



## Pushing activity and stability of LOHC dehydrogenation catalysts by strict LOHC quality protocols

F. Rullo<sup>a</sup>, C.-K. Beier<sup>b</sup>, J. Henseler<sup>a</sup>, A. Bösmann<sup>b</sup>, P. Preuster<sup>c,d</sup>, P. Wasserscheid<sup>a,b,e</sup>, M. Geißelbrecht<sup>a,\*</sup>

<sup>a</sup> Forschungszentrum Jülich, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IET-2), Cauerstraße 1, 91058, Erlangen, Germany

<sup>b</sup> Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058, Erlangen, Germany

<sup>c</sup> Rosenheim Technical University of Applied Sciences, Faculty of Chemical Technology and Economics, Marktler Straße 50, 84489, Burghausen, Germany

<sup>d</sup> Fraunhofer IEG, Fraunhofer Research Institution for Energy Infrastructure and Geothermal Systems IEG, Am Hochschulcampus 1, 44801, Bochum, Germany

<sup>e</sup> Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy, Am Brainergy Park 4, 52428, Jülich, Germany

### ARTICLE INFO

Handling Editor: Dr F Gallucci

#### Keywords:

LOHC  
Perhydro benzyltoluene  
Dehydrogenation  
Catalyst deactivation  
Quality control

### ABSTRACT

Hydrogen storage and transportation using liquid organic hydrogen carrier (LOHC) systems is a promising way to make use of the existing infrastructure for fuels (tank farms, tank vehicles) for the ramp-up of a future hydrogen economy. For a cost-efficient implementation of LOHC-based technologies the stability of both the hydrogen carrier compounds and the applied hydrogenation/dehydrogenation catalysts is of critical relevance. Herein, we show that catalyst stability in the continuous dehydrogenation of the LOHC compound perhydro benzyltoluene (H12-BT) benefits strongly from a combination of catalyst material pretreatment (drying and reduction) and LOHC purification (removal of volatiles and selective adsorption of oxygenated impurities). This has been demonstrated by using a pellet string reactor with only 30 catalyst pellets (commercial Elemax D101, Clariant), in which only one pellet fills the cross-section of the reactor that is hardly wider than the diameter of the applied catalyst pellets. With this specific reactor the ratio of feed flow to catalyst mass is 20–60 times higher than in a typical technical dehydrogenation reactor allowing us to quantify detrimental effects of impurities on catalyst stability faster and more accurately. Our study demonstrates that all impurities leading to CO formation in the reactor have a significant negative influence on the catalyst stability. Removing such impurities from the catalyst and the LOHC feed enables almost stable dehydrogenation performance in the string reactor for 50 h time-on-stream.

### 1. Introduction

Hydrogen will play a key role in future for seasonal energy storage, as a fuel for heavy-duty mobility, an energy carrier for the transport of energy equivalents over wide distances, and as feedstock and reduction equivalent in major industries [1–3]. Hydrogen can be produced without CO<sub>2</sub>-emissions if electrolysis with electricity from renewable power sources is applied. While H<sub>2</sub> has a very high gravimetric energy density (33.3 kWh/kg), several challenges relate to its very low volumetric energy density at ambient conditions (3 Wh/L). To increase the volumetric energy density compression, liquefaction or chemical hydrogen storage via hydrogen binding to carrier molecules are possible technical options. Next to chemical hydrogen storage using CO<sub>2</sub> or N<sub>2</sub> as energy-lean carrier (and methane, methanol, DME or NH<sub>3</sub> as the

hydrogen-rich carrier, respectively), the liquid organic hydrogen carrier (LOHC) technology offers a very attractive way for hydrogen storage and transportation [4,5]. An LOHC-system always consists of at least one hydrogen-lean and one hydrogen-rich molecule, both liquid at ambient conditions. In an exothermal hydrogenation reaction H<sub>2</sub> reacts with the hydrogen-lean molecule to form its hydrogen-rich counterpart. The so-stored hydrogen can be released in times and at locations of energy shortage or hydrogen need in an endothermal dehydrogenation reaction transforming the hydrogen-rich molecule back to the initial hydrogen-lean carrier compound. This closes the storage cycle that can be applied in many repetitive hydrogenation/dehydrogenation cycles.

The LOHC technology is particularly attractive when the used storage molecules are pure hydrocarbon compounds. In this case, the high physico-chemical similarity of the storage compounds to today's

\* Corresponding author.

E-mail address: [m.geisselbrecht@fz-juelich.de](mailto:m.geisselbrecht@fz-juelich.de) (M. Geißelbrecht).

