Viewpoint

Liquid Organic Hydrogen Carriers or Organic Liquid Hydrides: 40 Years of History

Valérie Meille 1,* and Isabelle Pitault 2,*

1 CNRS, IRCELYON, Univ Lyon, Université Claude Bernard Lyon 1, F-69626 Villeurbanne, France
2 CNRS, LAGEPP UMR 5007, Univ Lyon, Université Claude Bernard Lyon 1, 43 Boulevard du 11 Novembre 1918, F-69100 Villeurbanne, France
* Correspondence: valerie.meille@ircelyon.univ-lyon1.fr (V.M.); isabelle.pitault@univ-lyon1.fr (I.P.)

Abstract: The term LOHC stands for Liquid Organic Hydrogen Carriers. The term has been so well accepted by the scientific community that the studies published before the existence of this name are not very visible. In this mini-review, we have tried to rehabilitate various studies that deserve to be put back in the spotlight in the present context. Studies indeed began in the early 1980s and many publications have compared the use of various organic carriers, various catalysts and reactors. Recent reviews also include the economic aspects of this concept.

Keywords: LOHC; hydrogen storage; hydrogen carriers; liquid hydrides; MCH/TOL system

1. Introduction

The term LOHC (Liquid Organic hydrogen carriers) appeared less than 10 years ago [1], with only 135 references up to now, 2/3 of them in the three last years (source: webofknowledge). However, studies dedicated to the storage of hydrogen in organic molecules have been published for more than 40 years. Simultaneous studies in the 1980s appeared in Canada (Quebec) [2], in Switzerland [3] and in Italy [4] and the term “Liquid organic hydride” was often used. Since the adoption of the term LOHC, these pioneering studies are much less cited just because they are not referenced under this term, but some of them really deserve being considered. The objective of this article is not to make an nth review of the work conducted in recent years on LOHC systems but to retrace the history that led to the development of this system and to give another point of view on the storage of hydrogen in organic liquids.

Hydrogen storage in liquid organic compounds is illustrated in Figure 1. When hydrogen is produced and not used immediately, it has to be stored and potentially transported. To gain in safety and ease of transportation, hydrogen can be used to hydrogenate a hydrogen-lean molecule, producing a hydrogen-rich molecule wherein hydrogen is safely stored. Later and in another place, hydrogen can be released by a dehydrogenation reaction. Both hydrogenation and dehydrogenation reactions are catalyzed; the former is exothermic and the latter is endothermic. Whereas catalytic hydrogenations are common, dehydrogenation, and especially when carried out on-board of a vehicle, requires in-depth studies of the appropriate catalyst, reaction conditions and reactor.
2. 40 Years History

The idea of storing hydrogen in organic liquid molecules first appeared in a technical report from Exxon studies [5]. Note that previous studies about dehydrogenation reactions exist (e.g., [6]), but the formation of hydrogen was not the objective. Several studies were then conducted quasimultaneously in three main research groups: one in Italy, one in Switzerland and one in Quebec, Canada. The latter group filed a Canadian patent in 1981 and studied the dehydrogenation of cyclohexane [2,7]. Studies continued until the mid 1990s, with some collaborative contribution from Institut Français du Pétrole concerning the catalyst deactivation studies [8–10].

In Switzerland, at the Paul Scherrer Institut, the use of a liquid organic carrier of hydrogen as a fuel for automobiles was proposed in 1981 [3]. The so-called MTH system (Methylcyclohexane—Toluene—Hydrogen) was used. The team studied the complete economic and technical feasibility of using $H_2$ combustion engines and proposed prototype trucks [11–13]. One of the main difficulties encountered was due to the catalyst stability. The last publications of the group in the late 1990s, also with ETH-Zurich, concerned the use of a coated reactor to improve heat-transfer and the development of a predictive model to take into account the catalyst deactivation [14,15]. A technicoeconomic study was also published [16].

Extensive studies were also conducted in Italy with the objective of hydrogen storage and long-distance transportation [4,17–19]. Kinetic studies, as well as studies to understand the deactivation of the catalyst were performed [20–22]. The studies also concerned the benzene/cyclohexane and the toluene/methylcyclohexane couples.

