

# Autothermal Hydrogen Release from Liquid Organic Hydrogen Carrier Systems

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## Abstract

A typical feature that the LOHC technology shares with other types of chemical hydrogen storage is that the release of hydrogen from the carrier requires an input of heat. In many use cases where waste heat from external sources is not available (e.g. in heavy-duty mobility), this is seen as a major drawback. In this paper, we show that autothermal LOHC dehydrogenation offers a very attractive way to overcome this drawback. In detail, we demonstrate autothermal hydrogen release from dicyclohexylmethane using diphenylmethane oxidation to benzophenone as source of heat. The full storage cycle involves benzophenone hydrodeoxygenation to dicyclohexylmethane, dicyclohexylmethane dehydrogenation to diphenylmethane, and diphenylmethane oxidation to benzophenone. We studied both the individual reaction steps using pure feedstocks and the integral cycle in which the intermediates and by-products of each reaction remain in the system for the subsequent reaction step. Although no efforts have yet been made to develop special catalyst materials for this purpose, the results with the applied commercial hydrodeoxygenation (Pd/C), dehydrogenation (Pt on alumina) and partial oxidation (VO<sub>x</sub>/TiO<sub>2</sub>) catalysts are already very promising. The storage cycle can be closed with high selectivity and with only minor total oxidation losses. The proposed concept of autothermal LOHC dehydrogenation offers the potential to increase the amount of usable hydrogen from a given amount of charged hydrogen carrier by up to 30%.

## Keywords

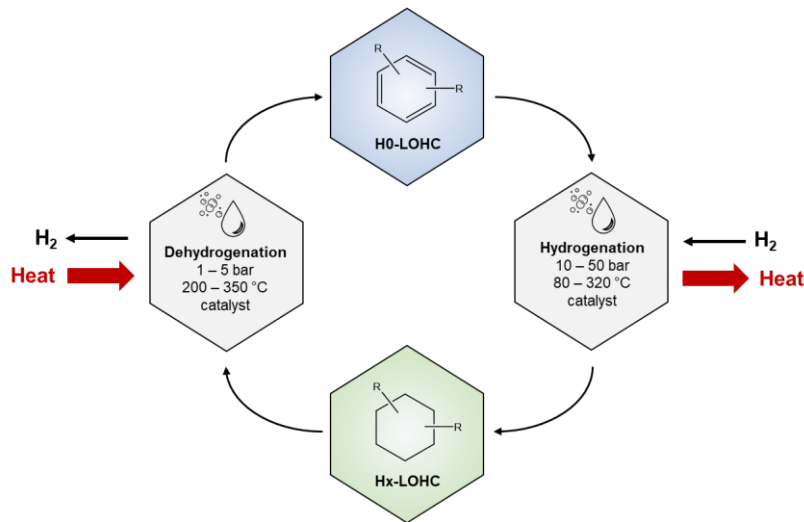
LOHC, autothermal hydrogen release, benzyltoluene, partial oxidation, benzophenone

## Introduction

Despite its excellent gravimetric energy density of  $33 \text{ kWh kg}^{-1}$ , elemental hydrogen is not a suitable secondary energy carrier at ambient conditions due to its very low volumetric energy density of only  $3 \text{ Wh L}^{-1}$ .<sup>[1]</sup> Traditional hydrogen storage and transportation applications therefore use elemental hydrogen either at very high pressure (up to 700 bar, e.g. for automotive applications) or in liquefied form at very low temperatures (e.g. cryogenic hydrogen at  $-253 \text{ }^\circ\text{C}$ ).<sup>[2]</sup> These extreme conditions, however, afford sophisticated infrastructures, a fact that prevents the rapid adoption of these applications on the global scale. In fact, the widespread introduction of high-pressure or liquefied hydrogen would require enormous investments in a completely new infrastructure. For an efficient and rapid transformation towards a hydrogen society, it would therefore be of great advantage to adopt parts of the already existing infrastructures for liquid fuels storage and transport. Using existing tank farms, transport ships and tank trucks for future hydrogen logistics would greatly facilitate the implementation of emission-free hydrogen technologies in relevant scale and quantity for contributing substantially to the ongoing defossilization efforts around the world.

Liquid Organic Hydrogen Carrier (LOHC) technologies precisely address this issue of infrastructure compatibility. They offer an attractive technical option for the safe and energy-dense handling of hydrogen at ambient conditions in chemically bound, liquid form. This allows the further use of infrastructures for liquid fuels to which the populations of almost all countries around the world are accustomed and which enjoys excellent acceptance.<sup>[3,4]</sup> Moreover, these existing liquid fuel infrastructures will become available when crude oil and crude oil-based products will phase-out to reach  $\text{CO}_2$  emission targets and, finally, a fully defossilized global energy system in the future.

All LOHC technologies are based on the reversible binding of hydrogen to organic molecules that are liquid at ambient conditions. During the loading process, an exothermal catalytic hydrogenation reaction transforms the hydrogen-lean carrier (H0-LOHC) to its hydrogen-charged counterpart (Hx-LOHC). At locations and times of hydrogen or power demand, the stored hydrogen can be released from this Hx-LOHC in an endothermal catalytic dehydrogenation reaction. If the storage cycle is highly selective, this hydrogen release step leads to the same amount of carrier molecules that were initially used in the loading step. This regenerated H0-LOHC compound can then be used for another storage cycle. Indeed, the repetitive use of the liquid storage compounds is a very important technical feature of all LOHC technologies. Figure 1 shows schematically a general representation of LOHC-based hydrogen storage cycles. Note, that the hydrogenation and dehydrogenation catalysts can be identical, however, the storage and release conditions are different. The most important parameter to influence the hydrogenation/dehydrogenation equilibrium is the hydrogen partial pressure with high pressures favoring hydrogenation and low pressures favoring hydrogen release.



**Figure 1: General hydrocarbon-based LOHC hydrogen storage cycle with hydrogen-lean (H0-LOHC) and hydrogen-rich (Hx-LOHC) compounds.**

Hydrogen storage technologies must be designed in a way that strictly avoids unintended or uncontrolled release of the stored hydrogen. In case of hydrogen storage in LOHC systems, hydrogen can only be released if the required dehydrogenation heat is continuously supplied in the presence of a suitable dehydrogenation catalyst at a thermodynamically suitable temperature. For the dehydrogenation of pure hydrocarbon LOHC systems, such as for example perhydro benzyltoluene (H12-BT), the required reaction temperature for an effective hydrogen release against 1.5 bar hydrogen partial pressure is 280 °C.<sup>[5]</sup> Note, that the endothermal character of hydrogen release from LOHC systems represents an important safety feature as hydrogen production can quickly be interrupted by stopping the required heat supply.

