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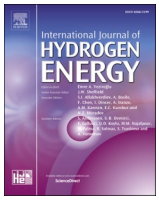

Storage stability in the liquid organic hydrogen carrier system benzyltoluene/perhydro benzyltoluene

Julian Henseler [a], Michael Geißelbrecht [b], Nils Tippkötter [c], Peter Wasserscheid [a,b,d,*]

[a] Forschungszentrum Jülich GmbH, Institut für nachhaltige Wasserstoffwirtschaft, An der deutschen Welle 7A, 52428, Jülich, Germany
[b] Forschungszentrum Jülich GmbH, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IET-2), Cauerstraße 1, 91058, Erlangen, Germany
[c] Fachbereich 3 - Chemie und Biotechnologie, Fachhochschule Aachen, Heinrich-Mußmann-Straße 1, 52428, Jülich, Germany
[d] Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058, Erlangen, Germany

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ABSTRACT

Liquid organic hydrogen carriers (LOHCs) offer a promising option for hydrogen logistics, as they use the existing distribution system for liquid energy carriers to transport hydrogen in chemically bound form. Compared to other technologies, LOHC systems are most competitive when hydrogen needs to be stored for extended periods of time or transported over longer distances. This means that the LOHC material spends most of its time in storage tanks or transport containers, while the time share under hydrogenation/dehydrogenation conditions is comparatively short. Although there are numerous studies that have investigated the stability of LOHC compounds under the conditions of catalytic hydrogenation/dehydrogenation reactions, there has been a lack of detailed investigations into the storage stability of these hydrogen storage compounds. With this article, we aim to close this gap for the specific example of the LOHC system benzyltoluene (H0-BT)/perhydro benzyltoluene (H12-BT), which has attracted considerable industrial interest in recent years. Specifically, we investigate the stability of this system against oxidation in the presence of air and determine the most relevant oxidation products. It turns out that H0-BT is more susceptible to oxidation than H12-BT. Low temperatures reduce the likelihood of oxidation upon contact with air while the presence of sunlight enhances the formation of oxidation products. Replacing air contact with a nitrogen atmosphere prevents any alteration of the stored LOHC material, even at elevated storage temperatures. All oxidation products from storage in air can be regenerated in the subsequent hydrogenation process, with these impurities having only a minor impact on the performance of the hydrogenation catalyst.

1. Introduction

Hydrogen plays a key role in the transition of our current fossil-based energy system to a fully renewable-based one for the future. Safe and cost-efficient storage and transport of hydrogen is a key element for making such transition economically successful. In its elemental form hydrogen storage and transportation is challenging due to its low volumetric storage density (even in pressurized form) and its wide explosion range. The liquid organic hydrogen carrier (LOHC) technology offers a promising solution. Herein, hydrogen is handled chemically bound to a liquid. The fuel-like nature of hydrogen-rich and hydrogen-lean LOHC compounds enable the further utilization of the storage and transportation infrastructure used today for fossil fuels [1]. The LOHC technology involves the catalytic hydrogenation of a hydrogen-lean LOHC compound at a time and location of energy and hydrogen availability producing the corresponding hydrogen-rich LOHC compound. The latter can be stored and transported like any fuel. At a time and location of hydrogen or energy need, the stored hydrogen can be released in a catalytic dehydrogenation reaction re-forming the hydrogen-lean LOHC compound that can be used for a subsequent storage cycle.

A key aspect of the LOHC technology is the utilization of a given quantity of LOHC material over many storage cycles and over long service time. In most anticipated use cases for LOHC systems, transportation over longer distances and storage over longer periods of time are foreseen [2–4]. A typical number of around 20 hydrogenation/dehydrogenation cycles per year of service has been proposed for technical use cases [5]. Thus, the LOHC material will spend a large proportion of its service time in storage tanks or transportation containers. It is critical for the cyclability of the LOHC material that during

* Corresponding author. Forschungszentrum Jülich GmbH, Institut für nachhaltige Wasserstoffwirtschaft, An der deutschen Welle 7A, 52428, Jülich, Germany.
E-mail address: p.wasserscheid@fz-juelich.de (P. Wasserscheid).

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these extended storage and transport times no deterioration of the LOHC material takes place. This aspect, however, has not been treated in the literature in detail so far.

The LOHC system investigated in this contribution is the benzyltoluene/perhydro benzyltoluene (H0-BT/H12-BT) system. This system has found significant industrial interest in recent times [6–8]. H0-BT/H12-BT is characterized by a very attractive volumetric storage density, wide liquid range, low vapor pressure, low viscosity, and good economic availability [1,2,9,10]. Due to its chemical structure, H0-BT is prone to oxidation at the methylene bridge of the molecule by air. This reactivity has been described in the literature for the structural very similar dibenzyltoluene (H0-DBT) to explain the presence of up to 1 wt% of oxidized compounds in technical H0-DBT [11]. For such catalyst-less, flame-less and spark-less oxidation of organic compounds by atmospheric oxygen the term "autoxidation" has been coined in the literature [12,13]. Autoxidation follows a radical or an ionic reaction pathway including three steps: initiation, propagation, and termination. Parameters like heat, light, and the presence of transition metals influence the formation of radicals or ions in the initiation step and can therefore influence the autoxidation rate of organic hydrocarbons [12,14]. Autoxidation is influenced in addition by the capability of the organic molecule to stabilize the reaction intermediates. In the case of hydrocarbons this capability increases in the order of primary < secondary < tertiary hydrocarbons [15,16]. For unsaturated bounds, the CH_X group adjacent to the bond is prone to autoxidation, as the reaction intermediate at this position can be stabilized by mesomerism [17]. This is the reason why in the H0-BT regioisomers, the methylene bridge (C9) and the methyl group (C14) are the most reactive sites for autoxidation (see Fig. 1, left). For the autoxidation of H12-BT molecules (see Fig. 1, right), in contrast, the tertiary carbon atoms C10, C13, and C1/C2/C3 (depending on the position of the methyl group) are the preferred sites for autoxidation.

Recently, studies by Rullo et al. [19] and Bulgarin et al. [11] reported that oxygen-containing impurities, like dicyclohexylmethanol can negatively affect the catalyst performance through the formation of CO during the dehydrogenation of H12-BT. Moreover, CO in the released hydrogen is critical, if this hydrogen is foreseen for generating power in a proton exchange membrane fuel cell (PEMFC). For this reason, the amount of oxygen-containing impurities in a technical LOHC material has been limited in the DIN specification to an amount of 5000 ppmw for the sourced virgin H0-BT material and to 1000 ppmw for recycled LOHC material [20]. Note, that the higher limit for oxygen-containing impurities for the sourced virgin material is set in the DIN specification expecting that a hydrogenation/dehydrogenation cycle of the LOHC material would reduce the amount of such oxygen-containing impurities [11].

One important piece of information that is currently lacking is whether the storage conditions of BT-based LOHC compounds also influence the amount of oxygen-containing impurities, e.g., through autoxidation processes. This information appears to be essential, as such oxidation products can also have an impact on catalyst activity and stability, both for the hydrogenation of H0-BT and for the dehydrogenation of H12-BT. Therefore, this study aims to i) reveal the general structure of the products formed by autoxidation processes from H0-BT and H12-BT; ii) to investigate the most important parameters influencing this autoxidation, such as, e.g., storage temperature or presence of UV radiation; iii) to provide insight into the influence and fate of LOHC autoxidation products in the catalytic hydrogenation of H0-BT.