At the beginning of year 2000, several groups published some contributions on the topic of hydrogen storage in organic liquids. Air Products proposed to extend the use of organic hydrogen carriers to heterocycles, including in particular N-ethylcarbazole [23,24]. Briefly, the main advantage was the possibility to dehydrogenate the molecule at a lower temperature due to a lower reaction enthalpy. The system was then studied by many researchers. A recent publication cites the history of the catalysts used for N-heterocycles (among which N-ethylcarbazole prevails) [25]. However, studies not using the keyword LOHC are not cited (e.g., [26]).

In the 2010s, the term LOHC appeared, together with the use of the pair dibenzyltoluene/perhydrodibenzyltoluene [1]. The studies concerning this family of compounds extended to other benzyltoluene compounds and are made easily accessible thanks to the use of the keyword LOHC, having become very popular and inescapable. Thus, on the other hand, older studies, and also those that do not use this keyword are totally invisible.
and seem to be erased from the history. It is the purpose of this paper to gather both groups of publications (those with and those without the LOHC keyword).

3. Literature Overview

Excellent recent reviews detail the contributions from several groups to the knowledge of hydrogen storage in LOHC, sorted by the chosen hydrogen carrier (e.g., [27,28]). The reader is advised to consult these papers to have an overview of the present situation. Newly considered LOHC couples, like e.g., n-(methylbenzyl)pyridine and methylindole appear in even more recent reviews [29]. The review of Modisha et al. [30] gathers some useful informations concerning catalysts and reactors but mostly in the case of dibenzyltoluene. For a complete review of catalysts and reactors used for the organic liquid hydrogen carriers, namely in the case of methycyclohexane/toluene and cyclohexane/benzene, it is useful to also consider studies (older or not) not mentioning the term LOHC. A recent paper concerning the couple MCH/TOL, which does not use the term LOHC but the term organic hydride, gives some references to many important papers that are never mentioned in all the LOHC-labeled works [31]. It cites all the kinetic studies carried out for the dehydrogenation of methycyclohexane, including the Canadian, Swiss and Italian pioneering studies. Since (methyl)cyclohexane dehydrogenation is an important model reaction in reforming of naphtha, many publications have been written for that specific process but can still be very useful in the case of hydrogen release (e.g., [32–36] and other references cited in [31]).

3.1. Hydrogen-Rich/Hydrogen-Lean Pairs

Apart from the well-known pairs that were already presented, new couples appeared in the very recent literature. Among the most promising molecules that can store hydrogen appears n-(methylbenzyl)pyridine, liquid in the range of use and less viscous than DBT [37]. A list of alkyl-indoles was also evaluated in the Sustainable Energy Laboratory of Wuhan with several papers that are reported in the review written by Rao et al. [29]. Among the products that could be obtained from natural products, trisphaeridine, present in amaryllidaceae alkaloids, also seems promising with a low reaction enthalpy [38]. The pair γ-butyrolactone/butane-diol is also envisioned [39], and this publication presenting a promising and cheap hydrogen carrier does not use the keyword “LOHC”. Verevkin et al. propose the use of diphenylether derivatives and furfuryl alcohol [40,41]. The use of methanol is also gaining some importance and can be used in different ways. Combined with urea, it can reversibly form ethylenediamine and hydrogen [42]. Produced from atmospheric carbon dioxide, methanol is called a “circular” hydrogen carrier [27] and is considered as the cheapest hydrogen storage solution [43]. Note that formic acid is also a circular hydrogen carrier [44]. Other promising molecules exist (1,2-dihydro-1,2-azaborine, phenazine) and can be found in the cited reviews [44]. Note that a recent paper also lists possible new H₂-rich/H₂-lean pairs based on a computational study [45].

3.2. Catalysts

A table of most used catalysts for the five most popular LOHC is presented in the review done by Modisha et al. [30]. The most studied system is methycyclohexane/toluene (or cyclohexane/benzene), briefly presented here, with 40 years of experience. Initially, the catalysts used for the dehydrogenation reaction were those traditionally used for gasoline reforming, that is Pt/alumina catalysts with a second element, metal or modifier. More recently, a diversification of the catalysts is proposed even if the active metals are still mostly Pt and Pd (see e.g., the review of Aakko-Saks et al. [27]). Many bimetallic catalysts are proposed both to decrease the amount of noble metal and/or improve the activity and selectivity of the reaction [46–49]. The role of the support was also investigated. Whereas most of the studied concern alumina, some composite supports, e.g., Al₂O₃−TiO₂ [50] have proved to be interesting thanks to the partial reducibility of TiO₂ and electron transfer.
from support to the metal facilitating the desorption of products and thus accelerating the reaction. Carbon is also considered as a potential metal support [51].

