals such as Pd, Pt and Ru, which provide high selectivity and activity. Initially, Ru, Pt or Ni based catalysts supported on alumina were reported as potential catalysts for the hydrogenation of DBT [24]. Various catalysts have been investigated to improve the efficiency of DBT hydrogenation (Table 2). Platinum-based catalysts (Pt/Al_2O_3) are the most extensively studied systems and demonstrate excellent performance across a range of conditions. For instance, the study by Shi et al. [25] revealed that 3% Pt/Al_2O_3, including H_2 and O_2 plasma-modified

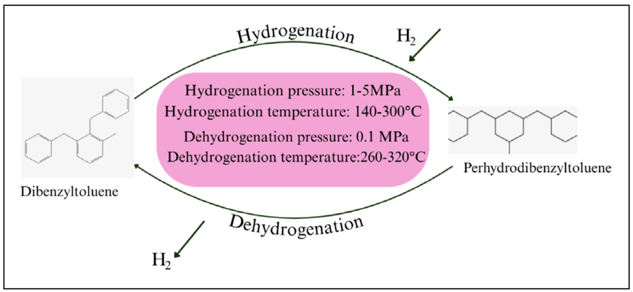

Figure 2. Hydrogenation and dehydrogenation cycles of LOHC compounds.

Table 2. Hydrogenation catalytic performance of some catalysts for DBT

LOHCs	Catalysts	T (°C)	P (MPa)	Conversion (%)	Selectivity (%)	References
DBT	0.3%Pt/Al_2O_3	270	30	100	100	[30]
	3%Pt/Al_2O_3	140	40	100	100	[25]
	3%Pt/Al_2O3-H_2 plasma	140	40	100	100	[25]
	3%Pt/Al_2O3-O_2 plasma	140	40	100	100	[25]
	5 wt. % Ru/Al_2O_3	170	5	-	100	[26]
	Raney-Ni	170	7	-	100	[31]
	Ni70/AlSiO-1/1	150	7	100	100	[32]
	0.3 wt% Pt/Al_2O_3	270	3	-	100	[33]
	0.3 wt. % Pt/Al_2O_3	230	3	100	-	[34]
	0.3 wt. % Pt/Al_2O_3	300	3	95	-	[35]
	13 wt. % Ni/Al_2O_3	200	4	100	-	[29]
BT	0.5 wt. % Ru/MgO	150	0.5	100	100	[27]
	5 wt. % Ru/Al_2O_3	150	0.5	% 99<	-	[36]

versions, achieved 100% conversion and selectivity at a relatively low temperature (140 °C) and high pressure (40 MPa) within just 15 minutes. This highlights the impact of catalyst pretreatment on reaction kinetics. Similarly, other studies using 0.3% Pt/Al_2O_3 at higher temperatures (230–300 °C) and moderate pressures (3 MPa) also reported conversion values close to 100%, although some lacked selectivity data. Nickel-based catalysts, such as Ni70/AlSiO and 13 wt.% Ni/Al_2O_3, provide a cost-effective alternative to noble metals. Despite being less active at low temperatures, these systems still achieved 100% conversion, albeit at slightly higher temperatures (150–200 °C) and pressures (4–7 MPa). Ruthenium-based catalysts also offer remarkable performance, particularly under milder conditions. For example, 5 wt.% Ru/Al_2O_3 [26] and 0.5 wt.% Ru/MgO [27] demonstrated nearly complete hydrogenation at only 150–170 °C and low pressures (0.5–5 MPa), with 100% selectivity. These results emphasize the high activity of Ru catalysts at lower energy requirements. Liu et al. [28] investigated the hydrogenation of DBT using Al_2O_3-supported catalysts containing 5 wt% of Pd, Pt, Ru, or Rh. The most active catalyst was found to be 5 wt% Rh/Al_2O_3, which achieved a turnover frequency (TOF) of 26.5 h^{-1} and a hydrogenation degree of 92.7% within 2 hours. Support materials also play a key role by influencing metal dispersion, hydrogen adsorption, and heat transfer. Porous supports like Al_2O_3, γ-Al_2O_3 and ZrO_2 are commonly used due to their thermal stability and surface area. In particular, highly acidic or mesoporous supports have been shown to enhance hydrogen diffusion and prevent aggregation of metal particles. In particular, highly acidic or mesoporous supports have been shown to enhance hydrogen diffusion and prevent aggregation of metal particles. These include slow diffusion within the large DBT molecule, metal sintering during prolonged operation, and catalyst deactivation due to impurities. To address these issues, recent research has focused on: i) bimetallic catalysts that balance activity and stability, ii) nano-structured supports that enhance mass transfer and iii) solvent-assisted hydrogenation methods that lower energy requirements [28, 29].