2. Experimental

2.1. H0-BT and H12-BT aging experiments under various conditions

Aging experiments of H0-BT and H12-BT were carried out by filling 250 mL of each liquid compound in two separate three-neck round-bottomed flasks. Each flask was heated to 120 °C for 24 h. During the entire time, compressed air was continuously bubbled into the LOHC material in both flasks using a glass pipe.

The long-term stability tests of H0-BT and H12-BT were carried out in 100 mL glass serum bottles, which were filled with 20 mL of the LOHC compound. For the tests at room temperature, the serum bottles were placed in an unheated shaker. For the tests at 55 °C, the serum bottles were placed in an incubation shaker set to 55 °C. For tests at 70 and 80 °C, the serum bottles were placed in a drying oven set to the respective temperature. Sampling was carried out twice a week. The overall test time was four weeks.

To investigate the influence of UV radiation on the aging of the two LOHC materials, the serum bottles were irradiated with UV light in a BioVanguard cleanbench from Baker Company. This cleanbench was equipped with a Philips TUV TL D 30W G13 UV C lamp emitting UV-C radiation mainly at 254 nm with a power of 12 W. The irradiance intensity onto the 1 m^2 lab bench is estimated to be 1.2 mW/cm^2. This translates roughly to a cumulative UV dose of 3 kJ/cm^2 or 62 kJ per sample container (20 cm^2 area) over the whole experimental duration. To put these numbers into context, a day with a medium UV index of 5 (= normal spring/summer day in central Europe) equals to an irradiance intensity of 0.0125 mW/cm^2, 100 times lower than the intensity in our experimental setup. Furthermore, note that sunlight only contains UV-A and UV-B radiation >280 nm. Sampling was carried out twice a week, the overall test time was four weeks.

The influence of a nitrogen atmosphere was investigated by sealing serum bottles airtight with a stopper and flushing them with nitrogen through cannulas for 5 min. The sampling was also carried out through a cannula, and the nitrogen atmosphere was renewed after each sampling. Sampling was carried out twice a week. The overall test time was 30 days.

2.2. Analytical methods

All samples were analyzed immediately after sampling using GC-MS (for identification of the autoxidation products) and the GC-FID (for quantification of the autoxidation products) methodologies described in the following.

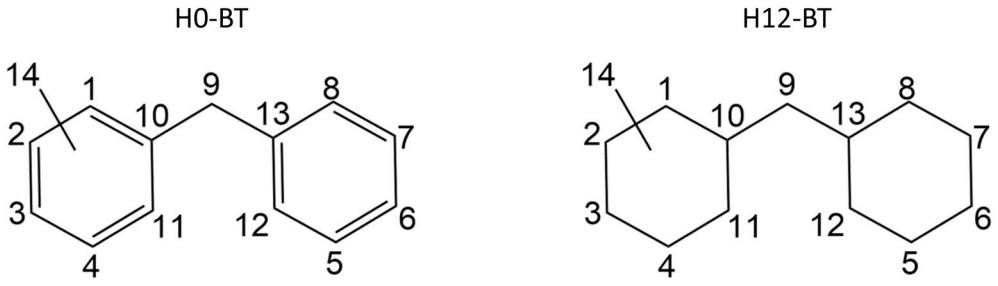

Fig. 1. Chemical structure of H0-BT (left) and H12-BT (right) molecule - the atom numbering was adapted from Henseler et al. [18] to keep consistency within investigations of the H0-BT/H12-BT LOHC system.

The GC-MS setup consisted of a PerkinElmer Clarus 690 GC and an SQ8T quadrupole mass spectrometer. The GC used a Restek Rxi-5HT column (30 m × 0.25 mm x 0.1 µm). The oven program started with an oven temperature of 50 °C, which was increased with a heating rate of 15 °C/min to a final temperature of 380 °C. This final temperature was maintained for 3 min. An injector temperature of 350 °C was set. The injection of 1 µL sample was performed with a split ratio of 1:50. The carrier gas was He, with a flow rate of 1 mL/min. For sample preparation, 20 µL of LOHC material was diluted with 980 µL of dichloromethane (DCM) (volume ratio 1:50). To prevent detector overload by the samples' main components, H0-BT and H12-BT, the mass spectrometric detector was turned off in the retention time range of 4.25–5.20 min. Molecular structures were identified based on a comparison of recorded mass spectra with existing reference spectra from the NIST spectrum library [21].

The GC-FID setup consisted of a Bruker 456 GC-FID equipped with a Restek Rxi-5HT column (30 m × 0.25 mm x 0.1 µm). The GC methodology including the oven temperature program, the sample preparation, sample injection etc. was identical to the GC-MS method above. The GC-FID method was only modified by raising the detector temperature to 380 °C and changing the carrier gas to hydrogen with a flow of 1.7 mL/min.

Due to the large number of degradation products not every single product could be quantified using identical reference material for calibration. Therefore, a mixed standard consisting of multiple aromatic hydrocarbons (see Table 1) spanning over a wide volatility range was used as reference. It was verified that the sensitivity of the heteroatom-free reference material was comparable to the sensitivity of analogous oxygen-containing degradation products (see ESI, Fig. S1). The reference material with the closest retention time to the target substance was chosen for quantification. The retention time and the range used for quantification of each reference substance is shown in Table 1.

A stock solution of the mixed standard was prepared by dissolving 20 mg of naphthalene, 20 mg of fluorene, 20 mg of benzo[a]anthracene, 20 mg of benzo[a]pyrene, 20 mg of coronene, and 10 mg of tetraphenylnaphthacene in 100 mL DCM. Standards were prepared by diluting 20, 40, 80, 160, 320, and 640 µL of the stock solution with DCM to a total volume of 1000 µL.

2.3. Hydrogenation experiments using aged H0-BT samples

To investigate the effect of impurities caused by autoxidation during LOHC storage on the hydrogenation of H0-BT, the reaction was studied comparing reaction rates and selectivities for the use of technical H0-BT (as purchased) and purposedly aged H0-BT (120 °C, 24 h, air) under otherwise identical conditions. For these experiments, 195 g of H0-BT and 6.45 g of a Pt/Pd on Al_2O_3 catalyst (EleMax H101, Clariant, 0.16 wt% Pt; 0.59 wt% Pd) were placed in the reactor. The reaction temperature for hydrogenation was 220 °C, and the hydrogen partial pressure in the reactor was 20 bar in both experiments. In the hydrogenation with purposedly aged H0-BT, the atmosphere in the reactor was replaced after 120 min by venting the reactor atmosphere, purging with nitrogen, and then adding fresh hydrogen up to the intended hydrogen partial pressure of 20 bar. This procedure allowed us to remove water vapor and other gaseous side products from the gas phase of the reactor. Liquid samples were taken and their degree of hydrogenation was determined using a GC-FID analysis protocol as described by Rüde et al. [10] The productivity of the catalyst was calculated in the degree of hydrogenation range of 20 to 50 % since the hydrogenation rate is constant in this range.

Table 1
Retention times, retention time windows for quantification, and boiling points of the reference substances contained in the mixed standard applied for our analyses.