The problem of catalyst deactivation due to coke formation is regularly highlighted and has been extensively studied and modeled in the case of MCH/TOL. Very early on, modifiers were added to avoid secondary reactions of cracking and isomerization leading to the formation of coke [10]. It has also been established that the presence of hydrogen in the gas phase prevents the deactivation of Pd nanoparticles by suppressing coke formation, in contrast to what has been observed in the absence of hydrogen [52–54]. In a study of toluene hydrogenation on Pt/Al₂O₃, Taimoor and Pitault [55] observed a slow and reversible deactivation even in the presence of hydrogen and demonstrated that this was due to a strong adsorption of toluene on alumina. In this context, interesting studies on the application of an electric field to a fixed bed of Pt/CeO₂ or Pt/TiO₂ are worth mentioning [56,57]. The electric field allows the dehydrogenation of MCH to be carried out at low temperature (423K) and the desorption of toluene is rapid, avoiding both the formation of coke (or a strong adsorption) and limiting the reverse reaction.

It is also worth mentioning a few publications using non-noble metal catalysts for the dehydrogenation of methylcyclohexane and cyclohexane [50,58–60].

Concerning N-ethylcarbazole, a list of screened mono and bimetallic catalysts is proposed in the review of Zhou et al. with the following elements: Pd, Pt, Ru, Rh, Ni, Au, Ir [61].

Besides heterogeneous catalysts, organometallic complexes can also be used for the dehydrogenation reactions, typically iridium [39] and ruthenium [42]. A review gathers many recent developments in that field but without ever using the word LOHC [62].

3.3. Reactors

Regarding the reactor design, many developments were proposed in the case of the most studied systems: MCH/TOL, H₀-DBT/H₁₈-DBT and N-Ethylcarbazole. The most classical reactors are summarized in the review from Modisha et al. [30]: spray-pulsed, fixed-bed, CSTR batch-type, structured monolith reactor, tubular and pressure swing reactors.

Apart from these reactors, studies often set aside (without the keyword “LOHC”) concern for the implementation of heat exchanger reactors to compensate the heat required by the dehydrogenation reaction [52,63]. It should be noted that the same coupling of MCH dehydrogenation and H₂ or toluene combustion has recently been reconsidered to generate power [64].

To handle pure hydrogen recovery (without LOHC vapors), membrane reactors [53,65–69] and integrated adsorption columns [70,71] were proposed.

It is worth mentioning that the global system was also studied at microreactor scale since this information seems to be lost [65,72,73].

3.4. Economical Studies

Recently, many studies concern the comparison of the economical aspects of storing hydrogen in LOHC compared to compressed gas or liquefied H₂ [74,75]. Some recent studies [43,76] conclude that if the heat needed for dehydrogenation is sustainably managed (e.g., waste heat), dibenzyltoluene or toluene are systems of choice both in terms of efficiency and costs. Nevertheless, thanks to a lower cost and a higher hydrogen transport capacity than other LOHC, methanol is the most economic solution [43,44]. However, in that case, an appropriate management of carbon dioxide and water has to be foreseen.

4. Conclusions

For an exhaustive review of the studies carried out in the framework of liquid organic hydrogen carriers, using the unique keyword “LOHC” is dangerous because it excludes all the studies carried out 30 years before the invention of this keyword, but also some recent exploratory studies from groups who are not familiar with this name. The missing informa-
tion when searching by the term “LOHC” ranges from molecules (e.g., [39,77]) to reactors (e.g., [52]) through catalysts (e.g., [26,45,50,62]) and kinetics (e.g., [31,36]). Important studies were namely conducted with the so-called MCH/TOL system, either for the development of more stable catalysts for a comprehensive kinetic analysis or for the design of the most appropriate reactor to cope with the high endothermicit of the dehydrogenation reaction.

In future studies, it is expected that an important place is given to the development of catalytic systems but also to processes allowing a better heat integration.