Dehydrogenation of DBT

Dehydrogenation of perhydrodibenzyltoluene (H_{18}-DBT) is a critical step in the LOHC cycle, where hydrogen is released through an endothermic catalytic process. This reaction typically occurs at temperatures ranging from 270 °C to 320 °C and pressures below 1 MPa (Fig. 2). DBT has a melting point of 34 °C and a boiling point of 390 °C, which helps minimize vapor losses due to hydrogen flow. Moreover, its low vapor pressure at room temperature enables the release of high-purity hydrogen. The main advantages of the DBT system include: (i) a high boiling point (~390 °C) and low vapor pressure, which minimize vapor losses and system inefficiencies, (ii) lower environmental and toxicity risks compared to nitrogen containing compounds like NEC, and (iii) its long-standing use as a heat transfer fluid, which demonstrates its scalability for industrial applications. However, the system also requires high dehydrogenation temperatures (>300 °C), and molecular diffusion in porous supports can be slow, limiting reaction kinetics. This endothermic reaction can be represented as Eq (2):

$C_{21}H_{36} \rightarrow C_{21}H_{20} + 8H_2$ (2)

Lee et al. [37] compared the dehydrogenation performance of 5 wt% Pt/Al_2O_3 and 5 wt% Pt/CeO_2 catalysts in the DBT–perhydrodibenzyltoluene system. The study achieved 100% selectivity, with Pt/Al_2O_3 showing full conversion, whereas Pt/CeO_2 achieved only 37% conversion. Additionally, Sievi et al. [12] developed innovative thermo-electrochemical hybrid systems that enable hydrogen recovery from DBT at lower temperatures. Recent studies have introduced several strategies to enhance the performance of DBT-based LOHC systems, including the development of bimetallic catalysts (e.g., Pd–Ni) to leverage synergistic effects and the utilization of nanostructured supports to increase surface area and improve mass diffusion [38, 39]. Efficient dehydrogenation of DBT remains critical for the practical implementation of LOHC technology. Accordingly, ongoing research efforts focus on optimizing catalyst activity, elucidating reaction mechanisms, and ensuring long-term system stability over multiple hydrogenation–dehydrogenation cycles. Nevertheless, key challenges such as catalyst deactivation (e.g., coke formation), high energy demand, and the necessity to maintain thermal stability continue to limit the widespread adoption of this technology [32].