Reference substance	Retention time of the reference substance in min	Retention time range for quantification in min	Boiling point in °C
Naphthalene	4.4	0.0-6.0	218 [22]
Fluorene	7.6	6.0-10.3	294 [23]
Benzo[a]anthracene	12.9	10.3–13.9	437 [24]
Benzo[a]pyrene	14.9	13.9-16.4	496 [25]
Coronene	17.9	16.4-19.5	525 [23]
Tetraphenylnaphthacene	21	19.5-24.0	n.a.

3. Results and discussion

3.1. Identification of oxidation products formed during atmospheric storage

To identify products formed in the presence of atmospheric oxygen during storage, H0-BT and H12-BT were purposedly aged by exposing them to air at 120 °C for 24 h. The GC-MS chromatograms aged samples are shown in Fig. 2.

Note, that the used technical H0-BT and the H12-BT derived thereof through hydrogenation are regioisomeric mixtures (e.g. ortho-H0-BT, meta-H0-BT, and para-H0-BT in the case of the H0-BT). Because autoxidation can occur at different carbon atoms of these regioisomers, countless products can result from oxidation reactions during storage.

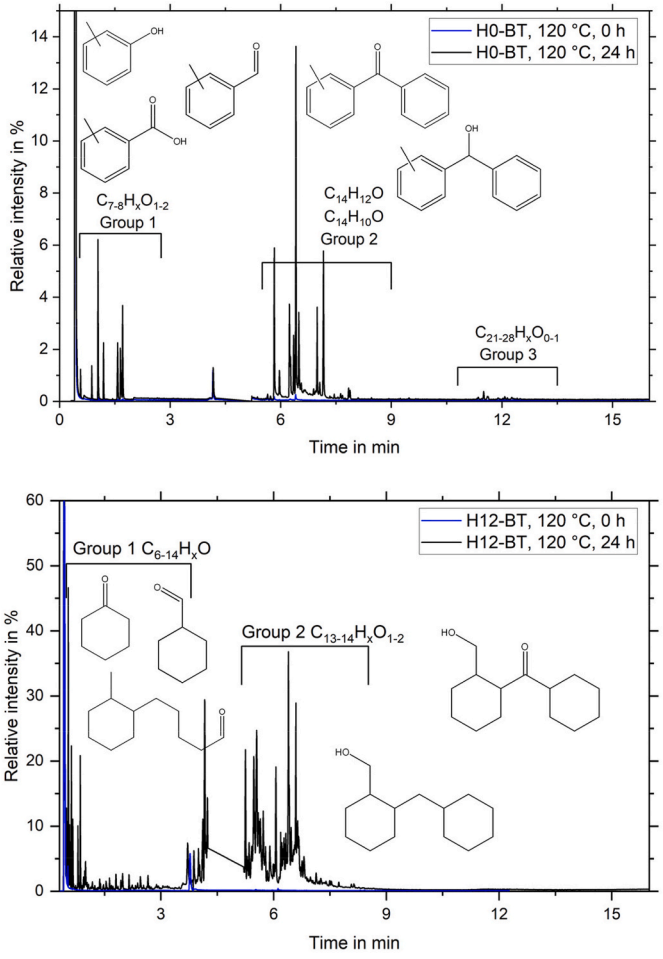

Fig. 2. GC-MS measurement of purposedly aged H0-BT (top) and H12-BT (bottom). Reaction conditions: T = 120 °C; t = 24 h; air atmosphere. It should be noted that the mass spectrometric detector was switched off in the retention time range of H0-BT and H12-BT (4.25-5.20 min) in order to avoid detector overload. These main components of the samples are therefore not visible in the chromatogram.

Due to this complexity, the aim of this contribution is not to identify each individual isomer, but rather to elucidate general autoxidation pathways and to quantify the main structural motifs formed. Therefore, the products identified from LOHC oxidation during storage have been divided into three general classes:

- Group 1 comprises products with a lower number of carbon atoms. The autoxidation can result in a cleavage of molecular structures. The resulting light products have an increased volatility and thus reduced retention time in the gas chromatography compared to the original LOHC molecules H0-BT and H12-BT.
- Group 2 includes substances, in which the basic structure of the initial LOHC molecule is retained but the oxidation of one or more carbon atoms has happened. These products have a slightly lower volatility compared to H0-BT and H12-BT. Therefore, the retention time is slightly increased compared to the two initial LOHC molecules.
- Group 3 comprises products with a higher number of carbon atoms. The autoxidation can lead to the oligomerization of two LOHC molecules, which results in products of higher molar mass, a significantly lower volatility, and, therefore, a significantly higher retention time.

A list of the identified oxidation products and their respective retention times in the chromatographic separation is found in the ESI (Table S1 and Table S2).

For the interpretation of Fig. 2 it is important to consider that the mass spectrometric detector was turned off between the retention time of 4.25 min and 5.20 min to prevent the detector from overloading with the regioisomers of H0-BT and H12-BT, respectively. Therefore, these components are not seen in the spectra shown in Fig. 2.

In the case of H0-BT (see Fig. 2, top), the oxidation products in group 1 consist mainly of molecules with one aromatic system and varying degrees of oxidation. Degradation products in this group are most likely formed by oxidative cleavage of the H0-BT molecule. This includes products such as methylphenols and methylbenzaldehydes, which were also detected in technical H0-BT at a lower concentration level (see ESI Fig. S2). In addition, other oxidation products, such as benzoic acid and acetophenone, are detected.

Group 2 mainly contains H0-BT regioisomers that have been functionalized with oxygen at their methylene bridge (C9), their methyl group (C14), or both. This results in the formation of either an alcohol-, keto-, or aldehyde -functionality.

The substances of group 3 cannot be fully identified by GC-MS analysis because the respective reference spectra for these substances are missing in the used spectrum library [21]. The substances in this group mainly have a mass-to-charge ratio (m/z) of 362 or 378. In the case of the ion m/z 362, this corresponds to twice the mass of the H0-BT molecule similar to the high-boiling condensation products observed in the dehydrogenation of H12-BT [18]. The ion m/z 378 corresponds to twice the mass of the H0-BT molecule plus the mass of an oxygen atom. Because the fragment mass spectra of these substances are very similar to that of H0-BT, we conclude that these substances are products of an oxygen-mediated condensation reaction.

The exact structure of these dimerization products cannot be determined from GC-MS analyses alone. Taking the known mechanism for autoxidation of organic compounds into account [12,17], we can assume that more stable reaction intermediates react preferentially and are particularly prone to recombination reactions. In the case of H0-BT isomers, the aromatic rings stabilize radical reaction intermediates at the methyl group (C14) and the methylene bridge (C9). The latter position is expected to be stabilized most effectively as both aromatic rings are available for stabilization. This position is therefore the most likely site for autoxidation and recombination reactions. A connection between two H0-BT molecules via their methylene bridge (C9) is therefore the most plausible pathway for the oxygen-induced formation of high-boiling side-products.

A GC-MS chromatogram of the purposedly aged H12-BT sample is seen in Fig. 2, bottom. The degradation products in group 1 consist mainly of cycloaliphatic compounds of varying degrees of oxidation, which are formed by the cleavage of the H12-BT isomers. Group 2 degradation products of H12-BT consist of molecules which acquire additional alcohol-, aldehyde-, or keto-functionalities analogous to the group 2 degradation products of H0-BT. However, products of the oxidative degradation of H12-BT shows a significantly greater variety. As qualitative analysis of the reaction products shows, a broad range of oxygenation and cleavage reactions of the aliphatic rings in H12-BT molecules is possible. Thus, as a first difference between H0-BT and H12-BT autoxidation we can state that H0-BT autoxidation offers two clearly preferred reaction sites (C9 and C14) which is not the case in H12-BT autoxidation leading to a broader range of possible oxidation products in the latter case.