Author Contributions: Writing—original draft preparation, review and editing, V.M., I.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank the CNRS for support in the frame of the 80|PRIME call, for the project NOSY-H2.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Teichmann, D.; Arlt, W.; Wasserscheid, P.; Freymann, R. A Future Energy Supply Based on Liquid Organic Hydrogen Carriers (LOHC). Energy Environ. Sci. 2011, 4, 2767–2773. [CrossRef]
2. Bélanger, G. Cyclohexane, a liquid hydride. Adv. Hydrogen Energy 1982, 3, 1335–1343.
3. Taube, M.; Taube, P. A liquid organic carrier of hydrogen as a fuel for automobiles. Adv. Hydrogen Energy 1981, 2, 1077–1085.
4. Parmaliana, A.; Crisafulli, C.; Maggiore, R.; Bart, J.C.J.; Giordano, N. Catalytic Activity of Honeycomb Catalysts, I. The Benzene-Cyclohexane (de)Hydrogenation Reaction. React. Kinet. Catal. Lett. 1981, 18, 295–299. [CrossRef]
5. Sultan, O.; Shaw, H. Study of Automotive Storage of Hydrogen Using Recyclable Liquid Chemical Carriers. [Catalytic Dethydrogenation of Napthenes]; Technical Report TEC-75/003; Exxon Research and Engineering Co.: Linden, NJ, USA, 1975.
6. Ritchie, A.W.; Bailey, J.E.; Nixon, A.C. Effect of pore size on the stability of platinum-alumina catalysts in naphthene dehydrogenation. Prepr. Am. Chem. Soc. Div. Pet. Chem. 1969, 14, B44–B51.
7. Bélanger, G. Hydrure Liquide Pour le Stockage de l’hydrogène. Patent CA 1146725, 24 May 1983.
8. Chaouki, J.; Touzani, A.; Klvana, D.; Bournonville, J.P.; Bélanger, G. Déshydrogénation du méthylcyclohexane sur le catalyseur industriel Pt-Sn/Al2O3. Revue de l’IFP 1988, 43, 873–881. [CrossRef]
9. Chaouki, J.; Klvana, D.; Pontier, T.; Bélanger, G. Modélisation de la désactivation du catalyseur Pt-Sn/Al2O3 lors de la déshydrogénation du méthylcyclohexane. Chem. Eng. J. 1991, 46, 109–118. [CrossRef]
10. Chaouki, J.; Klvana, D. Influence of the deactivation of an industrial Pt-Sn/Al2O3 catalyst on the performance of the dehydrogenation reactor. Chem. Eng. Sci. 1994, 49, 4639–4646. [CrossRef]
11. Taube, M.; Rippin, D.W.T.; Cresswell, D.L.; Knecht, W. A system of hydrogen-powered vehicles with liquid organic hydrides. Int. J. Hydrogen Energy 1983, 8, 213–225. [CrossRef]
12. Taube, M.; Rippin, D.; Knecht, W.; Hakimifard, D.; Milisavljevic, B.; Gruenenfelder, N. A prototype truck powered by hydrogen from organic liquid hydrides. Int. J. Hydrogen Energy 1985, 10, 595–599. [CrossRef]
13. Gruenenfelder, N.F.; Schucan, T.H. Seasonal storage of hydrogen in liquid organic hydrides: description of the second prototype vehicle. Int. J. Hydrogen Energy 1989, 14, 579–586.
14. Tschudin, S.; Shido, T.; Prins, R.; Wokaun, A. Characterisation of catalysts used in wall reactors for the catalytic dehydrogenation of methylcyclohexane. J. Catal. 1999, 181, 113–123. [CrossRef]
15. Maria, G.; Marin, A.; Wyss, C.; Muller, S.; Newson, E. Modelling and scaleup of the kinetics with deactivation of methylcyclohexane dehydrogenation for hydrogen energy storage. Chem. Eng. Sci. 1996, 51, 2891–2896. [CrossRef]
16. Scherer, G.W.H.; Newson, E. Analysis of the seasonal energy storage of hydrogen in liquid organic hydrides. Int. J. Hydrogen Energy 1998, 23, 19–25. [CrossRef]