<https://doi.org/10.1016/j.ijhydene.2024.12.104>

Received 15 November 2024; Received in revised form 2 December 2024; Accepted 6 December 2024

Available online 12 December 2024

0360-3199/© 2024 The Authors. Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

hydrocarbon fuels enables the rededication of the existing infrastructure for fuels to the transportation and storage of hydrogen using LOHC. Additionally, hydrogen storage via the LOHC-technology enhances the safety of hydrogen storage as hydrogen is part of the organic molecule and some of the hydrogen-rich LOHC compounds are even hardly flammable. Among the hydrocarbon LOHC systems discussed in literature, the systems toluene/methylcyclohexane (TOL/MCH), benzyltoluene/perhydro benzyltoluene (H0-BT/H12-BT), and dibenzyltoluene/perhydro dibenzyltoluene (H0-DBT/H18-DBT) are intensively discussed, investigated and evaluated in first pilot plant applications [6–10]. The H0-BT/H12-BT system combines the advantages of easy handling due to low viscosity and easy separation of LOHC and hydrogen by condensation due to low vapor pressure at ambient conditions [11]. In direct comparison to H0-DBT/H18-DBT, the H0-BT/H12-BT system shows higher activity and selectivity in both the hydrogenation and the dehydrogenation reaction. In direct comparison with toluene/methylcyclohexane H0-BT/H12-BT has a 13 % higher volumetric storage density. Based on these findings, we have decided to use the LOHC-system H0-BT/H12-BT for this study as this system combines most of the advantages of the LOHC-systems TOL/MCH and H0-DBT/H18-DBT.

The dehydrogenation of H12-BT is catalyzed by a heterogeneous catalyst, which typically consists of platinum nanoparticles supported on a porous, neutral alumina support [12]. The catalyst does not only determine the productivity of the hydrogen release reaction but also its selectivity, i.e. the almost complete suppression of side reaction that lead to a loss of LOHC carrier material. Therefore, significant research efforts have been devoted in the past to optimize the dehydrogenation catalyst with respect to its precious metal nanoparticle size, support material selection (acidity, pore structure, material), and preparation techniques (e.g. egg-shell impregnation) [12–15]. Additionally, selective poisoning of the catalyst and bimetallic catalysts has proven very successful to eliminate catalyst sites creating too strong product adsorption [16–19]. Such strategies enabled a very effective increase of both productivity and selectivity in deep unloading cycles, i.e. by strongly reducing fluorene formation from consecutive oxidative cyclization of H0-BT.

Besides productivity and selectivity, the stability and robustness of the applied dehydrogenation catalyst is decisive for the economics of hydrogen release from LOHC systems. The Pt-containing catalyst (typical Pt-loadings are 0.3–0.5 wt-%) is not only a part of the overall investment, changing the catalyst leads also to downtimes and low system availability. Recently, Lim et al. showed that time-on-stream (TOS) without catalyst change is a critical aspect to keep the dehydrogenation cost as low as possible [20]. Lim et al. found constant catalyst deactivation in their dehydrogenation study. As a countermeasure, they adjusted the temperature or the LOHC flow rate in order to continue to achieve the desired hydrogen release even with reduced catalyst activity [20]. For obvious reason this is not ideal because these countermeasures require a heat source of higher temperature or lead to a lower utilization of the hydrogen storage capacity of the applied LOHC material.

A deeper investigation of the most relevant deactivation mechanisms of LOHC dehydrogenation catalysts in close-to technical applications (including impurities and dynamic operation) is still in its infancy. Dao and coworkers have studied the stability of S-doped Pt-catalysts on alumina and concluded from their quantitative CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies that the preservation of terrace and step sites at the Pt nanoparticles is crucial to maintain a high catalyst activity over time [21]. They stated that deactivation of S-doped Pt catalysts is significantly reduced compared to S-free Pt catalysts on the same support, a finding that can be understood in the light of increased catalyst coking due to fluorene-type by-product formation with the S-free catalyst. Rude et al. conducted consecutive hydrogenation and dehydrogenation cycles in semi-batch experiments (one batch of LOHC mixture and catalyst remaining in the autoclave, hydrogen gas fed and released) and reported a relevant decrease in

productivity from the first to the second experiment but constant productivities afterwards [11]. These authors discuss the possibility of catalyst reactivation during the hydrogenation step of the storage cycle. Wunsch et al. investigated the liquid phase dehydrogenation of H18-DBT in a micro-structured reactor and reported declining productivity over the first 48 h TOS, followed by a constant productivity over the next 70 h TOS [22].

In a wider picture, deactivation studies of LOHC dehydrogenation catalysts depend strongly on the nature of the reaction. In reactions where only gaseous reactants contact the catalyst, coking is a major problem [23,24]. Coking starts with the formation of polycyclic hydrocarbons via condensation [25]. These polycyclic hydrocarbons can further oligomerize forming polyaromatic coke structures. Coking is favored by high concentrations of aromatic molecules (and thus degree of dehydrogenation) and by long residence times of aromatic products at the catalyst. The latter are often a direct consequence of the strong adsorption of aromatic compounds on the catalyst and of the low vapor pressures of polycyclic compounds preventing their removal from the catalyst surface via evaporation [18,26–28].