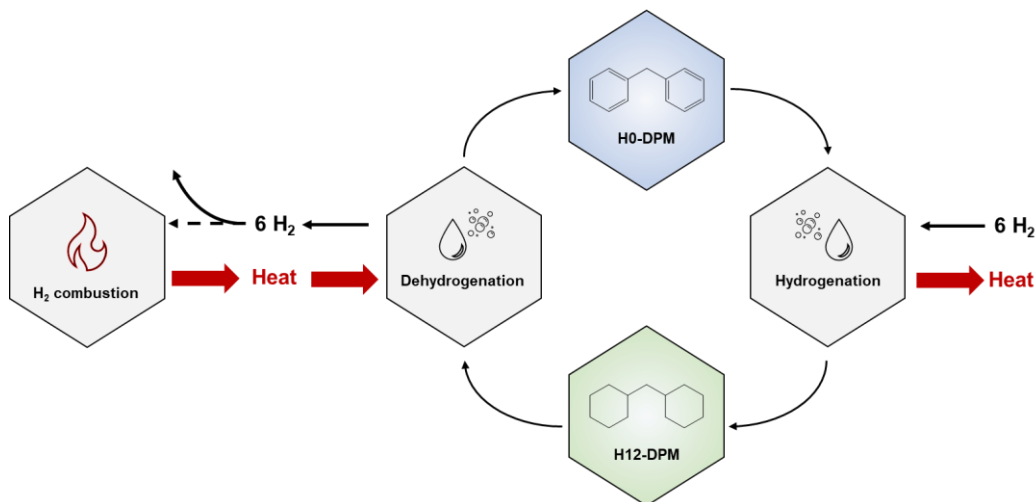
However, the need to provide reaction heat for hydrogen release in the range of 27% of the Lower Heating Value (LHV)<sup>[6]</sup> of the released hydrogen can strongly affect the efficiency of the storage cycle and is therefore seen by many authors of techno-economic studies as the major drawback of hydrogen storage using LOHC systems.<sup>[7-9]</sup> This aspect is especially important for the release of hydrogen from LOHC systems on vehicles, because on mobile units no external heat source is available and Polymer-Electrolyte-Membrane (PEM) fuel cells as the most interesting on-board hydrogen electrification technologies do not provide waste heat on the required temperature level for driving the hydrogen release reaction (PEM operation temperature is typically between 85 °C and 95 °C *vs.* required LOHC dehydrogenation temperatures of 270 °C to 320 °C). For the release of hydrogen from LOHC systems on board of vehicles, the following options have been therefore considered:<sup>[10]</sup>

- Electrical heating of the dehydrogenation reactor using the power generated in the on-board fuel cell;
- Combustion of a certain part of the released hydrogen;

- Conversion of the released hydrogen into electricity in a high-temperature fuel cell, e.g. a solid oxide fuel cell (SOFC), and utilisation of the waste heat from this fuel cell for hydrogen release;
- Use of a direct LOHC fuel cell (DLFC).

Electrical heating of the dehydrogenation reactor enables precise and dynamic temperature control and can be implemented very well from a technological point of view. This type of heating is therefore frequently used in kinetic investigations in the laboratory. For mobile applications, however, the electricity required for heating would have to be generated first by the onboard fuel cell with its heat losses making this technology much less efficient than heat provision by hydrogen combustion.

Partial combustion of the released hydrogen is well suited for providing the dehydrogenation heat for mobile or energy-autonomous applications but using this method, a relevant part of the LOHC-bound hydrogen is not available for the intended energetic use, e.g. for generating propulsion energy. Figure 2 exemplifies the provision of dehydrogenation heat by partial hydrogen combustion for the LOHC system perhydro diphenylmethane/diphenylmethane (H12-/H0-DPM).



**Figure 2: Hydrogen storage cycle using diphenylmethane/perhydro diphenylmethane as LOHC system and partial hydrogen combustion for heat provision in the dehydrogenation step.**

The use of a high temperature fuel cell that produces waste heat at a temperature level above the dehydrogenation temperature is another option for providing the heat for the hydrogen release reaction. This concept, however, comes with the requirement to operate a solid oxide fuel cell which does not fit well to the dynamic requirements of many types of vehicles. While such a solution can be seriously considered for shipping with its very constant power requirements over long periods of time, it is clearly much less suitable if the vehicle is operated in daily start-up and shut-down cycles.

The field of direct LOHC fuel cell research is fascinating and very promising, but to date the concept has only been convincingly demonstrated for ketone/secondary alcohol LOHC systems, such as the acetone/isopropanol pair.<sup>[11]</sup> Such system provides a much lower hydrogen capacity than the classical aromatic/alicyclic systems like the diphenylmethane/dicyclohexylmethane system (3.3 mass% vs. 6.7 mass% capacity).

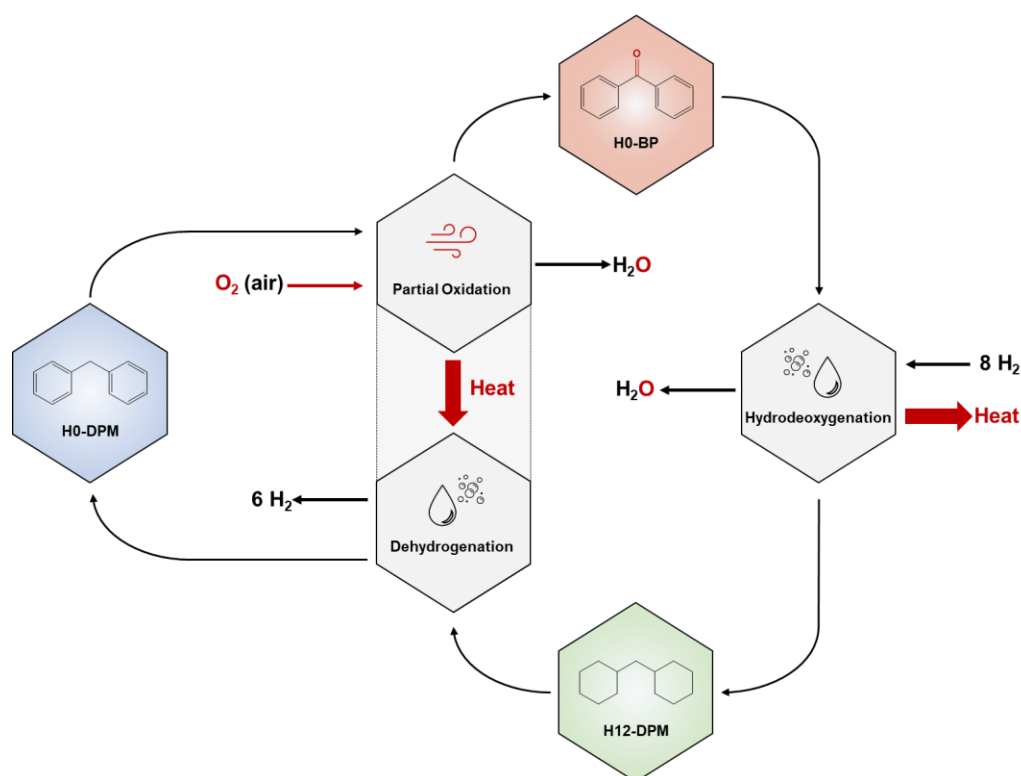
As a result of this analysis, it is fair to say that to date no method for onboard hydrogen release from LOHC systems provides the necessary dynamics for frequent (more than daily) start-stop cycles, maintains the high hydrogen capacity of alicyclic LOHC systems, and can use the entire LOHC-bound hydrogen for propulsion.