17. Giordano, N.; Cacciola, G.; Parmaliana, A. Catalytic and reaction engineering aspects in the storage of hydrogen through the reversible dehydrogenation of cyclohexane. Indian J. Technol. 1983, 21, 398–403.
18. Cacciola, G.; Giordano, N.; Restuccia, G. Cyclohexane as a Liquid Phase Carrier in Hydrogen Storage and Transport. Int. J. Hydrogen Energy 1984, 9, 411–419. [CrossRef]
19. Cacciola, G.; Recupero, V.; Giordano, N. Economic Evaluation of Long-Distance Hydrogen Transmission by Chemical Closed-Loop Cycle. Int. J. Hydrogen Energy 1985, 10, 325–331. [CrossRef]
20. El-Sawi, M.; Infortuna, F.; Lignola, P.; Parmaliana, A.; Frusteri, F.; Giordano, N. Parameter Estimation in the Kinetic Model of Methylcyclohexane Dehydrogenation on a P—Al2O3 Catalyst by Sequential Experiment Design. Chem. Eng. J. 1989, 42, 137–144. [CrossRef]
21. Frusteri, F.; Parmaliana, A.; Mezzapica, A.; Chuvilin, A.L.; Tsiakaras, P.; Giordano, N. Highly Dispersed Platinum Honeycomb Reforming Catalysts: Sintering Behavior and Activity. React. Kinet. Catal. Lett. 1992, 48, 315–323. [CrossRef]
22. Vitulli, G.; Falorni, R.; Salvadori, P.; Parmaliana, A.; Frusteri, F.; Giordano, N. Mesitylene Solvated Platinum Atoms in the Preparation of Efficient Supported Catalysts for the Dehydrogenation of Methylcyclohexane to Toluene. Catal. Lett. 1993, 17, 151–155. [CrossRef]
23. Cooper, A.C.; Bagzis, L.D.; Campbell, K.M.; Pez, G.P. Hydrogen storage and delivery by reversible hydrogenation of liquid-phase hydrogen carriers. Prepr. Papi. Am Chem. Soc. Div. Fuel Chem. 2005, 50, 271–273.
24. Cooper, A.C.; Campbell, K.M.; Pez, G.P. An Integrated Hydrogen Storage and Delivery Approach Using Organic Liquid-Phase Carriers. In Proceedings of the WHEC 16, Lyon, France, 13–16 June 2006.
25. Shuang, H.; Chen, H.; Wu, F.; Li, J.; Cheng, C.; Li, H.; Fu, J. Catalytic Dehydrogenation of Hydrogen-Rich Liquid Organic Hydrogen Carriers by Palladium Oxide Supported on Activated Carbon. Fuel 2020, 275, 117896. [CrossRef]
26. Wan, C.; An, Y.; Xu, G.; Kong, W. Study of Catalytic Hydrogenation of N-Ethylcarbazole over Ruthenium Catalyst. Int. J. Hydrogen Energy 2012, 37, 13092–13096. [CrossRef]
27. Aakko-Saks, P.T.; Cook, C.; Kiviharju, J.; Repo, T. Liquid Organic Hydrogen Carriers for Transportation and Storing of Renewable Energy – Review and Discussion. J. Power Sources 2018, 396, 803–823. [CrossRef]
28. Gianotti, E.; Taillades-Jacquin, M.; Rozière, J.; Jones, D.J. High-Purity Hydrogen Generation via Dehydrogenation of Organic Hydrogen Carriers: A Review on the Catalytic Process. ACS Catal. 2018, 8, 4660–4680. [CrossRef]
29. Rao, P.C.; Yoon, M. Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress. Energies 2020, 13, 6040. [CrossRef]
30. Modisha, P.M.; Ouma, C.N.M.; Garidzirai, R.; Wasserscheid, P.; Bessarabov, D. The Prospect of Hydrogen Storage Using Liquid Organic Hydrogen Carriers. Energy Fuels 2019, 33, 2778–2796. [CrossRef]
31. Akram, M.S.; Aslam, R.; Alhumaidan, F.S.; Usman, M.R. An Exclusive Kinetic Model for the Methylcyclohexane Dehydrogenation over Alumina-Supported Pt Catalysts. Int. J. Chem. Kinet. 2020, 52, 415–449. [CrossRef]
32. Ayo, D.B.; Susu, A.A. Platinum-rhenium/alumina catalyst. III. Mechanism of C6-ring hydrogenation/deshydrogenation reactions. Appl. Catal. 1988, 40, 1–16. [CrossRef]