For example, Chai and Kawakami showed that an Al<sub>2</sub>O<sub>3</sub>-supported platinum catalyst deactivated in the dehydrogenation of MCH strongly in the first 200 min TOS [29]. This deactivation could be reduced by the modification of the Pt catalyst with rhenium or sulphur. Further investigations showed that the overall deactivation of the investigated MCH dehydrogenation catalyst could be divided into two different deactivation phases during long-term experiments lasting over 600 h [30]. At the beginning of the experiment, a rapid drop in productivity was observed followed by a slower long-term deactivation [25]. A partial reactivation of the catalyst could be achieved by a reduction of the catalyst with a hydrogen flow [25].

The same condensation reactions of aromatic products also occur in multiphase dehydrogenation reactions with a partly liquid LOHC mixture. However, the removal of the resulting coke precursors can take place here by a hot wash with the liquid LOHC mixture, i.e. coke precursors dissolve in the LOHC mixture and are removed by the convective LOHC flow [16]. By the presence of liquid LOHC in the reactor the residence time of coke precursors can thus be significantly reduced resulting in much lower coke formation.

Apart from coke formation, catalyst poisoning by reactive gaseous side-products or impurities is another relevant deactivation mechanism for LOHC dehydrogenation catalysts in real-life use. The purity of hydrogen released from perhydro-dibenzyltoluene was investigated by Bulgarin et al. [31]. They detected small amounts of CO in the released hydrogen that can originate either from traces of water or traces of oxygenated hydrocarbon impurities in the system. The productivity of fresh H18-DBT with a higher amount of organic oxygenates was found lower compared to LOHC material after three consecutive hydrogenation/dehydrogenation cycles containing almost no organic oxygenate impurities. Organic oxygenates may also be formed in a new concept the so called autothermal dehydrogenation, if no complete reconversion of the oxidized LOHC molecule to the hydrogen-rich LOHC molecule is possible [32]. Besides the blocking of active Pt-sites by strong adsorption, CO can also form coke under typical dehydrogenation conditions [23,33,34]. In this reaction, coke is not formed from polycyclic hydrocarbon precursors, but by the deposition of atomic carbon via a CO cleavage reaction [35]. The solubility of coke from different origin (polycyclics condensation vs. CO cleavage) in the hot LOHC mixture may be different.

A very attractive method for testing catalyst stability in continuous operation offers the so-called pellet string reactor. This reactor type was already described in 1972 by Scott et al. and is characterized by the fact that the reactor cross-section is only slightly wider than the diameter of one of the applied catalyst pellets [36]. Therefore, the catalyst bed consists of a small number of catalyst pellets arranged as a string with maximum one catalyst pellet in the reactor cross-section. The liquid hourly space velocities (LHSV) of a pellet string reactor can be

comparable to industrial reactors and also their heat and mass transport characteristics can be similar [37,38]. The high ratio of reactor wall surface to volume makes isothermal operation easy. In addition, the small number of pellets allows one to immediately observe changes in the productivity of the catalyst pellets, and thus enables direct observation of catalyst deactivation effects. This makes a pellet string reactor very suitable for investigating catalyst stability.

In this contribution, we apply a pellet string reactor for investigating the stability of a commercial S-doped Pt/alumina dehydrogenation catalyst (Clariant, Elemax D101) in the dehydrogenation of H12-BT. Our work focuses on a detailed understanding of the role of impurities in the technical LOHC material and adsorbed species at the catalyst on catalyst stability. This study is the first one to systematically detect the influence of different impurities on catalyst stability. Furthermore, this is the first study to have addressed the development of a strict quality protocol for H12-BT dehydrogenation. Particularly in the context of industrial application, a quality protocol is essential for the successful commercial roll-out.

## 2. Material and methods

### 2.1. Experimental set-up

Our study was carried out in a continuous dehydrogenation reactor setup as previously described by Peters et al. [39] and schematically shown in Fig. 1. However, the dimensions of the reactor were chosen very specifically in order to realize a pellet string reactor with an inner diameter of 4.6 mm and a length of 105 mm (diameter of the applied Elemax D101 catalyst pellets ranged between 3.15 and 3.55 mm). The setup essentially consisted of a reactant and product tank as well as the tubular pellet string reactor, which was mounted and heated in a ventilated oven. The hydrogen-loaded H12-BT was pumped into the reactor using an HPLC pump, which was also coupled with a Coriolis mass flow meter from Bronkhorst. The reactor was operated in upflow mode, i.e. the H12-BT entered the reactor from the bottom. The released hydrogen was detected via a mass flow meter (MFM) with a measuring range of 200 Nml/min.