In this contribution, we demonstrate a very attractive concept to provide the heat for LOHC dehydrogenation by a selective partial oxidation of the dehydrogenated LOHC compound (H0-LOHC). Most importantly, this partial oxidation is fully reversible in the subsequent hydrogen charging step, so that the repetitive use of the LOHC carrier material is still maintained in this autothermal LOHC dehydrogenation process. The new concept allows in principle the full usage of the entire amount of LOHC-bound hydrogen for propulsion. Our work is based on earlier conceptual thoughts from the patent literature<sup>[12]</sup> and provides first evidence that autothermal LOHC dehydrogenation can indeed be achieved. We show that this concept may be relevant for practical applications if the right combination of carrier compound, reaction conditions and catalysts is selected. For practical relevance it is, for example, of high importance that all products and product mixtures formed in the cycle are liquid at room temperature. We here demonstrate a complete charging-release-recharging cycle for such a promising and applicable system and investigate in detail the particularly innovative partial oxidation and re-hydrogenation steps. We exemplify this exciting new concept for a drastically increased efficiency of LOHC-based hydrogen provision for the diphenylmethane (H0-DPM)/dicyclohexylmethane (H12-DPM)/benzophenone (H0-BP) LOHC system. Table 1 summarizes relevant material properties of the unloaded and oxidized form of the LOHC.

**Table 1: Important material properties of the studied LOHC molecules H0-DPM and H0-BP.**

| Material Property         | Diphenylmethane                     | Benzophenone                         |
|---------------------------|-------------------------------------|--------------------------------------|
| Self-ignition temperature | 485 °C <sup>[13]</sup>              | 560 °C <sup>[14]</sup>               |
| Melting Point             | 22 – 25 °C <sup>[13]</sup>          | 47 – 49 °C <sup>[15]</sup>           |
| Boiling Point             | 264 – 266 °C <sup>[13]</sup>        | 304 – 306 °C <sup>[15]</sup>         |
| Vapour Pressure           | 3225 mbar at 320 °C <sup>[16]</sup> | 1442 mbar bei 320 °C <sup>[16]</sup> |
| Density                   | 1006 g/L at 25 °C <sup>[13]</sup>   | 1085 g/L at 50 °C <sup>[17]</sup>    |
| Viscosity                 | 2.49 mPas at 30 °C <sup>[18]</sup>  | 5.49 mPas at 50 °C <sup>[17]</sup>   |

While H0-DPM melts at approx. 25 °C, H12-DPM melts at -19 °C, and H0-BP melts at 49 °C. Note, however, that mixtures of H0-DPM and H0-BP that are most relevant as products of the partial oxidation step (assuming incomplete conversion) show a strong melting point depression. Mixtures containing 60% of H0-BP and 40% H0-DPM (corresponding to 60% conversion in the partial oxidation reactions) show melting points below 25 °C. For details see Figure 2 in Section S4.3 of the ESI†. Thermal stability of the organic molecules during partial oxidation is ensured by operating temperatures far below the self-ignition temperature and short contact times in the reactor. The corresponding charging/uncharging/oxidation/reduction cycle for the H0-DPM/H12-DPM/H0-BP system is illustrated in Figure 3.



**Figure 3: Partial oxidation of H0-DPM as a way to provide the dehydrogenation heat for H12-DPM dehydrogenation resulting in an autothermal LOHC dehydrogenation process.**

Following the production of hydrogen and H0-DPM in the dehydrogenation reactor, hydrogen and H0-DPM are separated (e.g. by LOHC condensation) and the liquid H0-DPM is transferred to a second reaction chamber that is in close heat exchange with the dehydrogenation reactor. Ideally both reaction chambers are placed within one thermally insulated apparatus. In the oxidation chamber the exothermal partial oxidation of H0-DPM to H0-BP proceeds using air as oxidant and forming water as stoichiometric coupling product. The oxidation temperature is at least 20 °C above the dehydrogenation temperature to enable an effective heat flux from the exothermal oxidation to the endothermal dehydrogenation reaction. It is important to avoid overoxidation to CO<sub>2</sub> in the oxidation chamber as this would lead to a loss of the carrier molecule and to process-related CO<sub>2</sub> emissions. As both reaction chambers are separated, there

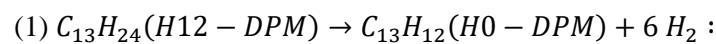
is no contact between hydrogen and oxygen at any time, which is important regarding process safety.

The here-proposed concept of autothermal LOHC dehydrogenation builds on the fact that the partially oxidized LOHC compound H0-BP can be fully regenerated to the originally hydrogen-loaded LOHC compound H12-DPM through a hydrodeoxygenation reaction with water as the stoichiometric coupling product. This reversibility of the oxidation process forms the basis to close the LOHC cycle and allows one to use the carrier medium over many storage cycles. Note, that the regeneration of one mol of H0-BP to form H12-DPM requires therefore 8 moles of hydrogen while the regeneration of H0-DPM to H12-DPM requires only 6 moles of hydrogen. Thus, for the energetic balance, the burning of 2 moles of hydrogen to water provides the energy for the endothermic dehydrogenation process. This extra-hydrogen is, however, invested at the location of the hydrogenation where in reasonable application scenarios energy is abundant, green and cheap. The concept of autothermal LOHC dehydrogenation can therefore be seen as a viable and new attempt to shift the energetic investment of chemical hydrogen storage fully to the hydrogen production site. From the consumer site perspective, the concept of autothermal hydrogen release increases the hydrogen yield from a given amount of transported LOHC material by at least 27% (the amount of hydrogen that would have to be burned to cover the reaction enthalpy). Moreover, the hydrogen release is not dependent on external heat sources or specific temperature levels of the fuel cell used for power generation from the released hydrogen. In our view, the concept of autothermal hydrogen release from LOHC systems therefore offers extremely promising potential to dramatically increase the cost efficiency of LOHC-based hydrogen storage, in particular for heavy-duty mobile applications.