Table 3 summarizes the catalytic performances of some catalysts used in the dehydrogenation of H18-DBT. Pt/Al_2O_3 (platinum supported alumina) catalysts were mainly used in the studies. However, one of the main findings noted is that higher platinum loading does not always result in higher performance. For example, a catalyst containing 5 wt.% Pt and tested in a flow-type reactor gave only 5% conversion, while a 0.5 wt.% Pt/Al_2O_3 catalyst prepared by precipitation method in supercritical CO_2 environment achieved 89% conversion at the same temperature and pressure. This reveals that the catalyst is directly related not only to the amount of active metal but also to parameters such as preparation method and metal dispersion. In Modisha et al. [40], among various catalyst preparation methods, Pt/Al_2O_3 prepared by SCD (supercritical CO_2 deposition) method stands out with both high conversion (89%) and acceptable selectivity (38%) values. In contrast, the catalyst prepared by wet impregnation with the same Pt ratio yielded only 31% conversion and 15% selectivity. This highlights the decisive influence of metal particle size and surface distribution on catalytic performance. Catalytic dehydrogenation of H_{18}-DBT is highly sensitive to parameters such as metal dispersion, catalyst preparation method, support material and additives. Although Pt-based systems are still the most widely used, their performance can be significantly improved by surface engineering and synthesis techniques. Future work should focus on the development of long-lasting and cost-effective catalyst systems that can operate at lower temperatures.

CONCLUSION

Dibenzyltoluene (DBT)-based Liquid Organic Hydrogen Carrier (LOHC) systems present significant potential for the safe, efficient, and scalable chemical storage and transportation of hydrogen. Thanks to their high thermal and chemical stability, low toxicity, and compatibility with existing energy infrastructure, DBT-based systems have considered as one of the most promising candidates for the commercialization of LOHC technology. The advancement of commercial applications further demonstrates the progress of this technology towards industrial maturity. However, several critical technical challenges continue to limit the large-scale applicability of LOHC systems. High dehydrogenation temperatures (>300 °C), catalyst deactivation (coke formation, sintering), and slow molecular diffusion within porous structures negatively affect the process efficiency and cycle life. Additionally, the high energy demand associated with the dehydrogenation step remains one of the main obstacles to achieving fully sustainable operation.

Table 3. Deydrogenation catalytic performance of some catalysts for H18-DBT.

Compond name	Catalysts	T (°C)	P (MPa)	Conversion (%)	Selectivity (%)	References
H18-DBT	Pt/Al_2O_3	270	0.1	-	58.1	[41]
	W0.22-Pt0.78/ Al_2O_3	270	0.1	-	64.8	[41]
	0.3 wt. % Pt/Al_2O_3	310	0.1	83	-	[42]
	0.5 wt. % Pt/Al_2O_3 (SCD/$scCO_2$)	298	0.1	89	38	[40]
	0.5 wt. % Pt/Al_2O_3 (Wet Impregnation)	299	0.0	31	15	[40]
	0.5 wt% Pt/Al_2O_3 (commercial catalysts)	300	0.1	88	42	[40]
	0.3%Pt/Al_2O_3	310	0.1	85	100	[43]
	5%Pt/Al_2O_3	300	0.1	5	100	[44]
	5%Pt/CeO_2	300	0.1	37	100	[44]
	5%Pt/Al_2O_3	270	0.1	58	100	[45]
	1%La,5%Pt/Al_2O_3	270	0.1	65	100	[45]
	5%Pt/Al_2O_3	300	0.1	48	-	[46]

In recent years, significant progress has been made in overcoming these challenges through the development of bimetallic catalysts (e.g., Pd–Ni, Pt–Ru), nanostructured supports, and thermo-electrochemical hybrid systems. However, further research is still required to ensure the scalability and long-term performance of these solutions. Future research should focus on the following key areas: i) Design of next-generation catalysts with high activity at low temperatures and reduced energy consumption, ii) Enhancement of mass and heat transfer through process intensification, iii) Integration of thermo-electrochemical hybrid systems to improve process efficiency, iv) Development of bio-based or sustainably sourced LOHC compounds, v) Long-term performance and cycle stability studies at commercial scale. In conclusion, LOHC technology — particularly DBT-based systems — has the potential to play a critical role in the future sustainable hydrogen economy. To fully realize this potential, it is essential to advance multidisciplinary research, innovative catalyst design, and integrated system development.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

STATEMENT ON THE USE OF ARTIFICIAL INTELLIGENCE

Artificial intelligence was not used in the preparation of the article.

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