33. Rochefort, A.; Peltier, F.L.; Boitiaux, J.P. Particle size Effect in supported platinum: methylcyclohexane dehydrogenation. J. Catal. 1992, 138, 482–490. [CrossRef]
34. Rochefort, A.; Peltier, F.L.; Boitiaux, J.P. The reconstruction of supported platinum particles monitored by methylcyclohexane dehydrogenation and H2 TPD. J. Catal. 1994, 145, 409–415. [CrossRef]
35. Ali, L.I.; Ali, A.G.A.; Aboul-Fotouh, S.M.; Aboul-Gheit, A.K. Dehydrogenation of cyclohexane on catalysts containing noble metals and their combinations with platinum on alumina support. Appl. Catal. A 1999, 177, 99–110.
36. Usman, M.R.; Cresswell, D.L.; Garforth, A.A. Dehydrogenation of Methylcyclohexane: Parametric Sensitivity of the Power Law Kinetics. 2013. Available online: https://www.hindawi.com/journals/ismr/2013/152893/ (accessed on 1 May 2021).
37. Oh, J.; Jeong, K.; Kim, T.W.; Kwon, H.; Han, J.W.; Park, J.H.; Suh, Y.W. 2-(N-Methylbenzyl)pyridine: A Potential Liquid Organic Hydrogen Carrier with Fast H2 Release and Stable Activity in Consecutive Cycles. ChemSusChem 2018, 11, 661–665. [CrossRef]
38. Tang, C.; Fei, S.; Lin, G.D.; Liu, Y. Natural Liquid Organic Hydrogen Carrier with Low Dehydrogenation Energy: A First Principles Study. Int. J. Hydrogen Energy 2015, 40, 32089–32097. [CrossRef]
39. Onoda, M.; Nagano, Y.; Fujita, K.i. Iridium-Catalyzed Dehydrogenative Lactonization of 1,4-Butanediol and Reversal Hy- drogenation: New Hydrogen Storage System Using Cheap Organic Resources. Int. J. Hydrogen Energy 2019, 44, 28514–28520. [CrossRef]
40. Verevkin, S.P.; Pimerzin, A.A.; Sun, L.X. Liquid Organic Hydrogen Carriers: Hydrogen Storage by Di-Phenyl Ether Derivatives: An Experimental and Theoretical Study. J. Chem. Thermodyn. 2020, 144, 106057. [CrossRef]
41. Verevkin, S.P.; Siewert, R.; Pimerzin, A.A. Furfuryl Alcohol as a Potential Liquid Organic Hydrogen Carrier (LOHC): Thermochemical and Computational Study. Fuel 2020, 266, 117067. [CrossRef]
42. Xie, Y.; Hu, P.; Ben-David, Y.; Milstein, D. A Reversible Liquid Organic Hydrogen Carrier System Based on Methanol-Ethylendiamine and Ethylene Urea. Angew. Chem. Int. Ed. 2019, 58, 5105–5109. [CrossRef]
43. Niermann, M.; Timmerberg, S.; Drüner, S.; Kaltsschmitt, M. Liquid Organic Hydrogen Carriers and Alternatives for International Transport of Renewable Hydrogen. Renew. Sustain. Energy Rev. 2021, 135, 110171. [CrossRef]
44. Niermann, M.; Beckendorff, A.; Kaltsschmitt, M.; Bonhoff, K. Liquid Organic Hydrogen Carrier (LOHC) – Assessment Based on Chemical and Economic Properties. Int. J. Hydrogen Energy 2019, 44, 6631–6654. [CrossRef]
45. Paragian, K.; Li, B.; Massino, M.; Rangarajan, S. A Computational Workflow to Discover Novel Liquid Organic Hydrogen Carriers and Their Dehydrogenation Routes. Mol. Syst. Des. Eng. 2020, 5, 1658–1670. [CrossRef]
46. Biniwale, R.B.; Kariya, N.; Ichikawa, M. Dehydrogenation of Cyclohexane Over Ni Based Catalysts Supported on Activated Carbon using Spray-pulsed Reactor and Enhancement in Activity by Addition of a Small Amount of Pt. Catal. Lett. 2005, 105, 83–87.
47. Mori, K.; Kanda, Y.; Uemichi, Y. Dehydrogenation of Methylcyclohexane over Zinc-Containing Platinum/Alumina Catalysts. J. Ipn. Pet. Inst. 2018, 61, 350–356. [CrossRef]