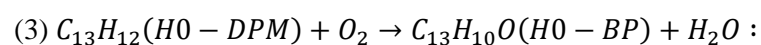
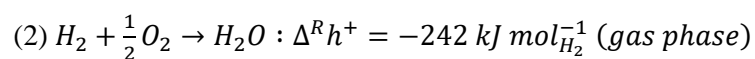
## Results and discussion

### Comparative energy assessment of different onboard hydrogen release concepts

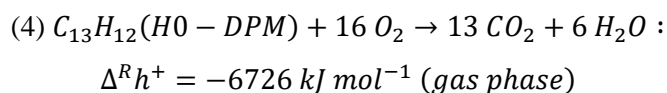
To realize an autothermal hydrogen release from H12-DPM, the endothermic dehydrogenation (Reaction 1<sup>[19]</sup>) can in principle be coupled with the exothermic hydrogen combustion (Reaction 2), the exothermic partial oxidation of H0-DPM to H0-BP (Reaction 3<sup>[20]</sup>), or the exothermic total oxidation of H0-DPM (Reaction 4<sup>[21]</sup>). Of course, these reactions can also proceed in parallel and simultaneous in the oxidation reactor.



$$\Delta^R h^+ = +65.3 \text{ kJ mol}_{H_2}^{-1} \text{ (liquid phase)}$$



$$\Delta^R h^+ = -357.1 \text{ kJ mol}^{-1} \text{ (gas phase)}$$



From these equations it can be seen that the dehydrogenation enthalpy for complete hydrogen release from H12-DPM could be provided by the total oxidation of 5.8% of the discharged carrier molecule H0-DPM. This is not a desired option for obvious economic and ecological reasons. It marks, however, an important boundary case for the concept of heat provision via partial oxidation. Any partial oxidation of practical relevance should result in clearly less total oxidation than 5.8% of the H0-DPM. Otherwise, it would be much easier to split the H0-DPM stream and to send 5.8% of it to a simple burner for heat generation.

Another relevant boundary case is the combustion of 27% of the released hydrogen. Also, this would provide the required heat for H12-DPM dehydrogenation but at the cost of a reduced hydrogen product yield as explained above. With the partial oxidation to H0-BP, which is energetically a deep discharge of the carrier system, up to 91% of the required dehydrogenation heat can be met. Only 5.8 kJ mol<sup>-1</sup> (H<sub>2</sub>) are left that have to be covered differently, e.g. by burning a much smaller amount of hydrogen (2.4% of the released hydrogen). Ultimately, 5.86 moles of H<sub>2</sub> per H12-DPM molecule could be used at the site of energy demand. In comparison, if hydrogen is burned to cover the full heat of dehydrogenation, only 4.38 moles H<sub>2</sub> per mole H12-DPM can be used at the site of energy demand. This number of usable moles of H<sub>2</sub> per mole LOHC is defined here as the usable storage capacity (USC, Equation 1) and will be used as the key performance indicator (KPI) for the here-described autothermal LOHC dehydrogenation throughout this paper.

$$USC = \frac{n_{H_2, \text{usable output}}}{n_{LOHC}} \quad (1)$$

Another key performance indicator is the overall storage efficiency (OSE). This KPI is defined as the number of usable H<sub>2</sub> molecules on the energy demand site divided by the number of H<sub>2</sub> molecules to close the storage cycle through re-hydrogenation on the supply site.

$$OSE = \frac{n_{H_2, \text{usable output on site of demand}}}{n_{H_2, \text{input on site of supply}}} \quad (2)$$

As shown above, 8 moles of H<sub>2</sub> are required in the rehydrogenation of H0-BP to H12-DPM. Therefore, the OSE is 5.86/8 = 73.2% and this is comparable to the efficiency of a scenario in which hydrogen is burned to provide the reaction enthalpy. However, these 8 H<sub>2</sub> are needed on the energy-rich location of LOHC regeneration, where green H<sub>2</sub> is available in high quantities and at low costs. The tremendous advantage of the autothermal hydrogen release concept is with regard to the USC. Here, we compare 5.86 moles usable H<sub>2</sub> per mole H12-DPM for the autothermal dehydrogenation process (partial oxidation with covering the small delta in heat production by hydrogen combustion) with 4.38 moles usable H<sub>2</sub> per mole H12-DPM for the



pure hydrogen combustion scenario. This offers the potential of increasing the USC by up to more than 34% for the H0-DPM/H12-DPM/H0-BP LOHC system. Note, that a higher USC has very strong implications on the cost of installing and operating a LOHC storage cycle for a given application for the following reasons:

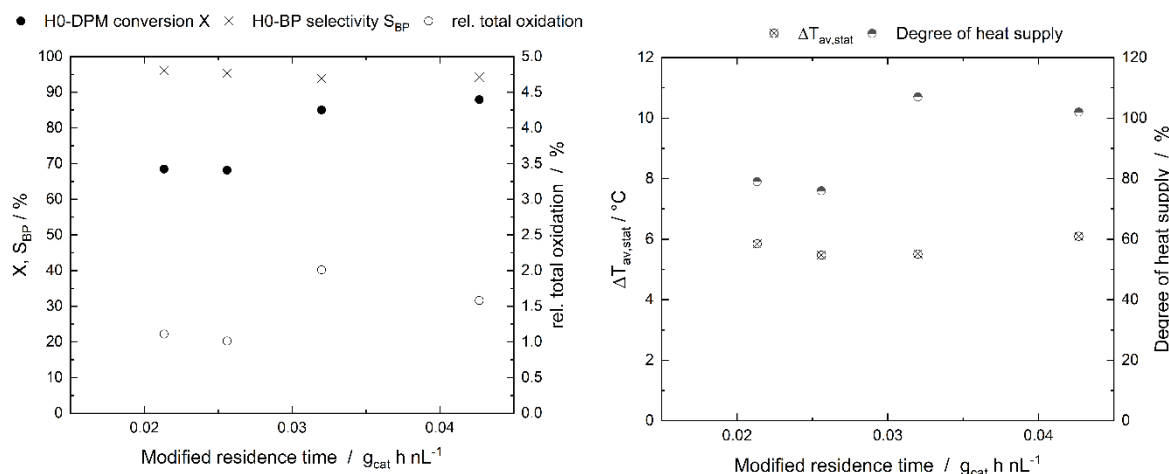
- i) The increase in USC leads to a strong decrease in LOHC investment as 25% less H0-DPM is required to store and transport the same mass of hydrogen;
- ii) The lower mass of H12-DPM required for the same amount of stored and transported hydrogen goes hand-in-hand with smaller LOHC storage volumes and lower transportation cost;
- iii) As up to 34% more hydrogen is released from the same amount of LOHC, hydrogenation and dehydrogenation equipment can be reduced in size, which saves cost and may increase practicability, in particular on the dehydrogenation side if heavy-duty mobility applications are in the focus.

### **Partial oxidation of H0-DPM**

In the following, the partial oxidation of H0-DPM is investigated and reaction parameters are optimized to enable the highest level of selectivity at sufficient productivity to realize the partial oxidation in a similar reactor volume than the respective dehydrogenation from H12-DPM to H0-DPM. Therefore, we present a variation of residence time and LOHC loading. We focus our analysis on the product spectrum formed with a special focus on conditions that reduce total oxidation of the carrier molecule to a minimum.