For some of our experiments the technical H12-BT was purified from by-products originating from the technical production or from the storage conditions. The purification was carried out to assess the influence of such impurities on the catalyst stability. The applied purification was performed in two steps. In the first step, purging of the technical H12-BT with nitrogen was executed. The H12-BT was placed for this purpose in heatable double jacket vessel for temperature control. Nitrogen was supplied to the setup and a vacuum pump allowed us to remove volatile impurities also at conditions below atmospheric pressure. In the second purification step the H12-BT was contacted with a defined amount of a 4 Å molecular sieve adsorber under an inert argon

atmosphere.

### 2.2. Experimental dehydrogenation procedure

The commercial S-doped Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (Clariant, EleMax D101) applied for this study has a platinum content of 0.3 wt-% and is doped with sulphur [16]. The applied H12-BT was a technical product purchased from Hydrogenious LOHC Technologies ([www.hydrogenious.net](http://www.hydrogenious.net)) with a degree of hydrogenation above 97 %. For our dehydrogenation experiments, the exact number of 30 catalyst pellets were filled into the reactor. The reactor was purged with cold hydrogen to remove any residual gases. Subsequently, the pressure was increased to reaction pressure. In experiments without catalyst preformation, the hydrogen flow was shut off prior to heating and pressurization. The reactor was heated to the desired reaction temperature under continuous H12-BT flow. To facilitate catalyst preformation, the reactor was heated to reaction temperature under a constant H<sub>2</sub> flow rate without H12-BT feeding for a period of 3 h. Following this, the hydrogen flow was stopped and the experiment was started with the addition of the H12-BT feed to the reactor. All dehydrogenation experiments were carried out at a mean reactor temperature of 284 °C and a pressure of 2.5 bara. A continuous flow of H12-BT of 0.3 g/min was fed into the reactor. The released hydrogen from the reaction  $\dot{V}_{H_2}$  was detected using a Bronkhorst mass flow meter.

The degree of dehydrogenation (DoDH) is defined as the ratio of released hydrogen to the maximum amount of releasable hydrogen. A DoDH of 0 thus means that no hydrogen has been released and H12-BT is the only LOHC compound present. A DoDH of 1 equals to complete dehydrogenation with H0-BT being the only LOHC compound present. The DoDH can be calculated based on the detected released hydrogen flow  $\dot{V}_{H_2}$  and the feed flow rate  $\dot{m}_{H12-BT}$  using equation (1).

$$DoDH = \frac{\dot{V}_{H_2} \cdot \rho_{H_2}}{\frac{\dot{m}_{H12-BT}}{M_{H12-BT}} \cdot 6 \cdot M_{H_2}} \quad (1)$$

The productivity is defined as the ratio of released hydrogen mass flow and active precious metal content of the catalyst. The productivity is frequently used to compare different reactors with a different catalyst mass and is dependent on the released hydrogen flow  $\dot{V}_{H_2}$ , the catalyst mass  $m_{cat}$  and can be calculated using equation (2). The used EleMax D101 catalyst has a precious metal loading  $w_{PM}$  of 0.003. Additionally, equation (2) shows the relationship between productivity and DoDH.

$$P = \frac{\dot{V}_{H_2} \cdot \rho_{H_2}}{m_{cat} \cdot w_{PM}} = \frac{\frac{\dot{m}_{H12-BT}}{M_{H12-BT}} \cdot 6 \cdot M_{H_2} \cdot \Delta DoDH}{m_{cat} \cdot w_{PM}} \quad (2)$$

The following experimental details have been applied for the purification of the H12-BT. Purging and evaporation of volatile impurities: The technical H12-BT was placed in a 2 L vessel and heated to 60 °C. A

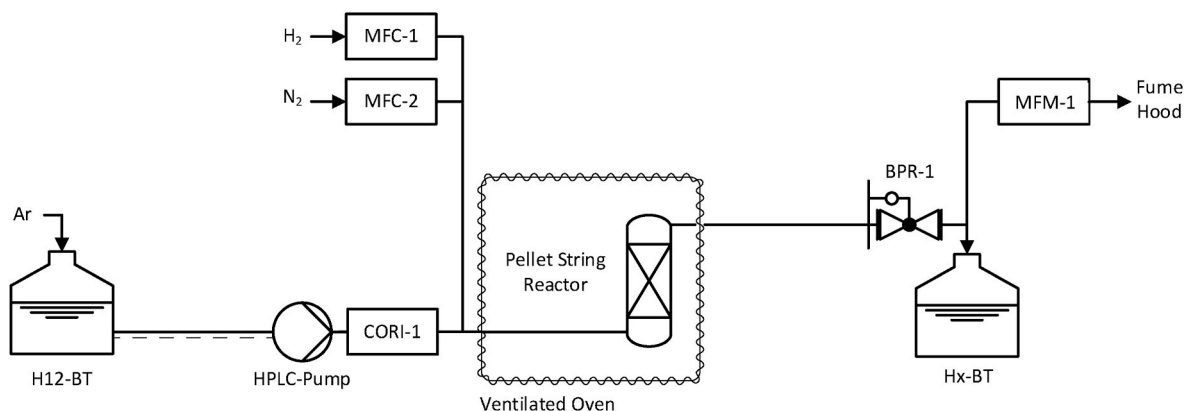


Fig. 1. Schematic illustration of the applied continuous dehydrogenation set-up with the pellet string reactor being placed in a heated oven.

