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Continuous (hydro-)dechlorination of aromatic chloride compounds in benzyltoluene

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ABSTRACT

Benzyltoluene is an attractive liquid organic hydrogen carrier (LOHC) compound but needs to be purified after its technical synthesis to remove chloride impurities that would harm the Pt-based hydrogenation and dehydrogenation catalysts used for the reversible LOHC loading and unloading with hydrogen. For this purpose the dechlorination of chlorobenzyltoluene in a benzyltoluene matrix was studied in a continuously operated trickle bed reactor using a commercially available nickel catalyst. The results indicate that the removal of chlorobenzyltoluene is mainly adsorption based. Rapid aging experiments with purposely added chloroaromatic compounds (chlorobenzene and chloronaphthalene) in quantities of up to 9000 ppm suggest that high chloroaromatic loadings lead to reduced dechlorination activity due to a rapid blocking of active sites. The dechlorination capacity per gram of the used catalyst material was determined to be in the range of 2 kg of technical benzyltoluene.

1. Introduction

The Liquid Organic Hydrogen Carrier (LOHC) technology enables safe hydrogen storage in liquids that can be handled in the existing infrastructure for liquid fossil fuels. Hydrogen is chemically bound to the carrier via a heterogeneously catalyzed hydrogenation reaction. Afterwards, the charged carrier compound can be catalytically dehydrogenated, releasing the hydrogen with transforming the carrier in its hydrogen-lean form, enabling a repetitive use in the next storage cycle [1–4]. Benzyltoluene (H0-BT) is discussed as hydrogen-lean LOHC compound, as it can store up to 6 mol molecular hydrogen per mol H0-BT, resulting in a hydrogen storage capacity of 6.2 wt% [5,6]. The system benzyltoluene/perhydro-benzyltoluene (H0-BT/H12-BT) is characterized by a broad liquid range, low viscosity, high thermal stability, and good technical availability [7,8].

In industrial scale, H0-BT is traded and applied as heat transfer fluid in form of a technical mixture of its different regioisomers, namely *o*-benzyltoluene, *m*-benzyltoluene, and *p*-benzyltoluene [7,9]. As reported recently, residues of chloroorganic impurities, such as chlorobenzyltoluene, are present in technical benzyltoluene mixtures. These impurities originate from the H0-BT synthesis route via Friedel-Crafts alkylation of benzylchloride and toluene [10,11]. Using H0-BT isomer mixtures in catalytic hydrogenation/dehydrogenation hydrogen storage cycles poses higher requirements in terms of purity than its technically established use as heat transfer fluid. The reason for this is that the presence of chloride compounds in the H0-BT under hydrogenation conditions can lead to deactivation of the catalyst and corrosion of the equipment [10,12].

A frequently discussed method for purifying chloroorganic mixtures is the hydrodechlorination, which is often described for the treatment of waste water or exhaust gases [13–15]. In this context, mainly palladium [15–17] and nickel-based [14,18,19] catalysts are used, often improving the dechlorination by the utilization of solvents or additives [13]. The application of the hydrodechlorination on the removal of chlorobenzyltoluene from the technical H0-BT mixture was demonstrated by Henseler et al. using supported transition metal catalysts [10]. Catalyst screening in a batch setup revealed that nickel catalysts are promising candidates for this process. Oxidative addition of chlorobenzyltoluene to the metal was assumed to be the key step in the dechlorination. It has also been shown that oxidized nickel centers can be regenerated in the

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presence of hydrogen for further use in the adsorption of chloroaromatic compounds [10]. Similar observations were published by Serguchev et al. who study the hydrogenolysis of chlorobenzenes over a nickel-chromia catalyst [19]. According to their studies, chloroaromatic compounds and hydrogen adsorb at different active centers. The adsorbed hydrogen then promotes the scission of the chloride carbon bond under formation of hydrogen chloride. While the chloride-free aromatic compound is released, desorption of HCl from the hydrogen adsorption site has been found to be comparatively slow.

The aim of this study is to realize the dechlorination of chlorobenzyltoluene in a continuous process, laying the foundation for a future technical application as LOHC-grade material. Our study builds on the use of a commercial nickel-based catalyst (in the following referred to as Ni-material) that has been recently described for the batch-mode version of this dechlorination [10]. We investigate the influence of temperature, residence time, and of the ratio of hydrogen to LOHC on the achievable degree of dechlorination. The (hydro-)dechlorination process is evaluated in terms of chloride removal and side product formation. To clarify whether poisoning of the active sites occurred during dechlorination, chlorobenzene or chloronaphthalene were artificially added to the pristine H0-BT. This served on the one hand to simulate higher throughputs of technical benzyltoluene. On the other hand, the product mixture could be checked for the dechlorinated reaction products of these added substances, namely benzene or naphthalene. A chloride balance was prepared to determine the fate of the chloride after removal from the liquid benzyltoluene.

2. Experimental

2.1. Dechlorination experiments

All dechlorination experiments were carried out under atmospheric pressure in a fixed bed glass reactor (inner diameter = 29 mm) equipped with a frit to retain the Ni-material. (see Fig. 1). The material was applied in form of extrudates (size 1.6 mm) with a nickel content of 52 ± 4 wt% on the aluminum silicate support. Benzyltoluene (supplier: Eastman Chemical Co., traded as Marlotherm LH) was dosed using a Techlab HPLC pump. Hydrogen and nitrogen flow were controlled by using Bronkhorst Mass Flow Controllers (MFCs). Liquid and gas were preheated in an inlet line to 100 °C, allowing the hydrogen to partly dissolve in the benzyltoluene on its way to the reactor. The liquid entered the reactor as a pulsed flow dripping down the fixed bed. The Ni-material was positioned on top of glass beads (diameter 2 mm) to ensure that the tip of the thermocouple was placed in the Ni-material. Glass beads were filled also on top of the Ni-material, supporting the preheating and radial distribution of the liquid. The total bed height summed up to 25 cm. The glass reactor was heated from the outside with an electric heating jacket, manually adjusting the heating power by temperature measurement of the thermocouple in the Ni-material. The liquid product and surplus gas left the reactor at the bottom towards the product flask. With a reflux chiller, benzyltoluene vapors were condensed, thus holding it back in the product flask. The gas was purged into the exhaust after flowing through a gas washing bottle filled with water. This allowed us to monitor the gas flow leaving and to prevent air from entering the setup. Liquid samples were taken from the product line throughout the experiment and from the product mixture in the flask at the end of the experiment.