Another striking observation in the aging of H12-BT under air at these harsh storage conditions is that no higher molecular weight products of group 3 are formed. This result suggests that the intermediates formed in the oxidation of H12-BT are much less stabilized. Obviously, this reduced level of stabilization shortens intermediate lifetimes in a way that prevents recombination of said intermediates to form dimerization products.

3.2. Impact of temperature

The qualitative investigation of the previous chapter shows that most of the oxidative degradation products in the LOHC material are small aromatic or cycloaliphatic compounds, with mostly one oxygen functionality per molecule. What remains to be investigated is the amount of these degradation products and thus the stability of the LOHC material under various storage conditions. It is known that factors such as high temperature, strong UV light irradiation, and the presence of transition metals can enhance the formation of radicals or ions and thus may accelerate autoxidation processes [12]. Of these factors, the presence of transition metals was not considered in this study assuming that storage tanks made of (stainless) steel or plastic will not lead to relevant levels of transition metal contamination in the LOHC material.

To investigate the influence of the storage temperature, both H0-BT and H12-BT were stored at room temperature, 55 °C, 70 °C, and 80 °C for an extended period of time exposed to an air atmosphere. The amount of oxidative degradation products in the LOHC material was monitored over time using GC-FID. Fig. 3 shows the temperature-dependent formation of oxidation products over time.

Over the extended period of our investigation (total investigation time of 28 days) H0-BT remained stable when stored at room temperature (approx. 23 °C). However, already a storage temperature of 55 °C led to a significant oxidative aging of H0-BT producing more than 2 wt% degradation products after 28 days. When the storage temperature was increased to 80 °C, more than 10 wt% oxygen-induced products (sum of group 1, 2, and 3) were formed.

In contrast, the amount of oxidative aging products is significantly smaller for H12-BT. Relevant amounts of autoxidation product of H12-BT are only seen for the stability experiment at 80 °C (Fig. 3 B). Below this temperature, H12-BT is stable under air atmosphere for the entire investigation time, indicating that these temperatures are insufficient to overcome the activation barrier needed for autoxidation of H12-BT. Thus, H12-BT offers more reaction sites for oxidation but their reactivity is much lower than for the preferred C9 and C14 sites in the case of H0-BT. This makes autoxidation in the case of H0-BT storage much more relevant for the practical application of the H0-BT/H12-BT LOHC system. It is important to note that these generalizations on the different reactivity of H0-BT and H12-BT only hold true for the investigated temperature range.

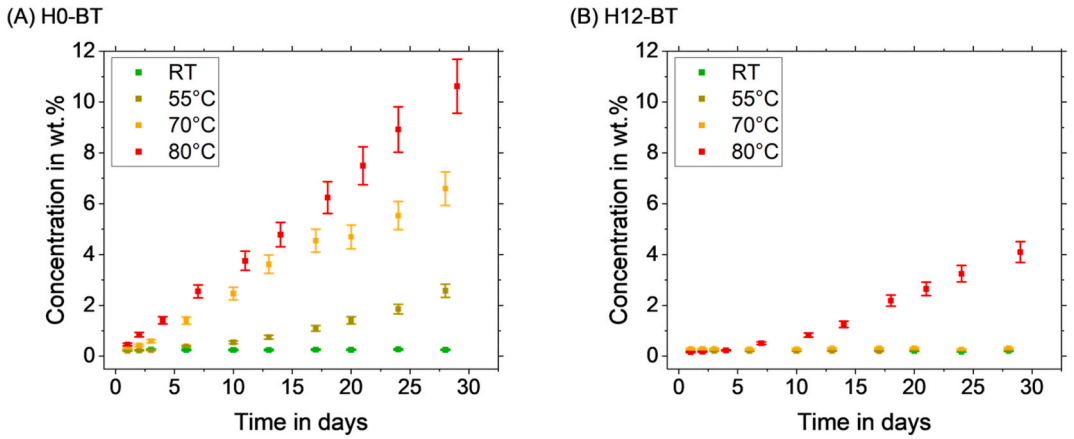

Fig. 3. Total concentration of oxidation products (sum of groups 1, 2, and 3) produced by storing H0-BT (left) and H12-BT (right) in an air atmosphere at different temperatures over time (total time of investigation being 28 days). Error bars indicate the general error resulting from the accuracy of the GC quantification method. Accuracy was measured by the recovery rate, which ranged from 90 to 110 %.

3.3. Impact of light

The influence of solar radiation can be a factor in the storage stability of H0-BT and H12-BT if the LOHC material is stored in light-transmissive tanks, such as intermediate bulk containers (IBCs). To simulate such solar radiation in our laboratory experiments, H0-BT and H12-BT were exposed to UV light at room temperature and the content of the resulting impurities was monitored over up to 30 days. In the H12-BT samples, no signs of oxidative degradation were detected, whether or not the samples were exposed to UV radiation. This is understandable given the fact that H12-BT shows very low UV light absorption properties and thus excitation does not occur. H0-BT, in contrast, absorbs UV light through its aromatic character. As can be seen in Fig. 4A this results in a significant product formation while without the UV light H0-BT proved fully stable at room temperature over the same period of time (see Fig. 4B).

H0-BT forms in total 6.9 wt% of group 1-3 products when exposed to the UV irradiation for 30 days. This amount is comparable to the storage at 70-80 °C in the absence of UV light. However, we need to mention that the UV light source applied in our study used UV light on a higher energy level and with an approximal 100 x higher irradiance intensity compared to a regular spring/summer day in central Europe (UV index of 5). The degradation effects of light irradiation observed in this study are therefore greatly enhanced in comparison to normal sunshine. Nevertheless, we show that light irradiation should not be neglected as a degradation factor during transport and storage of LOHC material. Note, that we took care in our experiment to exclude that the light source heats up the H0-BT sample over the course of the stability experiment (see temperature log in Fig. S3). Therefore, we can rule out an indirect influence on the temperature on the oxygen- and light-induced reactivity.

3.4. Storage stability of BT-based LOHC systems under nitrogen atmosphere

In practical use cases of the LOHC technology it may happen that storage at slightly elevated temperatures cannot be avoided easily, e.g. if hydrogen is to be stored and transported in countries with hot summer temperatures. Therefore, we were interested whether temperature-induced transformation of the BT-based LOHC material during storage can be fully suppressed using a nitrogen atmosphere in the storage tank. A similar approach is applied in the food industry to extend the shelf life of food [26]. For the respective experimental tests H0-BT and H12-BT samples were sealed in two different bottles under a nitrogen atmosphere and exposed to elevated temperature and UV light, respectively, in analogy to the experiments under atmospheric conditions described above.