#### *Residence time variation*

The gas flow in the oxidation reactor influences both the heat evolution and the heat transfer to the dehydrogenation process. Different gas flow velocities are also linked to different residence times of the reactants in the catalyst bed with the risk of overoxidation or total oxidation for too long residence times. To evaluate how sensitive the reaction responds to changes in the gas flow rate, the volumetric flow rate of air through the reactor was varied between 40 nL h<sup>-1</sup> and 90 nL h<sup>-1</sup> (nL h<sup>-1</sup> defined as normal Liters per hour) while the molar ratio of oxygen to H0-DPM, named  $\lambda$  (see section S3 of the ESI<sup>†</sup>) was always kept constant. The corresponding results for the H0-DPM conversion, the H0-BP selectivity and the relative total oxidation are shown in Figure 4 left. Figure 4 right gives information on the heat formation in the oxidation reactor and calculates the degree of heat supply for the corresponding total dehydrogenation of H12-DPM.

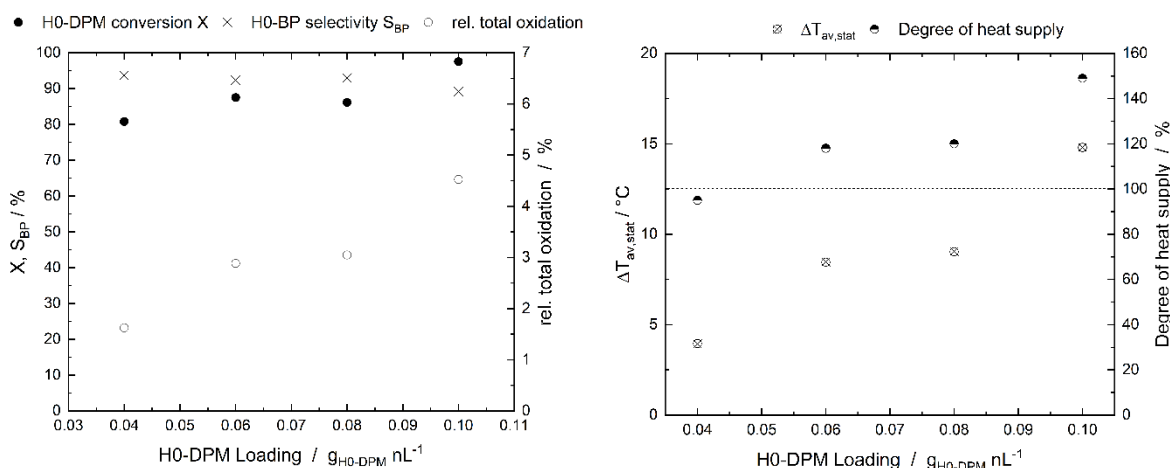


**Figure 4: Left: Conversion, selectivity to benzophenone (H0-BP), and relative total oxidation in the partial oxidation of H0-DPM at varying residence times. Right: Average temperature increases and calculated degree of heat supply for the H12-DPM dehydrogenation at varying residence times. (Set temperature 320 °C, reaction time 5 h, diluted catalyst bed 1:33 [Clariant OxyMax PA Layer 1], catalytic active mass 1.92 g,  $\lambda = 10$ , LOHC-load 0.06 g<sub>H0-DPM</sub> nL<sup>-1</sup>, further information in section S1.3 of the ESI<sup>†</sup>).<sup>[dataset] [26]</sup>**

Note, that the calculated heat formation in the oxidation reactor takes also into account the heat generated by the total oxidation reaction of H0-DPM to CO<sub>2</sub>. Figure 4 shows that with an increasing volumetric gas flow rate and thereby a shortening of the residence time in the reactor, the degree of H0-DPM conversion decreases as expected. More surprisingly, the H0-BP selectivity remains at a high level of over 95% even at low volumetric flow rates and consequently conversions above 85%. Still, a slight decrease in selectivity and slight increase in CO<sub>2</sub> formation can be seen for higher volumetric flows. The calculated degree of heat supply for dehydrogenation is increased at higher residence times which corresponds to the slightly higher total oxidation. Overall, these results lead to the conclusion that H0-DPM converts selectively to H0-BP at temperature conditions (320 °C) suitable for heat export to the H12-DPM dehydrogenation reaction. The formed H0-BP is stable under the applied reaction conditions with very little indication for overoxidation on the catalyst surface. This finding was further underpinned by an experiment, in which H0-BP was fed to the reactor as the starting material of the oxidation reaction. In this stability experiment only minor conversion, minor temperature increase, and very little total oxidation were detected.

#### *H0-DPM loading variation*

The loading of the gas flow with H0-DPM is another important parameter for the partial oxidation reaction. Because of its exothermal nature, a higher feed flow leads to a higher heat generation. The results of the corresponding H0-DPM loading variation between 0.04 and 0.1 g<sub>H0-DPM</sub> nL<sup>-1</sup> are shown in Figure 5.



**Figure 5: Left: Conversion, selectivity to benzophenone (H0-BP) and relative total oxidation in partial oxidation of H0-DPM at varying H0-DPM loadings. Right: Average temperature increase, and calculated degree of heat supply for dehydrogenation for the different experiments. (Set temperature 320 °C, reaction time 5 h, diluted catalyst bed 1:33 [Clariant OxyMax PA Layer 1], catalytic active mass 1.92 g,  $\lambda = 10$ , gas flow 60 nL h<sup>-1</sup>, further information in section S1.3 of the ESI<sup>†</sup>).<sup>[dataset] [26]</sup>**

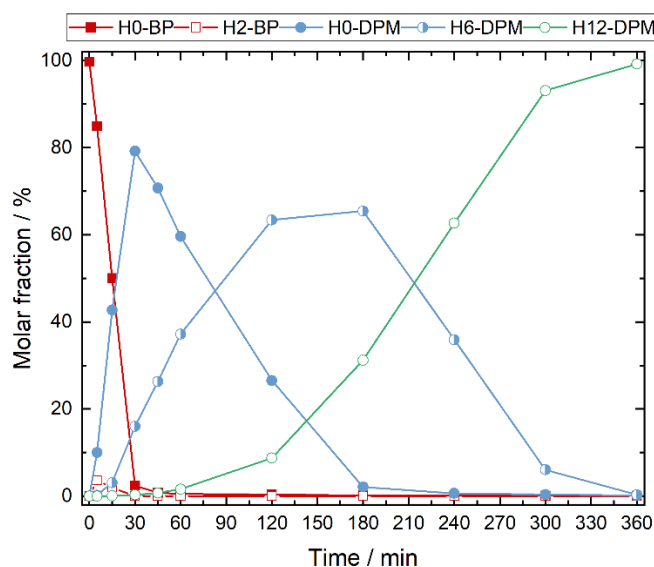
The results obtained are dominated by the incomplete heat removal from the reactor indicated by the increasing  $\Delta T_{av,stat}$  for higher H0-DPM flows (Figure 5, right). Therefore, the conversion and the relative total oxidation goes up with higher H0-DPM flows, while the selectivity drops below 90% for the highest loading. Due to the high degree of total oxidation at higher H0-DPM flow rates, the degree of heat supply is close to or above 100%. The results clearly indicate that a higher H0-DPM loading leads to an increased heat generation in the reactor. This requires an efficient heat transfer, e.g. to the H12-DPM dehydrogenation reaction, to maintain the reactor temperature at the intended level.