Before starting an experiment, the system was flushed with nitrogen

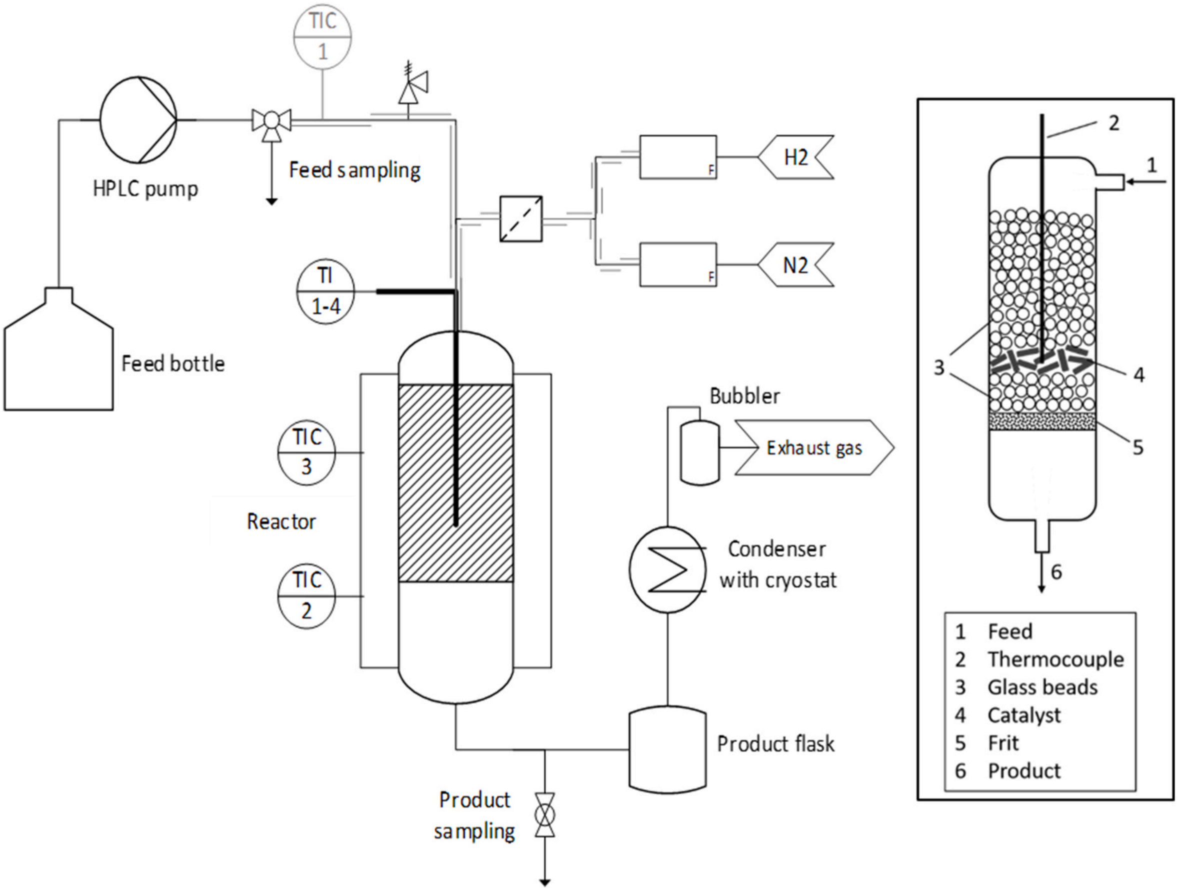


Fig. 1. Flow scheme of the continuous hydrodechlorination setup (left) and illustration of the reactor filling (right).

to ensure an inert atmosphere in the reactor. During the heating process, nitrogen flow was maintained. The day before the experiment, the Ni-material was preformed for 3 h at 200 °C, using a 1:1 mixture of hydrogen and nitrogen. The reactor heating was adjusted to 150 °C under nitrogen flow over night. The substrate was prepared in a feed bottle by either drying the technical benzyltoluene with a molecular sieve (0.4 nm, metal aluminum silicates, diameter 1.6–2.5 mm, purchased by Carl Roth) or by additionally adding chlorobenzene (Carl Roth, purity ≥99.5 %) or chloronaphthalene (Sigma Aldrich, purity 85–88 %). To start an experiment, the temperature was set to reaction conditions, hydrogen was introduced into the reactor to exchange the gas atmosphere and the benzyltoluene mixture was dosed with the pump, marking the start of the reaction.

2.2. Analytical methods for chlorinated compound quantification

The total content of chloroorganic compounds was measured with an NSX-2100H elemental analyzer, procured from A1-envirosciences GmbH as previously reported by Henseler et al. [10]. The Ni-material samples were ground using a mortar or a ball mill before analysis of their Cl-content in the NSX-2100H elemental analyzer.

As previously reported, chlorobenzyltoluene isomers are the only relevant impurities in technical H0-BT mixtures [10]. Quantification of chlorinated benzyltoluene species was carried out on the base of gas chromatography coupled with mass spectrometry (GC-MS) measurements. Quantification of chlorobenzene and benzene as well as chloronaphthalene and naphthalene was carried out on the base of gas chromatography with flame ionization detector (GC-FID) measurements. Detailed information on the GC configurations and the corresponding data evaluation are provided the ESI.

2.3. Analytical methods for side product analysis

Side product analysis also was carried out using a GC-FID setup (see ESI). The product mixture consists of the following components: 1. Hydrogenation products of the benzyltoluene isomeric mixture, including H6-BT and H12-BT, which can be expressed as degree of hydrogenation (DoH) in the context of the LOHC technology. 2. Light boiling components (LB) that exhibit a lower boiling point than benzyltoluene, thus eluting earlier from the GC column. Examples for LB components are benzene, toluene or xylene, expressed in this work as sum parameter due to the very low concentration of the single substances. Also, diphenylmethane (DPM) and its hydrogenated counterparts (Hx-DPM), which are formed by elimination of the methyl group in the Hx-BT compounds, are considered as LB components. 3. High boiling components (HB) that exhibit a higher boiling point than benzyltoluene, thus eluting later from the GC column. 4. Methylfluorene and fluorene species, which are covered by the definition of the high boiling components but represent defined compounds in the mixture. Since in the context of LOHC those fluorene-based species are increasingly discussed as precursors for further side product formation [7,20,21], special attention is paid to quantify their formation.

Additionally, fresh and used Ni-material was compared in terms of structural changes of the material, its Ni-content as well as its surface area. Further information on the used characterization methods XRD, TGA-MS, ICP-OES and BET can be found in the ESI.

3. Results and discussion

To prove that the dechlorination of technical benzyltoluene can be continuously operated in the chosen setup, an experiment was conducted with a total Ni-material mass of 75 g, at a temperature of 150 °C with 50 g h^{-1} liquid feed, 20 mL_n min^{-1} hydrogen and 10 mL_n min^{-1} nitrogen stream. The product stream was continuously collected in the product flask. The dechlorination of technical benzyltoluene was quantified via GC-MS measurements. Untreated benzyltoluene exhibits several peaks at retention times of 17.25–18.2 min, which can be assigned to isomers of the chlorobenzyltoluene species. Lower concentrations of chloride species in the liquid product lead to a decrease in detected signal strengths and peak areas. This is exemplified in Fig. 2a. Under the described reaction conditions, the concentration of chlorobenzyltoluene was significantly reduced, causing individual peaks to disappear below the detection limit.