Fig. 5 shows the concentration of group 1-3 products formed from H0-BT during storage at 80 °C under air atmosphere (Fig. 5A) and under nitrogen atmosphere (Fig. 5B). While significant oxidation of the BT-structure takes place in the case of storage under air forming mainly

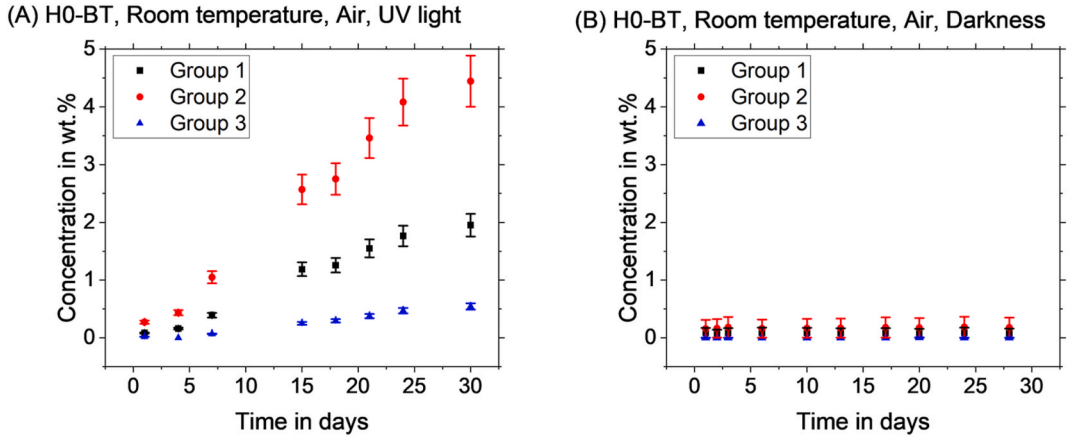

Fig. 4. Product formation from H0-BT (groups 1-3 are shown individually) under atmospheric conditions and at room temperature, (A) with and (B) without irradiation with UV light. Error bars indicate the general error resulting from the accuracy of the GC quantification method. Accuracy was measured by the recovery rate, which ranged from 90 to 110 %.

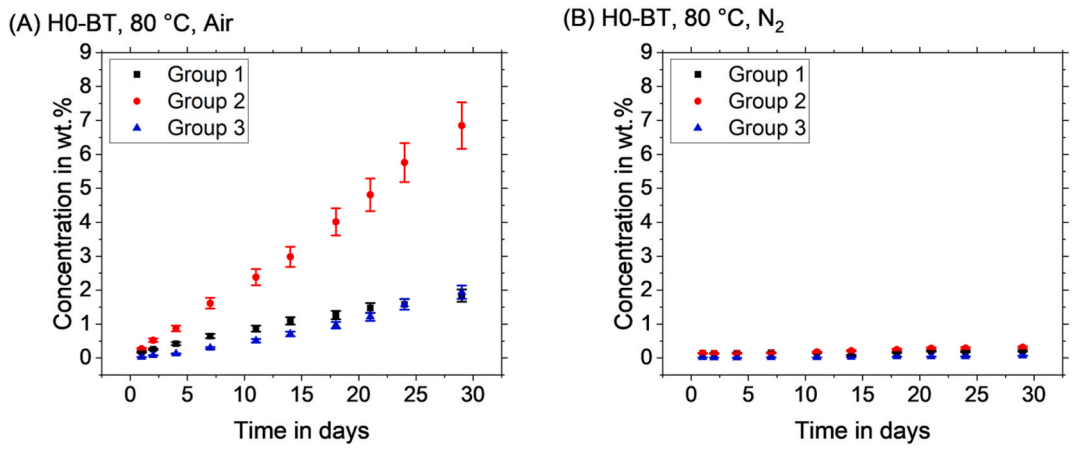

Fig. 5. Concentration of degradation products in H0-BT (separate group 1, 2, and 3) when stored at 80 °C under an air atmosphere (A) or under a nitrogen atmosphere (B). Error bars indicate the general error resulting from the accuracy of the GC quantification method. Accuracy was measured by the recovery rate, which ranged from 90 to 110 %.

group 2 products, full H0-BT stability is maintained over the complete testing time of 28 days. Thus, inertization prevents the formation of degradation products very effectively, which comes as no surprise given the established technical application of H0-BT as heat transfer oil. Full stability at 80 °C under nitrogen atmosphere was also observed for H12-BT (see ESI Fig. S4).

Fig. 6 extends our stability tests under nitrogen atmosphere to include the effect of irradiation with UV light. These experiments were conducted at ambient temperature. Fig. 6B demonstrates that also under UV light almost no side-product formation is observed during the storage period of 28 days if an inert nitrogen atmosphere is applied. On very close inspection, it can be found that the content of group 3 products increases during the storage time from 0.00 to 0.09 wt% despite the inertization with nitrogen. GC-MS analysis shows that these trace products have approximately twice the mass of the H0-BT molecule. We therefore assume that these trace products origin from the recombination of radicals formed by UV light excitation in the absence of oxygen. Due to the very small content of these dimer products under nitrogen atmosphere we conclude that inertization is a very effective way to prevent light-induced degradation of BT-based LOHC compounds. No measurable degradation of H12-BT was found under UV light irradiation and nitrogen atmosphere, as expected.

3.5. *Influence of oxygen-induced degradation products on H0-BT hydrogenation*

The previous sections have shown that under certain storage conditions oxygen-induced products form in significant amounts in BT-based LOHC systems. For the technical use of these LOHC systems it is therefore of high relevance to understand how these products influence the hydrogenation and dehydrogenation of such LOHC material. As storage effects were quantitatively much more pronounced for H0-BT storage we focus our investigation on the performance in the H0-BT hydrogenation process that has to cope with these impurities. It is worth mentioning in this context that studies on the effect of oxygen-containing impurities on the dehydrogenation of H12-BT have already been reported in the literature [19]. These studies have shown that such impurities reduce the productivity of the Pt/Al_2O_3 dehydrogenation catalyst.

To study the effect of oxygen-induced impurities on the H0-BT hydrogenation with relevant levels of impurity, the investigations have been carried out with a purposedly aged H0-BT sample (120 °C, 24 h, air) with a content of impurities in the sample of 6.6 wt% as determined by GC-FID. This level is about 20 times higher than the level of these impurities in the virgin commercial H0-BT material. During the hydrogenation reaction, the content of the oxygen-containing impurities was monitored via GC-MS. Fig. 7 shows the respective GC-MS chromatograms. The concentration of oxygen-containing products is significantly reduced already at a degree of hydrogenation (DOH) of 20 %. For a DOH

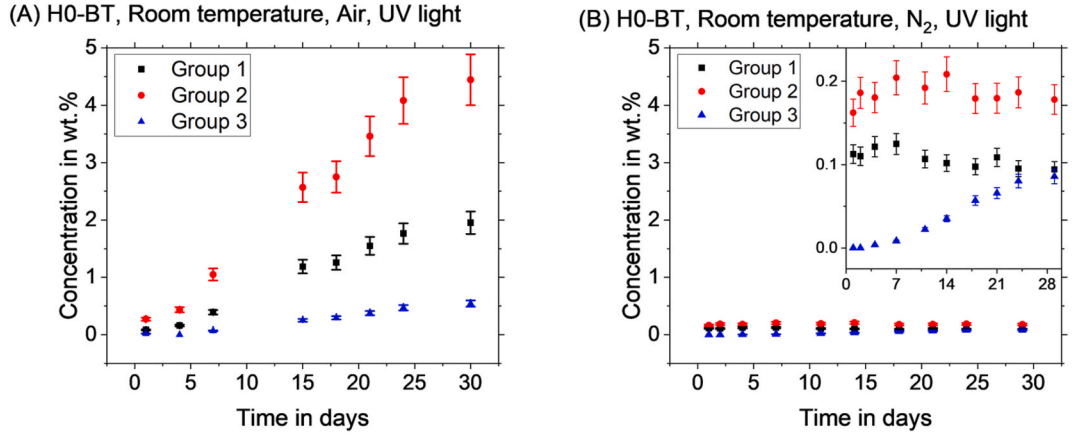

Fig. 6. Concentration of group 1-3 products formed from H0-BT stored at room temperature under UV radiation (A) and under nitrogen atmosphere (B). Error bars indicate the general error resulting from the accuracy of the GC quantification method. Accuracy was measured by the recovery rate, which ranged from 90 to 110 %.