It is noteworthy, that all partial oxidation reactions described here have been obtained with a commercial oxidation catalyst that has been optimized for the oxidation of o-xylene to phthalic anhydride. Even without any optimization of this catalyst to the particular demands of H0-DPM oxidation, most of our results indicate less than 3% total oxidation at high H0-DPM conversion and at temperatures suitable for heat transfer to the H12-DPM dehydrogenation reaction.

### Regeneration of H12-DPM from H0-BP by hydrodeoxygenation

To close the entire hydrogenation/dehydrogenation/partial oxidation/regeneration cycle for hydrogen storage with autothermal hydrogen release it is crucial to accomplish the last step, the re-hydrogenation of H0-BP to H12-DPM also in very high selectivity. This reaction represents a hydrodeoxygenation step where the ketone functionality is first hydrogenated, followed by water elimination and saturation of the so-formed double bond. Note, that the water formed during complete hydrodeoxygenation adds at the reaction conditions of 180 °C around 10 bar to the total pressure in the reactor.<sup>[22]</sup> As we have chosen 30 bar total pressure to

carry out this hydrodeoxygenation reaction, the hydrogen partial pressure in the reactor decreases to 20 bar after complete water release (neglecting the partial pressures of Hx-DPM and H0-BP at these conditions). However, this hydrogen partial pressure is still sufficient for the subsequent ring hydrogenation of the H0-DPM intermediate formed in the first step to obtain the final product H12-DPM. The course of the entire hydrogenation from H0-BP to H12-DPM is shown in Figure 6. This reaction has been described previously in the literature as undesired side reaction in attempts to hydrogenate H0-BP to dicyclohexylmethanol.<sup>[23]</sup>



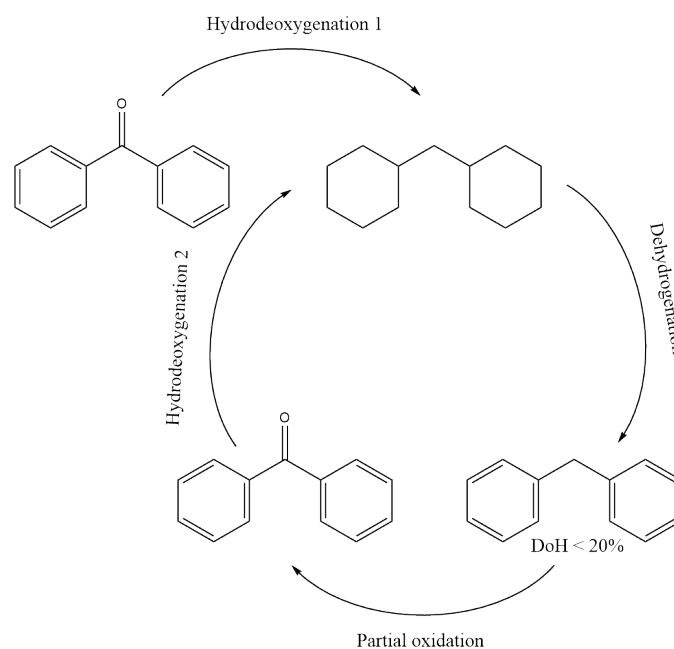
**Figure 6: Hydrodeoxygenation of H0-BP to H12-DPM to close the entire hydrogen storage cycle with autothermal hydrogen release – composition of the reaction mixture over time in a batch hydrodeoxygenation experiment (180 °C and 30 bar H<sub>2</sub>; catalyst Palladium on activated carbon (Sigma Aldrich 75993); H0-BP: Pd = 1000:1, further information in section S1.1 of the ESI<sup>†</sup>).[dataset] [26]**

As can be seen, H0-BP and the intermediate H2-BP undergo rapid dehydroxygenation to H0-DPM that itself is quickly consumed towards H12-DPM. The slowest step in the sequence is the hydrogenation of H6-DPM to H12-DPM. Most interestingly, the reaction sequence is highly selective and no products outside the intended consecutive path have been detected in our GC analysis. With the applied Pd/C catalyst, the hydrogenation of the oxygen functionality and the subsequent hydrodeoxygenation are clearly faster than the hydrogenation of the aromatic rings. As stated above, the hydrodeoxygenation of H0-BP requires two H<sub>2</sub> molecules more than the pure hydrogenation of H0-DPM. However, this extra hydrogen demand occurs at energy-rich locations with low energy prices and allows us to make use of all reversibly bound hydrogen at the LOHC carrier at the time and location of energy need and high energy cost. Figure 6 also demonstrates that the H0-BP hydrogenation time can be adjusted in a way that mainly H0-DPM (with a little bit of H6-DPM) forms in the hydrogenation. This offers the possibility to conduct the hydrodeoxygenation in a dedicated reactor optimized for water removal from H0-BP and merge the resulting largely oxygen-free product mixture then with

oxygen-free LOHC compounds from “normal” dehydrogenation in a reactor and under conditions optimized for aromatics hydrogenation.