Comparing the sum of peak areas of both samples in Fig. 2a, a reduction of chlorobenzyltoluene species by 92 % is observed, leading to an almost entirely dechlorinated H0-BT mixture. Fig. 2b shows the achieved degree of dechlorination that remained stable during the entire experiment. To confirm that the removal of chlorinated H0-BT species correlates with the total chloride content in the liquid phase, feed and product sample were measured in elemental analysis. The measurement resulted in an absolute chloride content of 8.7 mg L^{-1} for the feed and 0.8 mg L^{-1} for the dechlorinated product (reduction by 91 %). This confirms that the decreased concentration of chlorobenzyltoluene species goes hand-in-hand with the reduction of the total chloride content in the liquid phase. It furthermore confirms that chlorobenzyltoluenes represent the main part of the chloride impurities in the technical H0-BT mixture. Our study shows that continuous dechlorination of technical benzyltoluene is a viable purification approach.

3.1. Parameter variation

For a better understanding of the impact of operation parameters on the continuous dechlorination, the influence of temperature, residence time (mass of Ni-material), and the ratio of hydrogen to LOHC on the achievable degree of dechlorination was investigated. A Ni-material mass of 10 g, a technical H0-BT flow of 50 g h^{-1}, a hydrogen flow of 20 mL_n min^{-1} and a reactor temperature of 150 °C were chosen as reference conditions. During the parameter variation, those reference conditions were maintained constant except for one respective variable. After 6 h time-on-stream, the cumulative product samples were analyzed by GC-MS to detect the remaining Cl-BT peak area and elemental analysis was applied to quantify the total chloride content. The results shown in Fig. 3a–c give the medium value of both measurement methods and the respective standard deviation. At these reference conditions, a degree of dechlorination of approx. 44 % was obtained.

As can be seen in Fig. 3a, the degree of dechlorination increases with increasing temperature. However, in comparison to the experiments conducted in batch operation by Henseler et al., [10] the impact of temperature was found less pronounced in the present study. This can be explained by the different operating modes and flow conditions resulting in different mass transport limitations. Reactions in continuously operated trickle beds are generally described as significantly influenced by mass transport limitations [22], emphasizing the role of hydrogen solubility and hydrogen diffusion rate in the liquid benzyltoluene.

The variation of hydrogen flow (ratio gas to liquid) is shown in Fig. 3b. Without hydrogen supply, a degree of dechlorination of 29 % is observed, indicating that the chlorobenzyltoluene is partly removed from the mixture by a pure adsorption process. This is in accordance with the previously reported batch experiments published by Serguchev et al. and Henseler et al. [10,19] [10,19] We assume from the increasing dechlorination in the presence of hydrogen that the latter facilitates chloride desorption from the active Ni centers to regenerate these active sites. Increasing the hydrogen flow beyond 20 mL_n min^{-1} did not lead to a significant acceleration of the dechlorination process. We assume that dissolved hydrogen is mainly responsible for the enhanced regeneration of the Ni-material. Higher hydrogen flow rate does not lead to higher hydrogen solubility but results in a higher degree of LOHC evaporation thus decreasing the LOHC residence time in the Ni-material. To improve dechlorination rates, the driving force for hydrogen dissolution in benzyltoluene should be targeted, which might be possible by increasing hydrogen pressure [23,24]. Unfortunately this could not be tested in our glass setup.

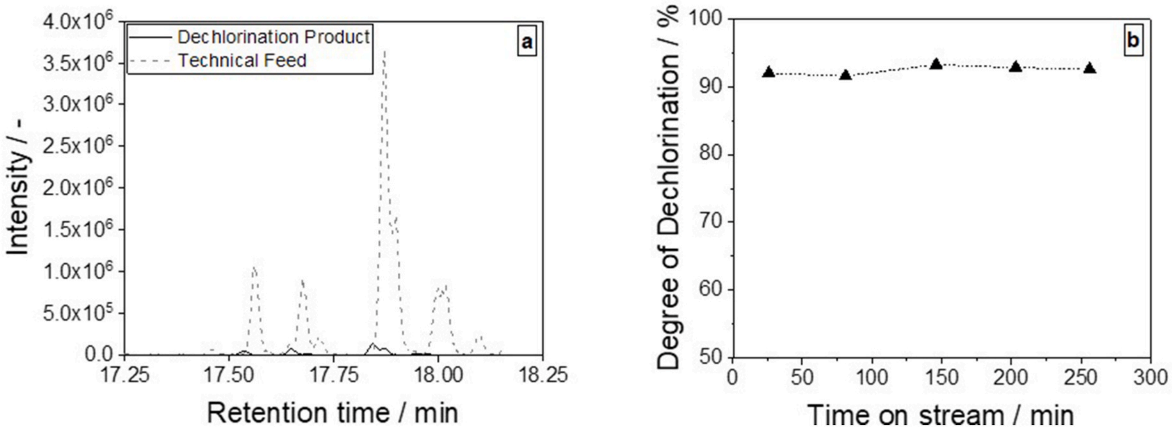


Fig. 2. Dechlorination results of an exemplary experiment using the following parameters: 75 g Ni-material, 150 °C, 50 g h^{-1} H0-BT, 20 mL_n min^{-1} H_2, 10 mL_n min^{-1} N_2. With a: Comparison of GC-MS results (m/z 216) for chlorobenzyltoluene peaks in technical feed sample and dechlorination product. With b: Calculated degree of dechlorination of collected samples over time on stream.