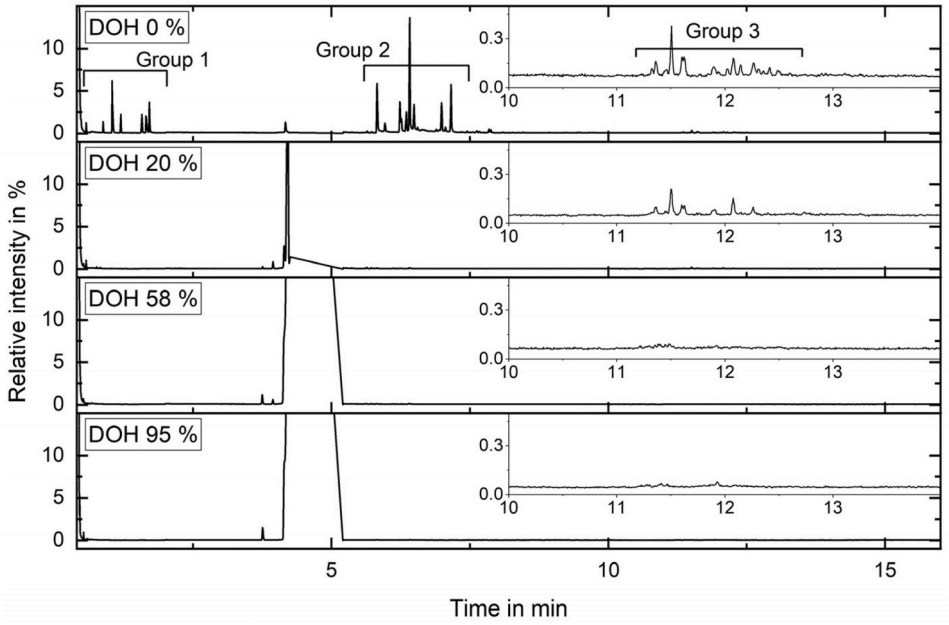

Fig. 7. GC-MS recordings of samples from the hydrogenation of purposedly aged H0-BT. Reaction conditions: T = 220 °C; p_{H2} = 20 bar; stirring speed = 1200 rpm; m_{kat} = 6.4 g; $m_{H0\text{-}BT}$ = 195 g; t = 280 min; catalyst = Pt + Pd/Al_2O_3. The reactor atmosphere was exchanged after a reaction time of 120 min (DOH approximately 20 %). The relative intensity scales all refer to the highest intensity measured in the first sample (DOH 0 %) and are therefore comparable between samples. To protect against high substance quantities, the mass spectrometric detector was switched off between a retention time of 4.25 and 5.20 min (retention time window H0-BT). The deflection between 4 and 5 min in the chromatograms with DOH 58 % and 95 % is triggered by a brief detection of H12-BT, followed by shutdown of the detector.

of 50 % no oxidized products can be detected in the reaction mixture.

Side-products of group 1 are less traceable over the course of the reaction since they have a high volatility and are thus not detected by sampling the liquid reaction mixture. Furthermore, these side products are potentially removed from the reactor through the exchange of the reactors atmosphere. Side-products of group 3 are also less traceable since they show an overall low intensity. Therefore, investigations focus on the side products of group 2 to elucidate the reaction pathway of oxygen-containing side-products during the hydrogenation of aged H0-BT. General trends observed for side products in group 2 are expected to be also applicable to groups 1 and 3.

There are two possible reasons for the disappearance of oxygen-containing product peaks from group 2:

- The aromatic molecules are hydrogenated and the original side-product peaks are exchanged with their hydrogenated versions which show a different retention time. The oxygen functionality remains in the hydrogenated LOHC molecule.
- Hydrodeoxygenation takes place and removes the oxygen functionality from the molecule. Side-product peaks are exchanged by their deoxygenated versions, which are identical with the initial LOHC molecule (H0-BT) and are therefore added to the peak of the bulk reactants. The oxygen functionality is removed from the side-products and water is formed as the reaction product.

Siegert et al. showed in their study of benzophenone hydrogenation (180 °C, 30 bar H_2, Pd/C) that hydrodeoxygenation (removal of the oxygen-functionality through water formation) proceeds significantly faster than the subsequent hydrogenation of the aromatic rings to form dicyclohexylmethane [27]. In our case, such hydrodeoxygenation activity of group 2 impurities would form H0-BT which is hard to quantify in the large excess of H0-BT. Nevertheless, oxygen-containing cycloaliphatic reaction products, such as dicyclohexylmethanol or dicyclohexylmethanone, were not detected in our hydrogenation experiments, which confirms that oxygen removal happens before aromatics hydrogenation.

What remains to be discussed is the impact of the hydrodeoxygenation and its reaction products on the performance of the H0-BT hydrogenation reaction. The first and foremost effect is the loss of valuable hydrogen through the hydrodeoxygenation reaction of oxygen-containing products from the storage process. Taking the extreme example of a 6.6 wt% methyl benzophenone content in H0-BT (quantity chosen according to the total group 1-3 content in our aging experiment), around 1.1 % of the storable hydrogen is lost through hydrodeoxygenation.

Fig. 8 shows other remarkable differences between the course of the

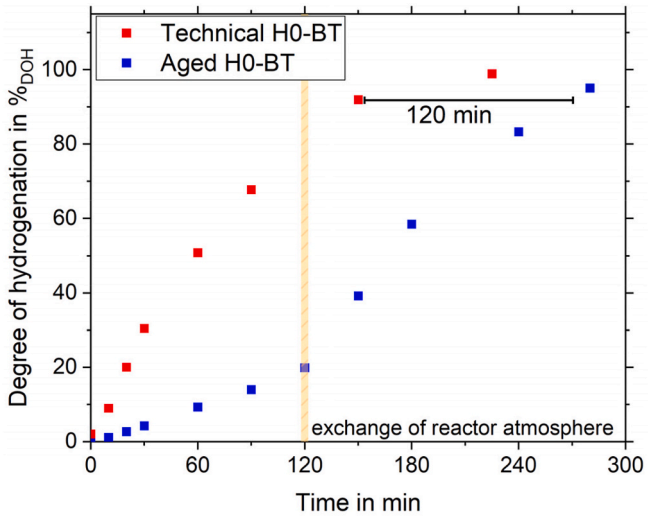

Fig. 8. Degree of hydrogenation in LOHC material as a function of reaction time during the hydrogenation of technical H0-BT and artificially aged H0-BT. Reaction conditions: T = 220 °C; p_{H2} = 20 bar; stirring speed = 1200 rpm; m_{kat} = 6.4 g; $m_{H0\text{-}BT}$ = 195 g; t = 225 min (technical H0-BT) 280 min (aged H0-BT); catalyst = Pt + Pd/Al_2O_3. The reactor atmosphere was exchanged after a reaction time of 120 min during the hydrogenation of aged H0-BT.

hydrogenation reaction of virgin technical H0-BT and our artificially aged (120 °C, 24 h, air) material. Especially at the beginning of the reaction (<120 min), the hydrogenation of the virgin H0-BT proceeds significantly faster than the hydrogenation of aged H0-BT. Only after exchanging the gas atmosphere of the reactor once (after 120 min), the hydrogenation reaction accelerated significantly. It is interesting to note that this 120-min time delay between the hydrogenation of aged material and the control experiment is found in the DOH differences at the later stages of the hydrogenation reaction again (see Fig. 8).