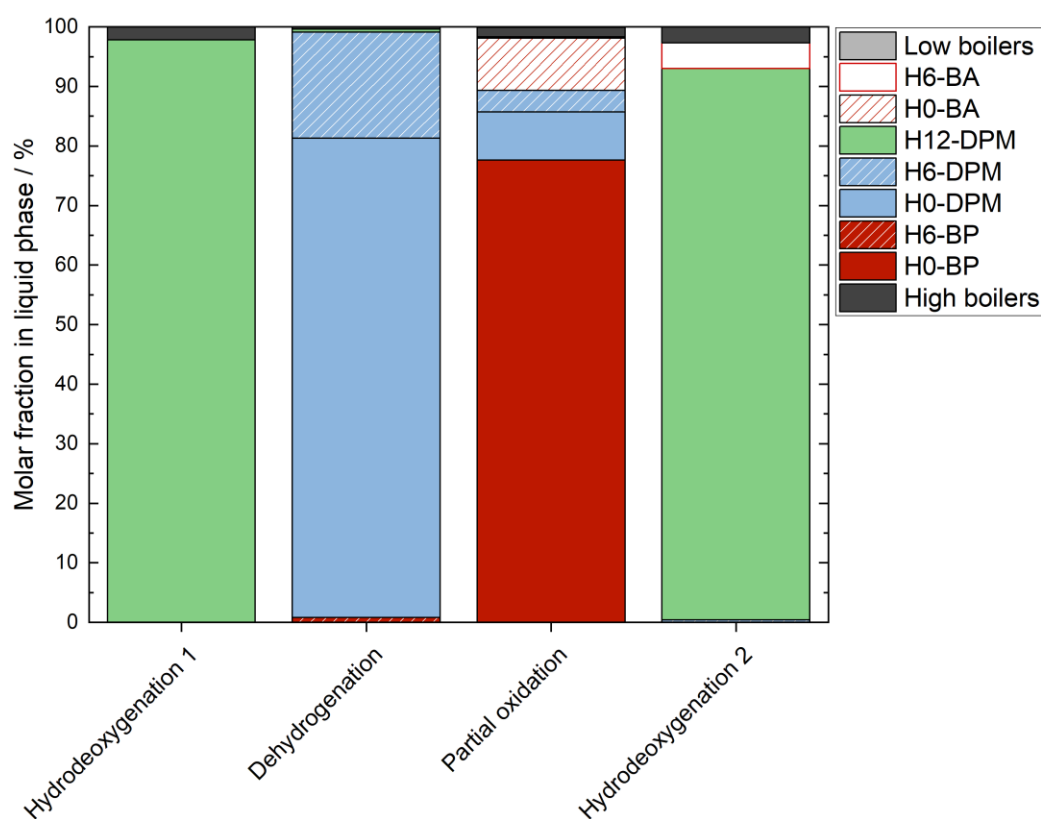
### Complete hydrogen storage cycle involving autothermal hydrogen release

To demonstrate the feasibility of the new LOHC storage cycle including autothermal hydrogen release and H12-DPM regeneration, a complete cycle with all reaction step in sequence was conducted. For this purpose, we used one defined starting sample and applied the reaction product of one step as starting material for the subsequent step. This allows us to reveal potential challenges that may occur from the different reactivity of reaction intermediates from the precedent step for the subsequent step or the entire sequence. Overall, four reaction steps were conducted, as shown schematically in Figure 7. As expected for hydrogen storage in a technical LOHC system, the H12-DPM dehydrogenation was carried out to reach a remaining degree of hydrogenation (DoH) of below 20% (corresponding to more than 80% release of the releasable hydrogen). Consequently, a technical mixture of H0-DPM and some H6-DPM with a DoH of 12% was used as feed for the partial oxidation reaction in this case.



**Figure 7: Schematic representation of the full LOHC storage cycle including autothermal hydrogen release and H12-DPM regeneration in the LOHC system H0-DPM/H12-DPM/H0-BP.**

All reactions were carried out in the same reaction equipment as used previously for the single individual reactions. After each reaction step the composition of the liquid LOHC phase was analyzed, and these results are shown in Figure 8. It should be noted that a certain loss of low-boiling substances during the transfer and handling of the reaction mixtures in the fume cupboard cannot be ruled out. The main products listed in Figure 8 should not be affected due to their very low vapor pressures.



**Figure 8:** Molar composition of the LOHC reaction mixture after each individual step of the hydrogenation/dehydrogenation/partial oxidation/regeneration cycle exemplified for the LOHC system H0-DPM/H12-DPM/H0-BP. Hydrodeoxygenation 1: 24 h in a 600 ml autoclave at 180 °C and 30 bar H<sub>2</sub>, Pd on activated carbon (Sigma Aldrich 75993), H0-BP: Pd = 1000:1. Dehydrogenation: 24 h in an semi-batch glas setup (section S1.2 of the ESI<sup>†</sup>), 255 °C, 200 mL min<sup>-1</sup> argon overflow, Pt on aluminum oxide [Clariant Elemax D102]. Partial oxidation: set temperature 320 °C, reaction time 5 h, diluted catalyst bed 1:33 [Clariant OxyMax PA Layer 1], catalytic active mass 1.92 g,  $\lambda = 10$ , gas flow 60 nL h<sup>-1</sup>, LOHC-load 0.06 g nL<sup>-1</sup>. Hydrodeoxygenation 2: 24 h in a 100 mL autoclave at 180 °C and 30 bar H<sub>2</sub>, Pd on activated carbon (Sigma Aldrich 75993); H0-BP: Pd = 750.[dataset] [26]

We started the sequence with a first hydrodeoxygenation reaction of H0-BP. The latter was applied in the purchased technical quality and contained 2% of high boiling compounds. As expected from our individual hydrodeoxygenation studies before, the reaction proceeded highly selectively and provided pure H12-DPM except for the high boilers that were presumably also hydrogenated to hydrogen-rich high boiling compounds.

During the subsequent dehydrogenation, the reaction mixture obtained from the first hydrodeoxygenation was used as starting material for hydrogen release. We adjusted the reaction time to obtain 80% of fully dehydrogenated H0-DPM. The rest of the reaction mixture was composed of H6-DPM and of the now mostly dehydrogenated high boiling components, only traces of H12-BT were presented in the obtained product mixture from dehydrogenation.

Using this reaction mixture as starting material for the subsequent partial oxidation allowed us to study not only the reaction of H0-DPM to H0-BP but also the influence of H6-DPM and of the other components in the mixture on catalyst stability and selectivity.

Interestingly, the subsequent partial oxidation step of this mixture with the here-applied  $\text{VO}_x/\text{TiO}_2$  catalyst was highly selective for the conversion of H0-DPM to H0-BP, but the presence of H6-DPM increased the formation of benzoic acid (H0-BA) and of  $\text{CO}_2$ . The amount of detected  $\text{CO}_2$  in the off-gas corresponded to a total oxidation of 6.8% (compared to less than 3% in the experiments with pure H0-DPM as feedstock). The formation of H0-BA can be explained by a C-C breaking reaction that splits the two rings of H6-DPM. While one aromatic part underwent oxidation to H0-BA, the other one led on the  $\text{VO}_x/\text{TiO}_2$  catalyst mostly to total oxidation. Similar reactivity of  $\text{VO}_x/\text{TiO}_2$  catalysts has been described in the literature by Dias et al.<sup>[24]</sup>, and Richter et. al.<sup>[25]</sup>. These previous findings provide interesting mechanistic insights for a targeted catalyst material development to enable more selective partial oxidation of H0-DPM/H6-DPM mixtures in the future. An alternative way to circumvent the problematic selectivity of the H6-DPM oxidation is to prolong the H12-DPM dehydrogenation times in the dehydrogenation step to minimize H6-DPM in the mixture that enters the partial oxidation reactor.

During the subsequent hydrodeoxygenation, all Hx-DPM and Hx-BP species were converted to H12-DPM. Part of the H0-BA formed during the oxidation step was hydrogenated to cyclohexyl carboxylic acid (H6-BA). While this compound, in theory, could contribute to the hydrogen storage capacity of the system, it should be the goal of future development work to limit the level of molecular transformation to C6 species in the partial oxidation step to a minimum. The formation of C6 species in the system may change the physico-chemical properties of the storage liquid over time which increases complexity in all subsequent reaction and separation steps. Overall, we were able to demonstrate the feasibility of the full autothermal LOHC cycle. While the investigated H0-DPM/H12-DPM/H0-BP system provides the necessary low melting points of the storage liquid in all states, room for improvement of the applied catalysts, reaction conditions and operation strategies has clearly been identified.