48. Boufaden, N.; Akkari, R.; Pawelec, B.; Fierro, J.L.G.; Zina, M.S.; Ghorbel, A. Dehydrogenation of Methylcyclohexane to Toluene over Partially Reduced silica-Supported Pt-Mo Catalysts. J. Mol. Catal. A Chem. 2016, 420, 96–106. [CrossRef]

49. Pande, J.V.; Prananto, L.A.; Biddinika, M.K.; Aziz, M. Combined Dehydrogenation and Hydrogen-Based Power Generation. RSC Adv. 2020, 10, 198–202. [CrossRef]

50. Zhu, G.; Yang, B.; Wang, S. Nanocrystallites-Forming Hierarchical Porous Ni/Al2O3–TiO2 Catalyst for Dehydrogenation of Organic Chemical Hydrides. Int. J. Hydrogen Energy 2011, 36, 13603–13613. [CrossRef]

51. Sebastián, D.; Alegre, C.; Calvillo, L.; Pérez, M.; Moliner, R.; Lázaro, M.J. Carbon Supports for the Catalytic Dehydrogenation of Liquid Organic Hydrides as Hydrogen Storage and Delivery System. Int. J. Hydrogen Energy 2014, 39, 4109–4115. [CrossRef]

52. Kerleau, P.; Swesi, Y.; Meille, V.; Pitault, I.; Heurtaux, F. Total catalytic oxidation of a side-product for an autotrophic restoring hydrogen process. Catal. Today 2010, 157, 321–326. [CrossRef]

53. Kreuder, H.; Müller, C.; Meier, J.; Gerhards, U.; Dittmeyer, R.; Pfeifer, P. Catalyst Development for the Dehydrogenation of MCH in a Microstructured Membrane Reactor—For Heat Storage by a Liquid Organic Reaction Cycle. Catal. Today 2015, 242, 211–220. [CrossRef]

54. Schuster, R.; Waidhas, F.; Bertram, M.; Runge, H.; Geile, S.; Shyaduk, R.; Abuin, M.; von V.; Noei, H.; Lykhach, Y.; et al. Dehydrogenation of Liquid Organic Hydrogen Carriers on Supported Pd Model Catalysts: Carbon Incorporation Under Operation Conditions. Catal. Lett. 2018, 148, 2901–2910. [CrossRef]

55. Taimoor, A.A.; Pitault, I. Kinetics of toluene hydrogenation—Integrating a dynamic approach regarding catalyst activity. React. Kinet. Mech. Catal. 2011, 102, 263–282. [CrossRef]

56. Takise, K.; Sato, A.; Murakami, K.; Ogo, S.; Gil Seo, J.; Imagawa, K.; Kado, S.; Sekine, Y. Irreversible Catalytic Methylcyclohexane Dehydrogenation by Surface Protons at Low Temperature. RSC Adv. 2019, 9, 5918–5924. [CrossRef]

57. Kosaka, M.; Higo, T.; Ogo, S.; Seo, J.G.; Kado, S.; Imagawa, K.; Sekine, Y. Low-Temperature Selective Dehydrogenation of Methylcyclohexane by Surface Protons over Pt//Anatase-TiO2 Catalyst. Int. J. Hydrogen Energy 2020, 45, 738–743. [CrossRef]

58. Yolcular, S.; Olgun, O. Ni//Al2O3 catalysts and their activity in dehydrogenation of methylcyclohexane for hydrogen production. Catal. Today 2008, 138, 198–202. [CrossRef]

59. Xia, Z.; Lu, H.; Liu, H.; Zhang, Z.; Chen, Y. Cyclohexane Dehydrogenation over Ni-Cu//SiO2 Catalyst: Effect of Copper Addition. Catal. Commun. 2017, 90, 39–42. [CrossRef]

60. Gulyaeva, Y.K.; Alekseeva, M.V.; Ermakov, D.Y.; Bulavchenko, O.A.; Zaikina, O.O.; Yakovlev, V.A. High-Loaded Nickel Based Sol–Gel Catalysts for Methylcyclohexane Dehydrogenation. Catal. Today 2010, 1198. [CrossRef]

61. Zhou, L.; Sun, L.; Xu, L.; Wan, C.; An, Y.; Ye, M. Recent Developments of Effective Catalysts for Hydrogen Storage Technology Using N-Ethylcarbazole. Catalysts 2020, 10, 648. [CrossRef]

62. Shimbayashi, T.; Fujita, K.i. Metal-Catalyzed Hydrogenation and Dehydrogenation Reactions for Efficient Hydrogen Storage. Tetrahedron 2020, 76, 130946. [CrossRef]

63. Heurtaux, F.; Kerleau, P.; Pitault, I.; Campoli, F. System for the Production of Hydrogen Loaded at an Edge of a Motor Vehicle, Comprises a Catalytic Reactor Equipped with a Subset Comprising First and Second Coupled Plates, a Supply Chamber, and an Evacuation Chamber. Patent FR2927323, 14 August 2009.