These results indicate that oxygen-containing degradation products have a significant influence on the performance of the hydrogenation reaction. However, this influence appears to be triggered primarily by the coupling product of hydrodeoxygenation, water. Note that the produced water is mainly present in gaseous form at the applied reaction conditions which reduces the hydrogen partial pressure in the reactor as the total pressure of the reactor is maintained in the experiment through a pressure regulator. During water formation in hydrodeoxygenation, hydrogen is replaced in the reactor by water vapor. The vapor pressure of water at 220 °C is approximately 24 bar [28], a sufficient amount of reaction water can therefore completely replace hydrogen at the applied total pressure of 20 bar in the reactor system thus preventing LOHC hydrogenation.

In our specific case, the total of 6.6 wt% of oxygen-containing impurities in the aged H0-BT results in a total amount of 0.066 mol of water (assuming methylbenzophenone as representative impurity) formed during complete hydrodeoxygenation. Assuming validity of the ideal gas law, this water would generate a partial pressure of 13.5 bar at a reactor gas volume of 200 mL and at the reaction temperature of 220 °C. With 20 bar total pressure the final gas mixture would only contain 6.5 bar H_2 because further hydrogen feeding stops when the total pressure of 20 bar is reached. At 6.5 bar H_2 partial pressure, the hydrogenation of the aromatic rings is at least severely hindered.

With exchanging the gas phase after a reaction time of about 120 min (DOH = 20 %), this gaseous water is removed from the reactor, which reestablishes a hydrogen partial pressure of around 20 bar (neglecting the vapor pressure of the organic feedstock) and consequently, the hydrogenation rate increases significantly. In detail, the productivity of the Pt + Pd/Al_2O_3 catalyst increases from 0.46 $g_{H2}/(g_{Pt+Pd}*min)$ between 0 and 20 % DOH to more than 1.79 $g_{H2}/(g_{Pt+Pd}*min)$ between 20 and 50 % DOH after the gas atmosphere has been replaced. Because all oxygen-containing impurities are hydrodeoxygenated after 120 min, no further water is formed, which maintains the hydrogen partial pressure close to 20 bar for the remaining reaction time. The productivity between 20 and 50 % DOH with the aged LOHC after reactor venting is similar to the productivity of the control experiment using virgin technical H0-BT, which reached a productivity of 2.01 $g_{H2}/(g_{Pt+Pd}*min)$ in the same DOH range. From previous experiments published by some of us [29] we know that such deviation is within the relative standard deviation of the catalyst productivity in the hydrogenation of technical H0-BT. This leads us to the conclusion that the hydrogenation of aged H0-BT is comparable to the hydrogenation of virgin technical H0-BT once the water from the initial hydrodeoxygenation has been removed from the gas phase of the reactor.

These findings are of great importance for the technical implementation of the H0-BT/H12-BT LOHC system because they demonstrate that group 2 products (the majority of autoxidation products) from unintentional oxidation of H0-BT during storage can be converted to H12-BT through a simple hydrodeoxygenation/hydrogenation sequence. The so-obtained H12-BT fraction is virtually free of any oxygen-containing impurities and can be used in the intended further hydrogen storage cycles. The applied catalyst shows little to no deactivation, enabling its long-term use.

4. Conclusion

Through its use in hydrogen logistic scenarios, LOHC material spends a large proportion of its service time in storage tanks, waiting to either store or release hydrogen. While from an economic point of view every reduction of LOHC quality through formation of impurities is undesired, it is particularly cumbersome when occurring during periods of inactivity, where no economic value is created.

This contribution quantifies through long-term stability experiments under air, inert gas and UV light the formation of oxygen-induced impurities in BT-based LOHC hydrogen storage systems at different temperature conditions. Heat and UV radiation have been found to be critical with H0-BT being less stable than H12-BT during storage. While H12-BT is unaffected by UV radiation and stable under air for 28 days up to a temperature of 70 °C (no detectable degradation products), the formation of oxygen-induced impurities in H0-BT occurs in air contact at temperatures slightly above room temperature. Storage of H0-BT under air at 80 °C for 30 days formed 10.6 wt% of oxidation and degradation products. In the presence of UV-light, H0-BT is even not stable under air at room temperature. Over 30 days of irradiation, 6.9 wt% of oxidation and degradation products were formed. Inertization by nitrogen prevents any heat- or UV-induced impurity formation for both H0-BT and H12-BT in the studied temperature range up to 80 °C.

The information gained in our study allows us to derive technical guidelines important for the future cost-effective design of Hx-BT storage and transportation tanks. Our results show that H0-BT storage requires inertization by nitrogen to prevent autoxidation at elevated temperatures or under light exposure. Nevertheless, this inertization can be avoided, and related costs can be saved, if heat and light is excluded. This can be realized in typical underground storage tanks. H12-BT storage needs less precautions than H0-BT storage. In this case, protective inertization measures are not necessary.

If, due to improper storage and handling, autoxidation of BT-based LOHC system occur to some extent, a sequence of hydrodeoxygenation and hydrogenation in the same reactor can be used to regenerate the material. Methylbenzophenones and similar oxidation products containing the BT base structure (group 2 product) can effectively be reconverted to H12-BT in this manner. However, the water vapor formed during the hydrodeoxygenation step reduces the hydrogen partial pressure in the reactor during dehydrooxygenation at fixed total pressure. Our results show that the productivity for H12-BT formation is comparable to virgin H0-BT hydrogenation once the dehydrooxygenation step is completed and the gas phase has been exchanged to pure hydrogen by venting and recompression of the reactor.

CRediT authorship contribution statement

Julian Henseler: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Michael Geißelbrecht:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Nils Tippkötter:** Writing – review & editing, Resources. **Peter Wasserscheid:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization.

Data availability statement

The data that supports the findings of this study are available in the electronic supplementary information of this article. Data for this article is made available on zenodo under https://doi.org/10.5281/zenodo.17369276.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Peter Wasserscheid reports financial support was provided by Ministry of Economic Affairs, Industry, Climate Action and Energy of the State of North Rhine Westphalia. Peter Wasserscheid reports financial support

was provided by Werner Siemens Foundation. Peter Wasserscheid reports a relationship with Hydrogenious LOHC Technologies GmbH that includes: equity or stocks. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2026.154460.