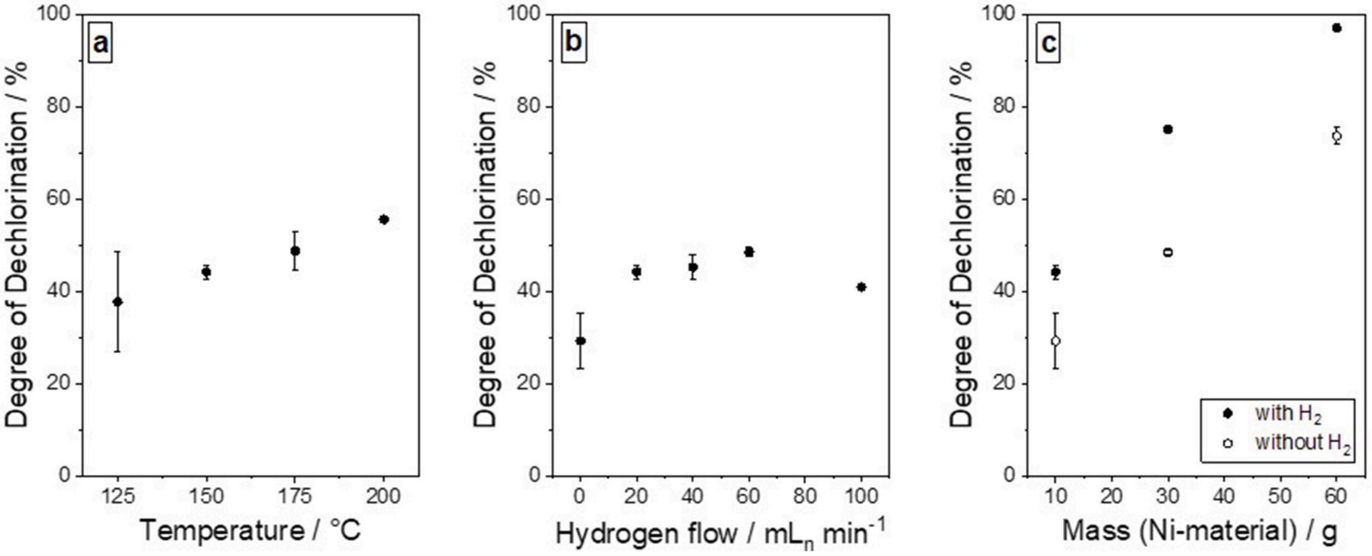


Fig. 3. Resulting degree of dechlorination of product mixture after 6 h on stream depending on a: temperature, b: hydrogen flow, c: Ni-material mass. Reference conditions for parameter variation: 10 g Ni-material, 150 °C, 20 mL_n min^{-1} hydrogen, 50 g h^{-1} technical benzyltoluene feed.

As can be seen in Fig. 3c, a higher mass of Ni-material can effectively improve the resulting degree of dechlorination. With raising mass, the residence time of reactants in the Ni-material and the number of active centers available for dechlorination are increased. Again, the presence of hydrogen in the reactor accelerates the dechlorination. To achieve a similar level of degree of dechlorination without the presence of hydrogen, a two-to threefold longer contact time is needed.

Besides the degree of dechlorination, the composition of the liquid mixture was also monitored to ensure high benzyltoluene quality for the subsequent LOHC application. Potential side product formation on the Ni-material was investigated via GC-FID analysis of collected product samples from the parameter variation experiments. The results are summarized in Fig. 4a–c.

In case of high boiling components and (methyl-)fluorene species, none of the varied parameters affects the concentration in the product mixture. Small fluctuations can be attributed to uncertainties in the GC-FID measurements and in the peak quantification close to its detection limit. Compared to the initial composition of the untreated H0-BT, the concentration of high-boilers and (methyl-)fluorenes is even reduced after contact with the Ni-material under the herein applied conditions. This indicates that organic impurities in the technical H0-BT are partly adsorbed to the Ni-material, leading to an additional purification of the benzyltoluene mixture during the dechlorination procedure.

Concentration of light boiling components, such as benzene, toluene and Hx-DPM, increased with increasing temperature (see Fig. 4a). However, except for the experiment conducted at 200 °C, the concentration of light boiling components does not exceed its initial value in the untreated H0-BT of 3000 ppm. The total side product concentration after dechlorination at 200 °C only sums up to 0.4 %, rendering a benzyltoluene purity of 99.6 %, which even exceeds the technical recommendations for LOHC application [25].

The variation of hydrogen flow (Fig. 4b) did not lead to significant changes in the product composition. Increasing mass of the Ni-material (Fig. 4c) caused an increase in light boiler concentration. During the experiment with 60 g Ni-material, two times the amount of light boiling components was observed in comparison to the reference experiment with 10 g Ni-material. The reason is that higher Ni-material mass leads to an increased residence time and to more active sites available for formation of light boiling components. We assume that the formation of light boiling components exceeds their adsorption in case of increased mass of Ni-material. In total, however, the benzyltoluene purity remained above 99.6 % for the highest monitored Ni-material mass of

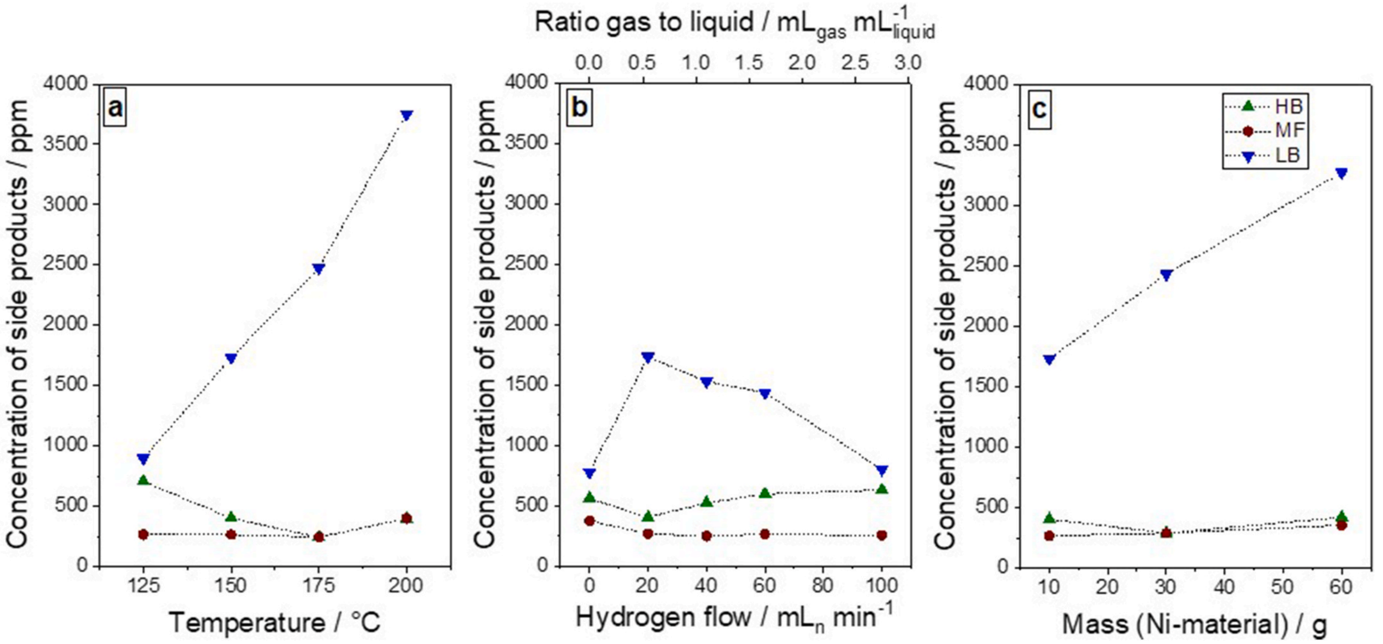


Fig. 4. Side product formation on the Ni-material during the dechlorination process as a function of process parameters. With a: temperature variation; b: hydrogen flow variation; c: Ni-material mass variation. Reference conditions: 10 g Ni-material, 150 °C, 20 mL$_n$ min^{-1} hydrogen, 50 g h^{-1} technical benzyltoluene feed. HB: high boiling components, LB: light boiling components, MF: methylfluorene and other fluorene species. Concentration of side products in the untreated, technical H0-BT denote as follows: LB: 3000 ppm, HB: 1000 ppm, MF: 500 ppm.