64. Prananto, L.A.; Biddinika, M.K.; Aziz, M. Combined Dehydrogenation and Hydrogen-Based Power Generation. Energy Procedia 2017, 142, 1603–1608. [CrossRef]

65. Yamamoto, S.; Hanaoka, T.; Hamakawa, S.; Sato, K.; Mizukami, F. Application of a microchannel to catalytic dehydrogenation of cyclohexane on Pd membrane. Catal. Today 2006, 118, 2–6. [CrossRef]

66. Ferreira-Aparicio, P.; Rodriguez-Ramos, I.; Guerrero-Ruiz, A. Pure hydrogen production from methylcyclohexane using a new high performance membrane reactor. Chem. Commun. 2002, 2082–2083. [CrossRef]

67. Ali, J.K.; Baiker, A. Dehydrogenation of methylcyclohexane to toluene in a pilot-scale membrane reactor. Appl. Catal. A 1997, 155, 41–57. [CrossRef]

68. Ali, J.K.; Rippin, D.W.T. Comparing mono- and bimetallic noble-metal catalysts in a catalytic membrane reactor for methylcyclohexane dehydrogenation. Ind. Eng. Chem. Res. 1995, 34, 722–729. [CrossRef]

69. Akamatsu, K.; Ohta, Y.; Sugiwara, H.; Hattori, T.; ichi Nakao, S. Production of Hydrogen by Dehydrogenation of Cyclohexane in High-Pressure (1–8 atm) Membrane Reactors Using Amorphous Silica Membranes with Controlled Pore Sizes. Ind. Eng. Chem. Res. 2008, 47, 9842–9847. [CrossRef]

70. Swesi, Y.; Ronze, D.; Pitault, I.; Dittmeyer, R.; Heurtaux, F. Purification Process for Chemical Storage of Hydrogen for Fuel Cell Vehicles Applications. Int. J. Hydrogen Energy 2007, 32, 5059–5066. [CrossRef]

71. Swesi, Y.; Kerleau, P.; Lamotte, V.; Pitault, I.; Ronze, D. Adsorption Parameters of Toluene on Amberlite Adsorbent for Purification Unit Useful in Vehicle Application. Ind. Eng. Chem. Res. 2010, 49, 817–821. [CrossRef]

72. Cui, T.; Fang, J.; Jones, F.; Reppond, A. Fabrication of microreactors for dehydrogenation of cyclohexane to benzene. Sens. Actuators B 2000, 71, 228–231. [CrossRef]

73. Roumanie, M.; Meille, V.; Pijolat, C.; Tournier, G.; de Bellefon, C.; Pouteau, P.; Delattre, C. Design and fabrication of a structured catalytic reactor at micrometer scale: example of methylcyclohexane dehydrogenation. Catal. Today 2005, 110, 164–170. [CrossRef]
74. Peschel, A. Industrial Perspective on Hydrogen Purification, Compression, Storage, and Distribution. *Fuel Cells* **2020**, *20*, 385–393. [CrossRef]

75. Makaryan, I.A.; Sedov, I.V.; Maksimov, A.L. Hydrogen Storage Using Liquid Organic Carriers. *Russ. J. Appl. Chem.* **2020**, *93*, 1815–1830. [CrossRef]

76. Hurskainen, M.; Ihonen, J. Techno-Economic Feasibility of Road Transport of Hydrogen Using Liquid Organic Hydrogen Carriers. *Int. J. Hydrogen Energy* **2020**, *45*, 32098–32112. [CrossRef]

77. Kalenchuk, A.; Bogdan, V.; Dunaev, S.; Kustov, L. Influence of Steric Factors on Reversible Reactions of Hydrogenation-Dehydrogenation of Polycyclic Aromatic Hydrocarbons on a Pt/C Catalyst in Hydrogen Storage Systems. *Fuel* **2020**, *280*, 118625. [CrossRef]