References

[1] Preuster P, Papp C, Wasserscheid P. Liquid organic hydrogen carriers (LOHCs): toward a hydrogen-free hydrogen economy. Accounts Chem Res 2017;50(1):74–85. https://doi.org/10.1021/acs.accounts.6b00474.
[2] Niermann M, Timmerberg S, Drünert S, Kaltschmitt M. Liquid organic hydrogen carriers and alternatives for international transport of renewable hydrogen. Renew Sustain Energy Rev 2021;135:110171. https://doi.org/10.1016/j.rser.2020.110171.
[3] Rong Y, Chen S, Li C, Chen X, Xie L, Chen J, Long R. Techno-economic analysis of hydrogen storage and transportation from hydrogen plant to terminal refueling station. Int J Hydrogen Energy 2024;52:547–58. https://doi.org/10.1016/j.ijhydene.2023.01.187.
[4] Reuß M, Grube T, Robinius M, Preuster P, Wasserscheid P, Stolten D. Seasonal storage and alternative carriers: a flexible hydrogen supply chain model. Appl Energy 2017;200:290–302. https://doi.org/10.1016/j.apenergy.2017.05.050.
[5] Jorschick H. Operational stability of a LOHC-based hot pressure swing reactor for hydrogen storage. Energy Technol 2018.
[6] Ellert A, Schmacks M, Braun MJ, Piccirilli L, Janssens TVW, Wasserscheid P, Schühle P. Continuous dehydrogenation of perhydro benzyltoluene in a catalytic finned tube reactor. Ind Eng Chem Res 2025;64(7):3714–27. https://doi.org/10.1021/acs.iecr.4c04254.
[7] Pappler S, Mader T, Blasius M, Gräser T, Rüde T, Geißelbrecht M, Seitz A, Wahl S, Wasserscheid P. Recovery of solid oxide fuel cell waste heat for hydrogen release from liquid organic hydrogen carriers. Int J Hydrogen Energy 2025;156:150245. https://doi.org/10.1016/j.ijhydene.2025.150245.
[8] Distel MM, Margutti JM, Obermeier J, Nuß A, Baumeister I, Hritsyshyna M, Weiß A, Neubert M. Large-Scale H 2 storage and transport with liquid organic hydrogen carrier technology: insights into current project developments and the future outlook. Energy Tech 2024. https://doi.org/10.1002/ente.202301042.
[9] Kwak Y, Moon S, Ahn C, Kim A-R, Park Y, Kim Y, Sohn H, Jeong H, Nam SW, Yoon CW, Jo YS. Effect of the support properties in dehydrogenation of biphenyl-based eutectic mixture as liquid organic hydrogen carrier (LOHC) over Pt/Al2O3 catalysts. Fuel 2021;284:119285. https://doi.org/10.1016/j.fuel.2020.119285.
[10] Rüde T, Dürr S, Preuster P, Wolf M, Wasserscheid P. Benzyltoluene/perhydro benzyltoluene – pushing the performance limits of pure hydrocarbon liquid organic hydrogen carrier (LOHC) systems. Sustain Energy Fuels 2022. https://doi.org/10.1039/D1SE01767E.
[11] Bulgarin A, Jorschick H, Preuster P, Bösmann A, Wasserscheid P. Purity of hydrogen released from the liquid organic hydrogen carrier compound perhydro dibenzyltoluene by catalytic dehydrogenation. Int J Hydrogen Energy 2020;45(1):712–20. https://doi.org/10.1016/j.ijhydene.2019.10.067.
[12] Frank C. Hydrocarbon autoxidation. Chem Rev 1950;46(1):155–69. https://doi.org/10.1021/cr60143a003.
[13] Waters WA. The chemistry of free radicals. Clarendon Press; 1946.
[14] Frimer AA. The reaction of singlet oxygen with olefins: the question of mechanism. Chem Rev 1979;79(5):359–87. https://doi.org/10.1021/cr60321a001.
[15] Walsh AD. Processes in the oxidation of hydrocarbon fuels.—I. Trans Faraday Soc 1946;42(0):269–79. https://doi.org/10.1039/TF9464200269.
[16] Walsh AD. Processes in the oxidation of hydrocarbon fuels—Ii. Trans Faraday Soc 1947;43(0):297–305. https://doi.org/10.1039/TF9474300297.
[17] Farmer EH, Sundralingam A. 22. The course of autoxidation reactions in polyisoprenes and allied compounds. Part I. The structure and reactive tendencies of the peroxides of simple olefins. J Chem Soc 1942:121–39. https://doi.org/10.1039/JR9420000121. 0.
[18] Henseler J, Schärfe T, Steffen J, Görling A, Geißelbrecht M, Wasserscheid P. Detailed analysis of coke precursor formation in catalytic perhydro benzyltoluene dehydrogenation processes. Fuel 2025;398:135500. https://doi.org/10.1016/j.fuel.2025.135500.
[19] Rullo F, Beier C-K, Henseler J, Bösmann A, Preuster P, Wasserscheid P, Geißelbrecht M. Pushing activity and stability of LOHC dehydrogenation catalysts by strict LOHC quality protocols. Int J Hydrogen Energy 2025;98:606–13. https://doi.org/10.1016/j.ijhydene.2024.12.104.
[20] DIN. DIN SPEC 91437:2023-05, Liquid Organic Hydrogen Carrier_(LOHC) auf Basis von Toluol_- Bewertung, Prüfung und Sicherstellung der LOHC-Qualität; Text Englisch; Beuth Verlag GmbH, Berlin.
[21] Stein, S. E. NIST/EPA/NIH mass spectral Library-PC version, NIST standard reference database 1A.
[22] Cooper AR, Crowne CWP, Farrell PG. Gas-liquid chromatographic studies of electron-donor-acceptor systems. Part 2.—Interactions of aromatic hydrocarbons and heterocycles with 2,4,7-trinitrofluorenone. Trans Faraday Soc 1967;63(0):447–54. https://doi.org/10.1039/TF9676300447.
[23] Grasselli JG, Lide DR, editors. Handbook of data on organic compounds. 2. ed. CRC Press; 1992.
[24] Wakayama N, Inokuchi H. Heats of sublimation of polycyclic aromatic hydrocarbons and their molecular packings. Bull Chem Soc Jpn 1967;40(10):2267–71. https://doi.org/10.1246/bcsj.40.2267.
[25] International Labour Organization. BENZO(a)PYRENE:International chemical safety card. https://chemicalsafety.ilo.org/dyn/icsc/showcard.display?p_version=2&p_card_id=0104 (accessed 2024-November-19).
[26] Marasca E, Greetham D, Herring SD, Fisk ID. Impact of nitrogen flushing and oil choice on the progression of lipid oxidation in unwashed fried sliced potato crisps. Food Chem 2016;199:81–6. https://doi.org/10.1016/j.foodchem.2015.11.136.
[27] Siegert F, Gundermann M, Maurer L, Hahn S, Hofmann J, Distel M, Schühle J, Müller K, Wolf M, Preuster P, Auer F, Geißelbrecht M, Wasserscheid P. Autothermal hydrogen release from liquid organic hydrogen carrier systems. Int J Hydrogen Energy 2024;91:834–42. https://doi.org/10.1016/j.ijhydene.2024.10.044.
[28] Liu C-T, Lindsay JR WT. Vapor pressure of deuterated water from 106 to 300.deg. J Chem Eng Data 1970;15(4):510–3. https://doi.org/10.1021/je60047a015.
[29] Henseler J, Rullo F, Mitländer K, Johner N, Wolf P, Schühle P, Geißelbrecht M, Wasserscheid P. Chloroorganic impurities in technical-grade benzyltoluene – influence on its use as LOHC compound and removal strategies. Int J Hydrogen Energy 2024;53:105–13. https://doi.org/10.1016/j.ijhydene.2023.11.344.