60 g. This proves that high quality LOHC can be obtained after the Ni-material-based dechlorination process.

In addition to potential side reactions leading to the decomposition of LOHC molecule, the competing hydrogenation of benzyltoluene was monitored. The effect of our reaction parameter variation on the degree of hydrogenation is summarized in Fig. 5a–c.

The observed hydrogenation activity depends mainly on reaction temperature and hydrogen flow. Under reference conditions, a degree of hydrogenation of 1.7 % was observed under the applied dechlorination conditions. Increasing the hydrogen input by factor 5 led to an increase of hydrogenated products by a factor of 2.5. Considering that the experiments were carried out at atmospheric pressure, the hydrogenation potential of the Ni-material to a DoH of up to 4.2 % is remarkable. Note that typical pressure ranges for the hydrogenation of benzyltoluene or dibenzyltoluene systems are 10–50 bar with a significant increase in reaction rate reported at elevated pressures [26,27]. Note further, that

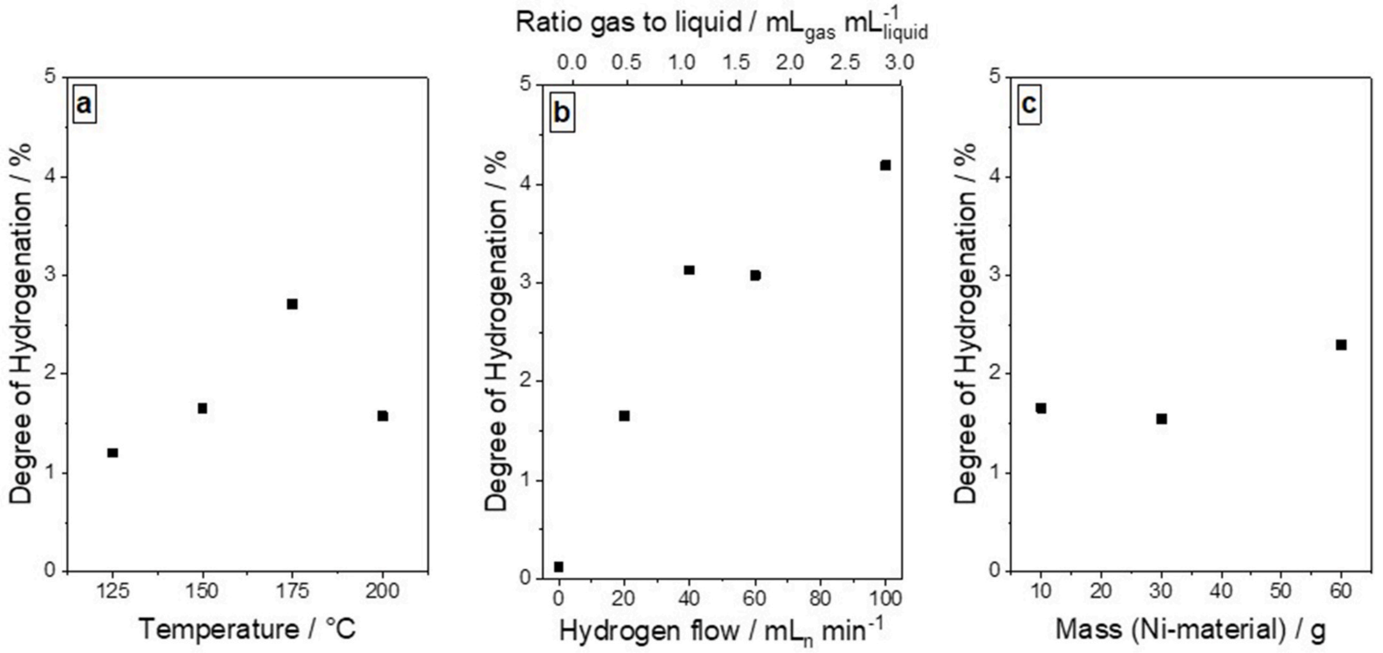


Fig. 5. Degree of hydrogenation obtained during dechlorination in the presence of hydrogen as a function of process parameters. With a: temperature variation; b: hydrogen flow variation; c: Ni-material mass variation. Reference conditions: 10 g Ni-material, 150 °C, 20 mL$_n$ min^{-1} hydrogen, 50 g h^{-1} technical benzyltoluene feed.

the observed hydrogenation of benzyltoluene is not an undesirable side reaction in the context of the LOHC technology, as the partially hydrogenated BT (Hx-BT) can enter the envisaged LOHC-based hydrogen storage cycle. Nevertheless, the monitoring of BT hydrogenation is relevant as this reaction competes with the hydrodechlorination for active centers and available hydrogen.

3.2. Chloride mass balance

In the present study, continuous dechlorination of technical H0-BT over a commercial nickel-based catalyst was proven a practical approach for eliminating chloride compounds which represent relevant catalyst poisons for LOHC hydrogenation and dehydrogenation processes. In order to monitor the fate of the removed chloride, dechlorination was carried out using the same Ni-material for several consecutive days of operation. The Ni-material was then screened for its chloride content to establish a chloride mass balance. Additionally, the dechlorination activity was monitored over time to identify possible saturation or deactivation phenomena at the used Ni-material.

During 13 experimental days, a Ni-material bed with a total mass of 75.28 g was exposed to technical benzyltoluene feeds. Using the chloride content of the feed (8.7 mg L^{-1} according to elemental analysis), the daily liquid throughput, and the remaining chloride level of the products (as monitored on a daily basis), the total removed chloride was calculated. Table 1 shows a summary of all days on stream and their respective removed chloride from the liquid phase. In total the removed chloride sums up to 35.9 mg.

After day 13, the Ni-material was analyzed for its chloride content using elemental analysis. Three samples were taken at different positions of the fixed bed: at the top of the bed (inlet zone), at the bottom of the bed (outlet zone) and in the middle of the bed. Also fresh Ni-material was characterized for comparison. The results are summarized in Table 2.

After use in dechlorination the chloride content of the Ni-material significantly increased compared to the fresh material. Accumulation of chloride was more pronounced at the top of the reactor, resulting in a 13 times higher chloride content at the inlet compared to the outlet. This suggests that the chloride capacity of Ni-material was not yet depleted and chloride accumulation propagates from top (close to the inlet) to bottom (close to the outlet).