vacuum of less than  $\leq 100$  mbar was then applied for 4 h and afterwards nitrogen stream of 1 NL/min was used to purge the vessel for a period of 70 h via a gas inlet nozzle. Adsorption: The pre-purified H12-BT was stored in a separate container for 24 h at room temperature under argon atmosphere in contact with a 4 Å molecular sieve (180 g molecular sieve on 1 L of H12-BT).

A MultiGas 2031 FTIR spectrometer from MKS Instruments was used to analyze the composition of the released hydrogen. The device was equipped with a multi-pass gas cell. The effective wavelength was 5.11  $\mu\text{m}$  and an MCT detector cooled with liquid nitrogen was applied. The spectra were collected with a resolution of 0.5  $\text{cm}^{-1}$ . To ensure a higher sensitivity and to enable the collection of background spectra, a temperature of 35  $^{\circ}\text{C}$  was set in the gas cell and the cell was purged with nitrogen ( $>99.999\%$ , Linde AG). The water content in the liquid samples was determined using coulometric Karl Fischer titration. For this purpose, the sample was weighed and injected into a Metrohm 831 KF coulometer. Hydranal-Coulomat AK from Sigma-Aldrich was selected as the reagent.

### 3. Results and discussion

#### 3.1. Catalyst stability in the continuous dehydrogenation of technical perhydro benzyltoluene

First, we performed long-term experiments in the tubular pellet string reactor to test the catalyst stability in the dehydrogenation of technical quality H12-BT as a reference. These experiments were carried out with small amounts of catalyst (0.6 g, 30 pellets) and a relatively high H12-BT feed flow rate (0.3  $\text{g}/\text{min}$ ) to be able to observe deactivation phenomena quickly while the catalyst operates at low DoDH with reasonably high Pt-based productivities. Note that under these conditions the H12-BT loading per mass of catalyst and time is higher than in a typical technical LOHC dehydrogenation reactor. In our experiment the ratio of feed flow rate to catalyst mass was  $30 \text{ g}_{\text{H12-BT}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$  compared to typical values of 0.5–3  $\text{g}_{\text{H12-BT}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$  reported for technical reactors [40,41]. This intensifies the effect of impurities in our setup, i.e. the effects of impurities on catalyst stability can be detected in shorter operation times with 1 h of TOS in our setup simulating 10–60 h TOS for the same operation conditions in a typical technical reactor.

Fig. 2 shows the productivity vs. TOS plot for a continuous H12-BT dehydrogenation experiment at 284  $^{\circ}\text{C}$  over 70 h. This experiment was performed with untreated catalyst and technical H12-BT used as received from the manufacturer. This run provides a benchmark for assessing the influence of different pretreatment processes and LOHC

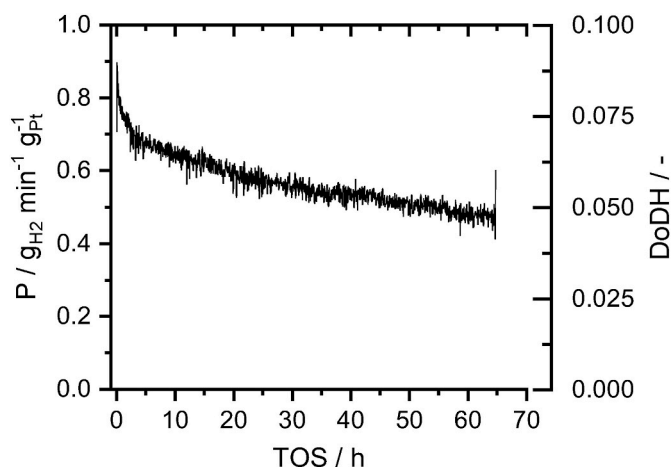


Fig. 2. Stability of the dehydrogenation of H12-BT over TOS for a non-preformed catalyst and non-purified H12-BT ( $T = 284$   $^{\circ}\text{C}$ ,  $p = 2.5$  bara,  $\dot{m}_{\text{H12-BT}} = 0.3$   $\text{g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/ $\text{Al}_2\text{O}_3$ ,  $m_{\text{cat}} = 0.6$  g).

purification measures on catalyst stability.