## Conclusion and outlook

The use of hydrocarbon-based LOHC systems is a promising option for the infrastructure-compatible chemical storage and transport of hydrogen. However, for hydrogen applications where no waste heat above 250 °C is available, the provision of the required reaction heat for the endothermic hydrogen release poses a challenge that has for such cases complicated the effective and efficient use of this technology so far.

Herein, we have demonstrated the concept of autothermal LOHC dehydrogenation, an innovative concept that enables hydrogen release from the LOHC system without burning part

of the released hydrogen and without using any external heat supply. The concept involves a deep energetic discharge of the LOHC carrier in two, heat integrated steps: i) the release of the reversibly bound hydrogen in an endothermal dehydrogenation reaction; ii) the exothermal partial oxidation of the uncharged carrier (after separation from hydrogen) at a temperature level that allows heat transfer to the dehydrogenation reactor. This innovative concept has been exemplified and evidenced for the low-melting system dicyclohexylmethane (H12-DPM)/diphenylmethane (H0-DPM)/benzophenone (H0-BP). From a technological perspective the new concept increases the usability of the released hydrogen for this LOHC system by up to 30% compared to heat provision by hydrogen combustion.

We first investigated the two critical new steps (partial oxidation, hydrodeoxygenation, dehydrogenation) of the new autothermal storage cycle individually using pure compounds as starting materials. The partial oxidation of H0-DPM to H0-BP was found to proceed in a very stable and selective manner using a commercial  $\text{VO}_x/\text{TiO}_2$  catalyst at temperatures of 320 °C. For a specific parameter combination matching the dehydrogenation heat demand by the exothermal partial oxidation (set temperature: 320 °C, reaction time: 5 h, diluted catalyst bed 1:33 [Clariant OxyMax PA Layer 1], catalytic active mass: 1.92 g,  $\lambda = 10$ , gas flow: 60  $\text{nL h}^{-1}$ , LOHC-load: 0.08  $\text{g}_{\text{H0-DPM}} \text{nL}^{-1}$ ) a H0-DPM conversion of 80% resulted in a H0-BP selectivity of 93% with less than 1.7% of total oxidation. The regeneration of the oxidized LOHC compounds through hydrodeoxygenation and hydrogenation was first tested by converting pure H0-BP to H12-DPM. Using a Pd on C catalyst at 30 bar hydrogen pressure and 180 °C, the reaction proceeded with over 99% selectivity and sufficiently high rates. The coupling product water is then separated from the LOHC material prior to the subsequent dehydrogenation by phase separation. In view of the very low water solubility of H12-DPM, this is a simple process step.

Finally, the full cycle of hydrodeoxygenation, dehydrogenation, partial oxidation and a second hydrodeoxygenation was conducted starting with technical quality H0-BP. Our aim was to find out whether real product mixtures from the cycle (including reaction intermediates and side products) would affect the autothermal storage cycle. While the need for a specific catalyst development becomes visible - in particular for the partial oxidation reaction in the presence of H6-DPM – the obtained results are very encouraging as still all steps proceeded with high activity and very good selectivity. Thus, the results obtained so far represent an excellent starting point for further catalyst and process optimization. We also anticipate that specific hardware developments can further improve the proposed process scheme. A more effective heat transfer from the exothermal partial oxidation to the endothermal dehydrogenation will help to avoid hot spots, which still occurred in our current reaction setup.

Overall, this fundamental study shows the very high potential of autothermal hydrogen release from LOHC systems by partial oxidation. We anticipate that this new approach is particularly



suitable for applications that i) benefit from the higher usable proportion of LOHC-bound hydrogen, ii) where no external heat supply is available, and iii) where a power-dense and compact design of the release unit is desired. These specific characteristics are fulfilled in most heavy-duty mobility applications where the installation space is very limited and usually no external high-temperature heat sources is available.

Based on the positive results shown for the partial oxidation of H0-DPM, the partial oxidation of technically used LOHC molecules like benzyltoluene will be studied next to get the concept one step closer to commercial application. The similarity of the molecules H0-DPM and H0-BT – only one additional methyl-group – promises feasibility of the concept also for this LOHC system, even if a more complex reaction network is expected for benzyltoluene. Adapting the catalyst and the reaction conditions to the new reactant is necessary and a current focus of our research.

## Author contributions

**Fabian Siegert<sup>†</sup>**: conceptualization; investigation, data curation, data discussion, and analysis (selective oxidation, hydrogen storage cycle); methodology (definitions); writing – original draft.

**Michael Gundermann<sup>†</sup>**: conceptualization; investigations (DSC); data curation, data discussion, and analysis (selective oxidation); methodology (gas phase analysis, DSC, SLE modeling, definitions); visualization; writing – original draft.

**Lukas Maurer**: conceptualization; investigation, data curation, data discussion and formal analysis (hydrodeoxygenation, dehydrogenation, hydrogen storage cycle); methodology (gas chromatographic analysis hydrodeoxygenation and dehydrogenation); visualization; writing – original draft.

**Simon Hahn**: formal analysis (energy assessment); visualization; writing – original draft.

**Jonas Hofmann**: preliminary investigation (hydrodeoxygenation), data curation (hydrodeoxygenation).

**Max Distel**: conceptualization; investigations (selective oxidation), methodology (gas chromatographic analysis selective oxidation).

**Johannes Ascherl**: investigations (selective oxidation).

**Karsten Müller**: formal analysis (thermodynamics, substance data); project administration.

**Moritz Wolf**: conceptualization; project administration; supervision.

**Patrick Preuster:** conceptualization; project administration; supervision.

**Franziska Auer:** conceptualization; data curation and discussion (hydrogen storage cycle); visualization; project administration; supervision; writing – original draft.

**Michael Geisselbrecht:** project administration; data discussion; supervision; writing – review & editing.

**Peter Wasserscheid:** conceptualization; data discussion; funding acquisition; project administration; resources; writing - review, editing.

† shared first authorship

## Conflicts of interest

Peter Wasserscheid is founder and minority shareholder of the company Hydrogenious LOHC technologies ([www.hydrogenious.net](http://www.hydrogenious.net)) that offers commercially hydrogen storage systems based on the LOHC technology. There is no conflict of interest to declare with regard to the specific scientific results reported in this paper.

## Data availability

Data for this article, including GC data and datasets for diagrams are available at zenodo under DOI 10.5281/zenodo.13132266. Further data used to support the findings of this study can be made available by the corresponding authors upon request.

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## Notes and references

‡ These authors contributed equally to this work.

† Electronic supplementary information (ESI) available.

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