Table 1
Throughput of technical benzyltoluene over 75.28 g Ni-material and achieved dechlorination as monitored on a daily basis. Reactor temperature 150–200 °C, H_2 supply 20–80 mL_n min^{-1}, N_2 supply 0–10 mL_n min^{-1}.

	Mass flow technical H0-BT	Run time	Throughput technical H0-BT	Degree of Dechlorination	Removed chloride
	$g\ h^{-1}$	min	g	%	µg
Day 1	50	390	325	99.7	2827
Day 2	50	330	275	99.1	2378
Day 3	50	406	338	99.7	2943
Day 4	100	274	457	98.6	3928
Day 5	100	274	457	98.6	3928
Day 6	50	256	213	95.5	1777
Day 7	50	395	329	99.6	2860
Day 8	50	352	293	99.4	2544
Day 9	50	370	308	99.7	2682
Day 10	50	391	326	98.6	2803
Day 11	50	318	265	95.5	2208
Day 12	50	397	331	97.0	2800
Day 13	50	310	258	98.0	2209

Table 2
Chloride content of Ni-material samples according to elemental analysis.

	Chloride content/ppm
Fresh Ni-material (as purchased)	12
Used Ni-material, reactor top	1521
Used Ni-material, reactor middle	694
Used Ni-material, reactor bottom	116

Assuming the value from the reactor middle (694 ppm) to be the medium chloride concentration over the total bed height, a total restrained chloride amount in the bed of 51.3 mg can be assumed. In such rough estimation, the chloride amount assigned to the Ni-material exceeds the removed amount from the liquid phase (35.9 mg) by 43 %. This overestimation is probably due to a non-linear distribution of chloride over the Ni-material bed. The result still indicates that the majority of chloride removed from the liquid phase accumulates on the Ni-material. Chloride removal via gaseous HCl plays certainly a minor role in this system (see also Henseler et al. [10]). With regard to future application of the dechlorination technology, this fact reduces also the risk of environmentally harmful HCl emission, while HCl traces could anyways be easily captured in aqueous solutions and neutralized with suitable bases.

3.3. Dechlorination of model substances

The before-mentioned experiments did not lead to a decrease in dechlorination activity over 13 days on stream, indicating that the chloride capacity of the Ni-material bed exceeded the purification requirements of technical benzyltoluene by orders of magnitude. To simulate a higher feedstock throughput and to accelerate aging of the Ni-material, the H0-BT feed was purposely enriched with chlorobenzene and chloronaphthalene. These additives were used in initial concentrations of 0.07–0.90 mol% while the initial molar chloride compound concentration in technical benzyltoluene is only 0.0045 mol% (8.7 mg L^{-1}). Thus, the use of these additives allowed us to accelerate Ni-material poisoning by a factor of up to 200 times. The quantification of the added chloride compounds was carried out using GC-FID analysis. To increase conversion of added chloroaromatics, the following experiments with chlorobenzene and chloronaphthalene were conducted at 200 °C. The results are shown in Fig. 6a–b.

Fig. 6a shows the degree of dechlorination in form of chlorobenzene conversion over time-on-stream in the continuous dechlorination experiment with varying chlorobenzene concentrations in the feed. For all cases and short operation times the degree of dechlorination is clearly above 90 %. Over time and with increasing chlorobenzene contents, the degree of dechlorination decreases considerably. We attribute this to a continuous blocking of active sites by chloride species, leading to Ni-material deactivation.

By comparing the composition of feed and product samples, the total amount of chlorobenzene being removed from the liquid phase, as well as the amount of benzene being formed can be quantified (see Fig. 6b). The removed amount of chlorobenzene increases with the feed concentration, explaining the more rapid decrease of activity for higher feed concentrations, as more of the chloride containing species occupy active centers.

Under chosen reaction conditions, decomposition of benzyltoluene can produce traces of benzene (see also Fig. 4). This small amount (0.2 mmol) compares to up to 3.7 mmol detected with added chlorobenzene in the feed. This indicates that the Ni-material -mediated dechlorination

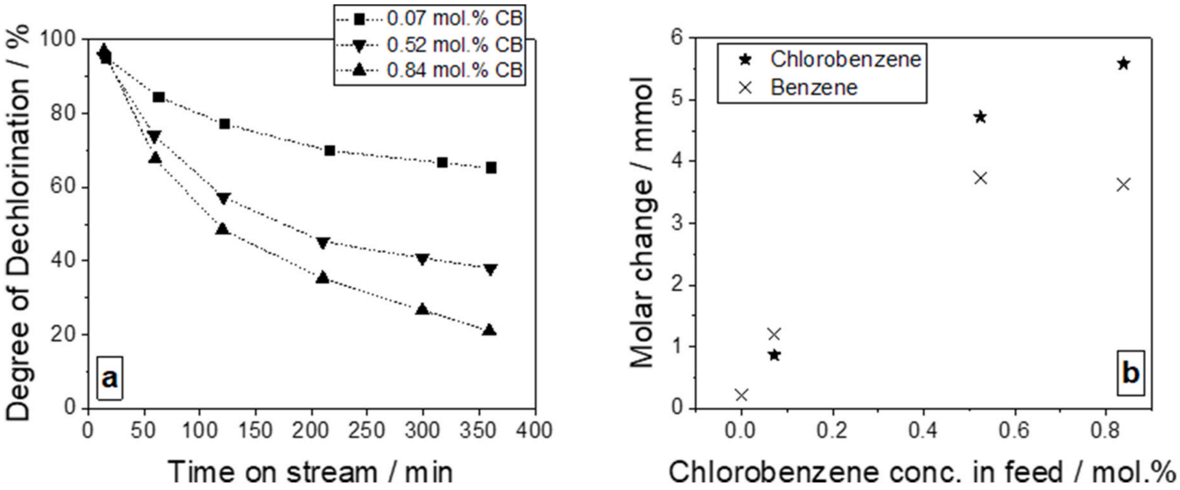


Fig. 6. Concentration variation in the dechlorination of chlorobenzene (CB) from a H0-BT matrix. Conditions: 5 g Ni-material, 200 °C, 50 g h^{-1} feed mixture, 20 mL_n min^{-1} H_2. With a: Degree of dechlorination vs. time on stream. With b: Molar change of chlorobenzene (removal) and benzene (formation) in the product mixture after 6 h on stream.

mechanism is not solely based on adsorption, but also cleavage of the chloride-carbon bond and benzene formation according to Scheme 1 takes place. This observation is in-line with results published by Serguchev et al. [19] These authors postulated that the chloroaromatic compound and the hydrogen adsorb primarily to different active sites. The hydrogen adsorption sites are claimed to firmly bind the formed HCl after the hydrodechlorination step.