The obvious deactivation behavior can be split into two phases. In the first 5 h TOS the productivity decreases rapidly  $0.9 \text{ g}_{\text{H}_2} \cdot \text{min}^{-1} \cdot \text{g}_{\text{Pt}}^{-1}$  to  $0.7 \text{ g}_{\text{H}_2} \cdot \text{min}^{-1} \cdot \text{g}_{\text{Pt}}^{-1}$ . Afterwards, an almost linear further decrease is observed but with much lower negative gradient. Fitting of the productivity data points between a TOS of 40 h and 60 h by linear regression results in a Pt-specific deactivation rate of  $-2.73 \cdot 10^{-3} \text{ g}_{\text{H}_2} \cdot \text{min}^{-1} \cdot \text{g}_{\text{Pt}}^{-1} \cdot \text{h}^{-1}$ . These findings indicate that in this particular setup no steady-state operation is reached in the first 65 TOS.

In searching for possible reasons of the observed deactivation we tend to exclude a major influence of coke formation for several reasons: i) Under the applied conditions the DoD is below 10% excluding the formation of significant amount of aromatic H0-BT product that, however, is the known as the starting material for polyaromatics and coke formation; ii) Evaporation of Hx-BT is not very pronounced at the applied conditions and resulting DoDH according to VLE equations developed by Kadar et al. [42] and a significant part of the LOHC mixture is therefore present in the liquid phase in the pellet string reactor; thus, coke precursors – if formed at all – would be washed away from the catalyst surface.

Instead, we considered catalyst deactivation by poisoning of the Pt-catalyst with CO. Such deactivation mechanism has been previously reported by Bulgarin et al. [31]. The formation of CO in the dehydrogenation of H12-BT requires an oxygen source. This oxygen source can be found in technical systems either in the LOHC feedstock or in the catalyst material. The LOHC feedstock may contain traces of organic oxygenates from storage, transport, and handling under air. The alumina support of the catalyst is known to effectively adsorb water which can serve as source of oxygen for CO formation under dehydrogenation conditions [31]. To validate this assumption, and to exclude that all CO formed undergoes very rapid methanation under the applied dehydrogenation conditions, we measured the CO content in the released hydrogen from the dehydrogenation experiment with technical H12-BT and non-pretreated catalyst (as shown in Fig. 2) by FTIR. The results are shown in Fig. 3.

It is noteworthy that the concentration of CO in the released hydrogen increases over the whole TOS. This is probably due to a reduced CO adsorption capacity over TOS. In the beginning the most active sites of the Pt catalyst strongly adsorb CO. With ongoing saturation of these sites, the CO released into the gas phase and detected by FTIR therefore increases with time. Note, that the CO concentrations are

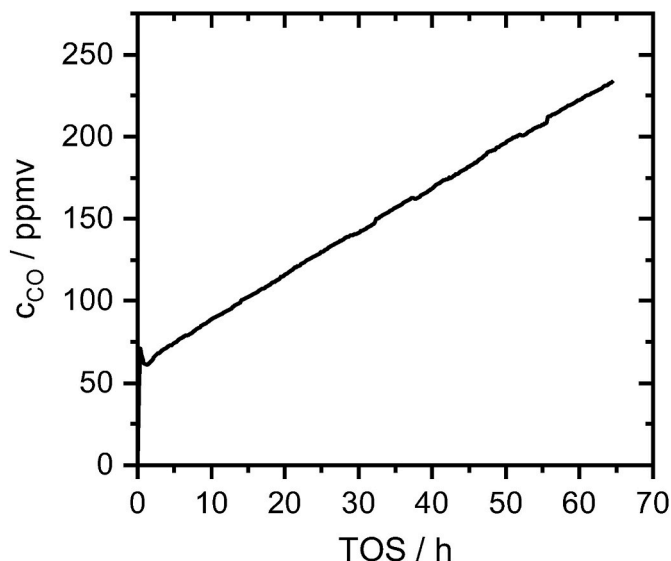


Fig. 3. Temporal progress of the CO concentration in the released hydrogen ( $T = 284$   $^{\circ}\text{C}$ ,  $p = 2.5$  bara,  $\dot{m}_{\text{H12-BT}} = 0.3$   $\text{g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/ $\text{Al}_2\text{O}_3$ ,  $m_{\text{cat}} = 0.6$  g).

high compared to earlier reports [31] as the amount of catalyst in the reactor for CO adsorption is low and the overall amount of released hydrogen is low (low temperature, low catalyst amount) thus leading to high CO concentrations in the product gas. Moreover, the residence time in the pellet string reactor is obviously too low to convert the formed CO to methane in a methanation as described by Bulgarin et al. [31]. These measurements proved the presence of the catalyst poison CO in our dehydrogenation reactor. In a next step, we therefore explored strategies to avoid the formation of CO by catalyst preformation and purification of the technical H12-BT feedstock.