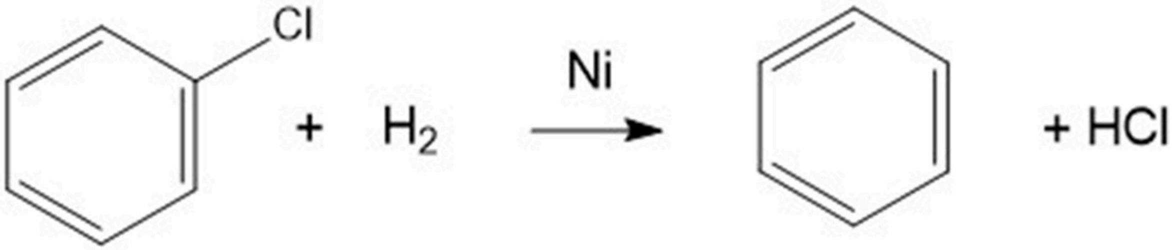
For higher chlorobenzene concentrations in the feed, especially for 0.84 mol% chlorobenzene in H0-BT, the difference between removed chlorobenzene and formed benzene increases. We assume that the adsorption of chlorobenzene is faster than its conversion under the applied reaction conditions, leaving part of the active centers occupied by chlorobenzene. Thus, the observed Ni-material deactivation is supposed to be related to continuously increasing poisoning of hydrogen adsorption sites by HCl and further occupation of active sites by unconverted chlorobenzene.

Further investigations were conducted with chloronaphthalene as additive. This substance was chosen due to its similarity to chlorobenzyltoluene as two-ring based aromatic system, attempting to transfer experimental results to real chlorobenzyltoluene impurities. Additionally, the chloride-free naphthalene occurring in the product mixture can directly be attributed to dechlorination reaction of chloronaphthalene as this compound cannot form from H0-BT side-reactions. Scheme 2 shows the expected reaction for chloronaphthalene dechlorination and naphthalene formation.

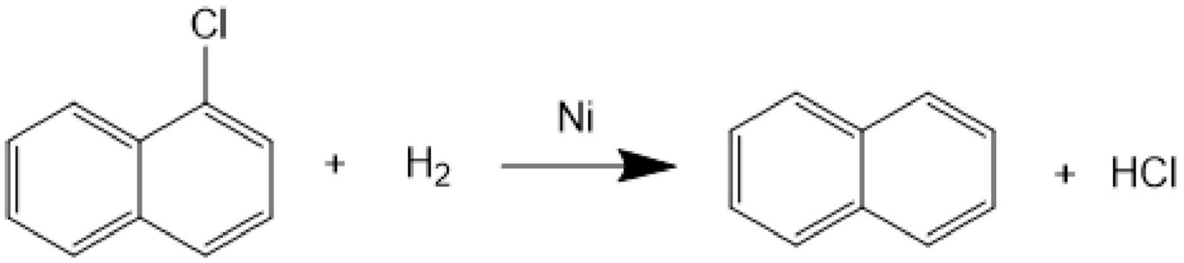
During time-on-stream, the degree of dechlorination decreases, with the most rapid decrease for the highest feed concentration of 0.84 mol% (see Fig. 7a). As for the previously described chlorobenzene experiments, we attribute this behavior to continuous blocking of active sites with chloronaphthalene and formed HCl. With increasing chloride concentration in the feed, more rapid catalyst occupation and deactivation is observed. In general, lower degrees of dechlorination were observed after 6 h for experiments with chloronaphthalene (below 20 %) than of chlorobenzene (below 40 %) for similar molar chloride concentrations in the feed. This indicates that the accessibility of active centers and adsorption are limited by molecular size, leading to an almost halved degree of dechlorination. Removed amount of chloronaphthalene and formed amount of naphthalene increase with the feed concentration (see Fig. 7b), confirming once more the actual cleavage of chloride-carbon bond according to Scheme 2. However, the naphthalene amount is always lower than the chloronaphthalene consumed with an increasing discrepancy at higher feed concentration. In analogy to chlorobenzene experiments, we assume that part of the adsorbed chloronaphthalene remains bound to the Ni-material, continuously blocking active centers for further dechlorination reactions.

Further characterization of fresh and used Ni-material was conducted via TGA-MS, XRD, ICP-OES and BET measurements (see ESI for more information). Therein, neither coking effects, nor structural changes or a decreasing surface area, induced by the presence of chloroorganic substances, could be verified. The results support our conclusion, that the deactivation of the used Ni-material is mainly attributed to blocking of active centers by adsorbed chlorine-containing species.

To estimate the chloride capacity of the Ni-material, the experiment with a chloronaphthalene concentration of 0.84 mol% was chosen as reference case. Due to its size and two aromatic rings, we assume dechlorination of chloronaphthalene to be somehow similar to dechlorination of chlorobenzyltoluene. From the values given in Fig. 7a we can conclude that the degree of dechlorination decreased in the regarded experiment to 17 % during the first 2 h on stream. Thus, 83 % of the dechlorination activity was lost during this time. From concentration measurements in the product stream, the medium amount of restrained



Scheme 1.



Scheme 2.

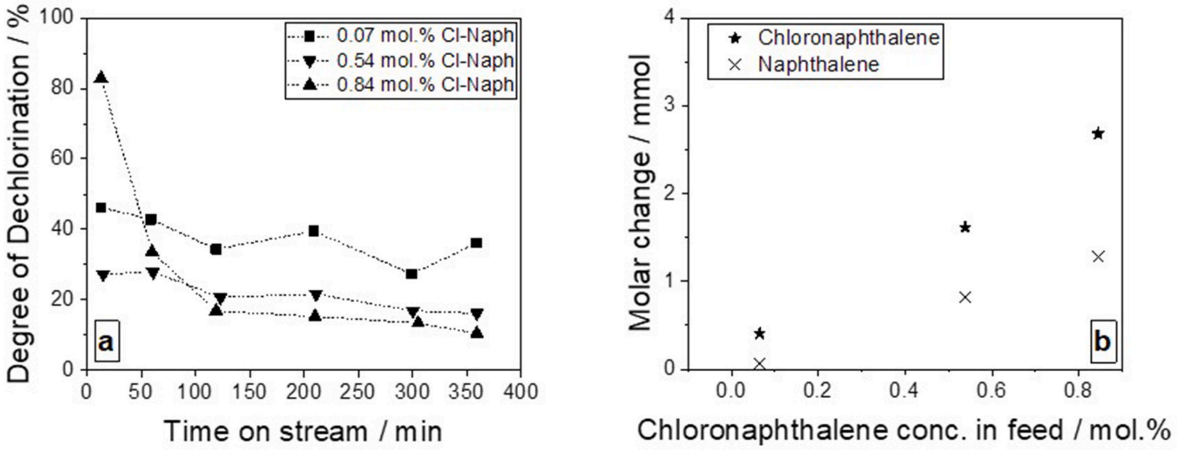


Fig. 7. Concentration variation in the dechlorination of chloronaphtalene (Cl-Naph) from a H0-BT matrix. Conditions: 5 g Ni-material 310 RS, 200 °C, 50 g h^{-1} feed mixture, 20 mL_n min^{-1} H_2. With a: Degree of dechlorination during time on stream. With b: Molar change of chloronaphthalene (removal) and naphthalene (formation) in the product mixture after 6 h on stream.

chloronaphthalene was calculated, resulting in a theoretical chloride capacity of 0.48 $mmol_{Cl}$ per gram Ni-material. For a chloride concentration in technical benzyltoluene of 8.7 mg L^{-1} (equals 0.0045 mol% in benzyltoluene), we calculate a dechlorination capacity of 10.7 mol H0-BT (1947 g H0-BT) per gram Ni-material. We are fully aware that a successful dechlorination process is not only dependent on the applied Ni-material mass. Still our investigation gives a first idea about the needed amount of adsorbent/catalyst for an efficient removal of chloro-impurities from technical H0-BT feeds for its application as liquid organic hydrogen carrier.