### 3.2. Influence of catalyst preformation on catalyst stability

In a first step, the catalyst was dried and reduced previously to the experiment to exclude that the catalyst material acts as the oxygen source for CO-formation. For the preformation the dry catalyst was heated under H<sub>2</sub> flow to the reaction temperature and kept at the temperature as described in the experimental section. The stability of the dehydrogenation of H12-BT with dried and reduced catalyst is shown in Fig. 4.

Obviously, the drying and preformation of the catalyst has no major influence on the long-term stability of the catalyst as the productivity is very similar between 40 and 65 h TOS. However, the decrease of the productivity in the first 5 h TOS is less pronounced after drying and reduction of the catalyst in our setup prior to H12-BT contact. One obvious explanation for the reduced short-term deactivation is that the drying and reduction of the catalyst eliminates one source of oxygen which, however, is not the dominant one in the system as can be seen from the fact that over longer TOS a continuous deactivation takes over that seems to be related to feedstock impurities.

### 3.3. Influence of LOHC purification on catalyst stability

Since the only source for the continuous oxygen supply to the reactor is the LOHC feedstock itself, our next set of experiments targeted the removal of water and oxygenates from the applied technical H12-BT. For this purpose, we applied the two-step procedure described in the experimental part including removing of volatile impurities and adsorption of remaining water and organic oxygenates. We could demonstrate by our Karl-Fisher titration measurements that the applied

procedure reduces the water content of the applied H12-BT from 26 ppm (without purification) to almost water-free after the purification (detected water amount below the quantification limit of 10 ppm). Additionally, the oxygen containing hydrocarbons were removed by adsorption to the molecular sieve. This purification effect was proven indirectly by adding purposely dicyclohexylmethanol proving its removal by adsorption. Direct and quantitative detection of the different oxygen-containing compounds present in the technical H12-BT (different compounds and different regioisomers) by gas chromatography was not possible due to detection limits and lack of correction factors. From our removal of dicyclohexylmethanol to quantities below detection limit we assume that most oxygen containing organic compounds are removed by our adsorptive purification method.

The influence of the purification of H12-BT was first tested without drying and reduction of the catalyst material to separate effects and to better understand the influence of each individual step. The influence of the H12-BT purification on the catalyst stability is shown in Fig. 4.

Interestingly, the removal of oxygen containing impurities from the H12-BT feed does not prevent the rapid decrease of the dehydrogenation productivity in the first 5 h TOS. This indicates again that the rapid deactivation in the first hours is related to impurities introduced into the reactor by the catalyst material itself. The linear regression of the productivity decrease between 45 and 60 h TOS gives, however, a significantly lower deactivation rate ( $-0.93 \cdot 10^{-3} \text{ g}_{\text{H}_2} \text{ min}^{-1} \text{ g}_{\text{Pt}}^{-1} \text{ h}^{-1}$ ) compared to the experiment without purification of the H12-BT feed (see comparison with Figs. 2 and 4).

This clearly indicates that the second deactivation period that dominates at longer TOS, is related to the quality of the LOHC feed. Again, CO formation from water and oxygenated compounds introduced by the LOHC feed is a very likely explanation. This is further confirmed by our FTIR measurements conducted with the product gas from the experiment shown in Fig. 5 with pretreated LOHC feed. The concentration of CO in the released hydrogen flow decreases to below 10 ppm in this experiment with purified H12-BT compared to up to 220 ppm in the case without purification (see Fig. 3).

To further test our hypothesis, we added purposely the oxygen containing model impurity dicyclohexylmethanol (DCHM) to the purified LOHC. The resulting concentration of dicyclohexylmethanol in the contaminated LOHC was 0.1 wt-%. Interestingly, the deactivation