3.4. Regeneration approaches

In the next set of experiments, we aimed to regenerate the Ni-material after its use in dechlorination. For this purpose, a 6 h dechlorination experiment was carried out over three days in a row. A chloronaphthalene concentration of 0.8 mol% was adjusted in the feed to investigate the regeneration after rapid poisoning conditions. In-between these experimental days, two different regeneration strategies were tested over night. In the first strategy, the reactor was flushed with pure nitrogen overnight to evaporate the chloronaphtalene from the system under inert conditions. In the second strategy, a 1:1 mixture of hydrogen and nitrogen was used to keep the Ni-material under reductive atmosphere. The results of both experimental series are shown in Fig. 8.

Starting with a fresh Ni-material, a rapid decrease in the degree of dechlorination was observed leading to 16 % degree of dechlorination after only 3 h time-on-stream. The difference in the first measurement point can be traced back to small variations in the sampling time, combined with the steep slope of the curve. Overnight regeneration by hot nitrogen flow resulted in minimal improvement of the dechlorination performance (full circles). This shows that the blocking of active sites after Ni-material utilization cannot be leveraged by a hot gas purge.

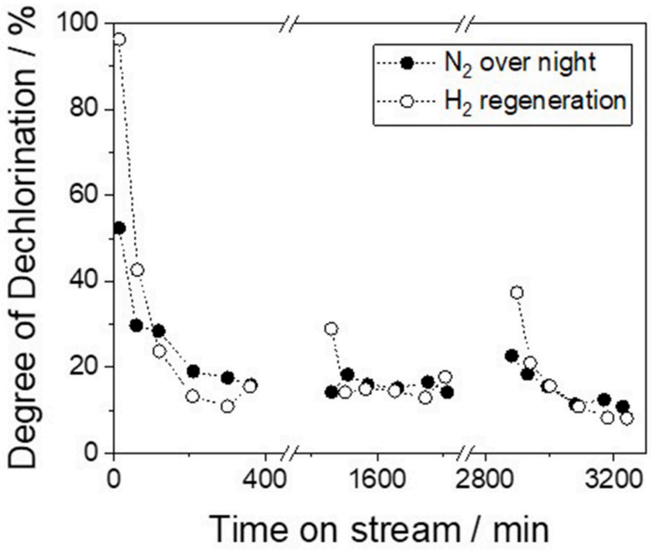


Fig. 8. Degree of dechlorination achieved during three days of dechlorination experiments with attempts to regenerate the Ni-material overnight. Dechlorination conditions: 5 g Ni-material, 200 °C, 0.8 mol% chloronaphthalene in the H0-BT feed, 50 g h^{-1} feed mixture, 20 mL_n min^{-1} H_2. Regeneration conditions overnight: Drying under nitrogen flow at 150 °C (full circles); drying/reduction at 200 °C using a 1:1 mixture of nitrogen and hydrogen (open circles).

Regeneration of the same materials with the reductive mixture of hydrogen and nitrogen (1:1) at 200 °C showed only some minor regeneration effects for the first data points of day two and three. This positive effect could not be maintained for longer than 1 h. After that a certain baseline dechlorination activity was found that was independent on the regeneration protocol applied.

Consequently, the regeneration is not possible under applied conditions using hydrogen and would need to be studied at higher temperatures in the future. Regeneration would enable to recover the Ni-material for the dechlorination process and HCl that could be recycled for the BT production process, to increase material efficiency and to reduce environmental impacts.

4. Conclusion

Dechlorination of chlorobenzyltoluene was successfully demonstrated in a continuously operated trickle bed reactor using a commercial nickel-based material as adsorbent and catalyst. Interestingly, dechlorination was also observed in experiments without hydrogen supply, indicating that partial removal of chlorobenzyltoluene from the liquid mixture proceeds via adsorption. By introducing hydrogen into the system, dechlorination is accelerated by factor 3, what can be attributed to the better regeneration of nickel centers in the presence of hydrogen.

To simulate a high liquid throughput and accelerate Ni-material aging, the chloride concentration was increased by adding the model substances chlorobenzene and chloronaphthalene to the H0-BT feed. Both substances increased deactivation with increasing feed concentrations due to more rapid blocking of active centers. The presence of benzene and naphthalene in the liquid product phase, confirms the cleavage of the chloride-carbon bond in these additives. The dechlorination capacity of per gram of Ni-material was estimated to ~2 kg of technical grade H0-BT.

In total, our study demonstrates that technical quality H0-BT that contains traces of chloroaromatic compounds from its production can be purified to almost chloride-free qualities by contact with commercial Ni-based hydrogenation catalyst materials that serve both as adsorbent and catalyst material. This allows us to convert this technical quality into a liquid organic hydrogen carrier of better quality for the use in repetitive hydrogenation/dehydrogenation cycles for the storage and transportation of hydrogen. It is important to note that this kind of purification and pre-treatment of the benzyltoluene is only necessary for the first use of technical H0-BT as LOHC compound. Given the usual application of LOHC compounds in many hundreds of hydrogenation and dehydrogenation cycles this is an important aspect for the scale in which such purification process might be industrially needed with further development of LOHC-based hydrogen storage technologies.

CRediT authorship contribution statement

K. Mitländer: Writing – original draft, Investigation, Formal analysis, Data curation. **J. Henseler:** Writing – review & editing, Investigation. **F. Rullo:** Writing – review & editing, Investigation. **P. Nathrath:** Investigation. **M. Geißelbrecht:** Writing – review & editing, Supervision. **P. Wasserscheid:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **P. Schühle:** Writing – review & editing, Supervision, Conceptualization.

Data availability statement

Additional research data is made available on the public depository Zenodo via the https://doi.org/10.5281/zenodo.14879559.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Peter Wasserscheid is co-founder and minority shareholder of Hydrogenious LOHC Technologies GmbH, Erlangen, a company that has commercialized equipment for hydrogen storage using the LOHC technology. 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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