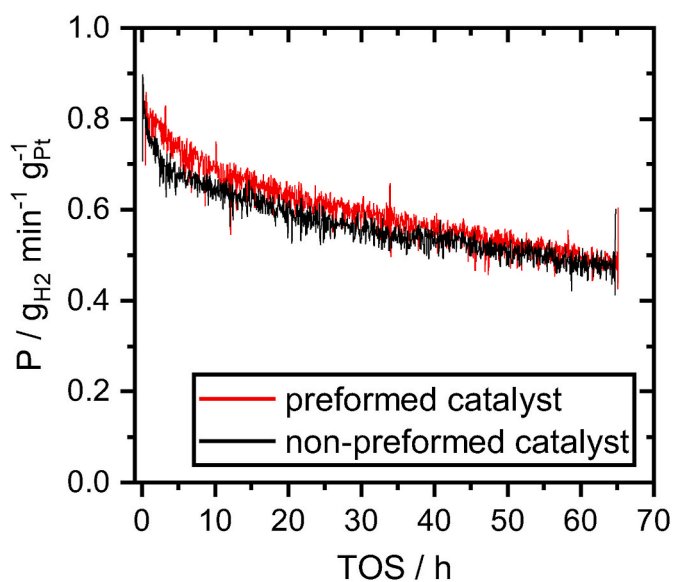


Fig. 4. Influence of the catalyst preformation on the stability of the dehydrogenation of H12-BT for non-purified H12-BT ( $T = 284 \text{ }^\circ\text{C}$ ,  $p = 2.5 \text{ bara}$ ,  $\dot{m}_{\text{H12-BT}} = 0.3 \text{ g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/Al<sub>2</sub>O<sub>3</sub>,  $m_{\text{cat}} = 0.6 \text{ g}$ ).

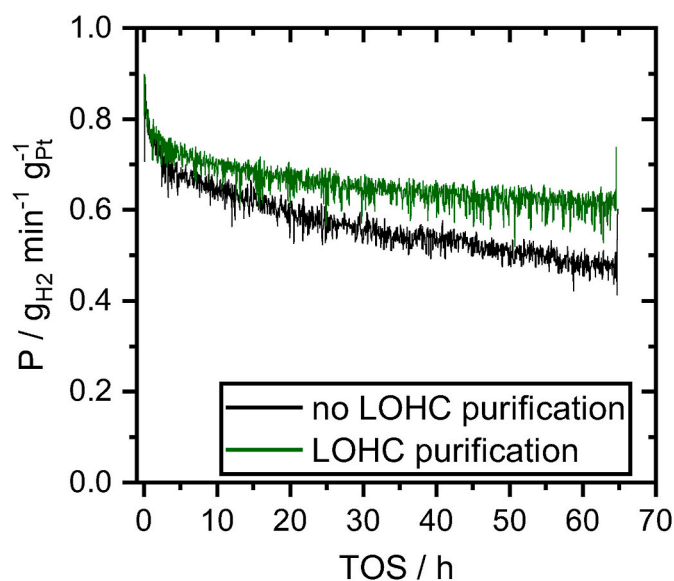


Fig. 5. Influence of the H12-BT purification on the stability of the dehydrogenation process in the pellet string reactor for the use of a non-dried and non-reduced catalyst ( $T = 284 \text{ }^\circ\text{C}$ ,  $p = 2.5 \text{ bara}$ ,  $\dot{m}_{\text{H12-BT}} = 0.3 \text{ g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/Al<sub>2</sub>O<sub>3</sub>,  $m_{\text{cat}} = 0.6 \text{ g}$ ).

behavior of the contaminated H12-BT was very similar to the reference scenario with the non-purified, technical H12-BT (see Fig. 6). The absolute productivity is higher over the entire TOS for the experiment with the synthetically contaminated H12-BT. This may be since only a few pellets of the commercial catalyst were used for each experiment and each individual catalyst pellet has slight differences in productivity. The concentration of CO in the product hydrogen stream increased to 30–50 ppm with the contaminated H12-BT. Despite the fact that this value is slightly lower than in the reference scenario with unpurified technical H12-BT, this finding clearly shows the dependency of the CO formation on the concentration of oxygen containing impurities in the LOHC feedstock. Moreover, our hypothesis that oxygen containing impurities in the H12-BT are responsible for the observed long-term deactivation could be clearly supported.

### 3.4. Combined effect of catalyst preformation and LOHC purification on catalyst stability

Finally, we combined the catalyst material preformation and the H12-BT purification method. This combination appeared reasonable to us as the catalyst material preformation prevents the initial rapid deactivation period while the LOHC purification reduces long-term deactivation effects as shown in the sections before. The effect of all individual treatments and of the combined treatment are shown in Fig. 7.

Very remarkably, the combination of catalyst preforming and LOHC purification did indeed completely avoid the short-term deactivation of the catalytic system with almost no decrease of activity in the first 5 h TOS. Afterwards, a very moderate decrease in the productivity over TOS was observed starting from the high, very initial productivity level. The linear regression of the deactivation rate between 40 and 50 h TOS resulted in a value of  $-1.3 \cdot 10^{-3} \text{ g}_{\text{H}_2} \text{ min}^{-1} \text{ g}_{\text{Pt}}^{-1} \text{ h}^{-1}$ . This deactivation is significantly less pronounced than for the reference scenario and comparable to the long-term deactivation of the experiment with purified H12-BT. The CO content in the released hydrogen of this experiment combining catalyst preforming and LOHC purification was below 5 ppm. It is not excluded that the low level of remaining deactivation is still due to the remaining low-level contamination of the purified H12-BT with oxygenated organic compounds.

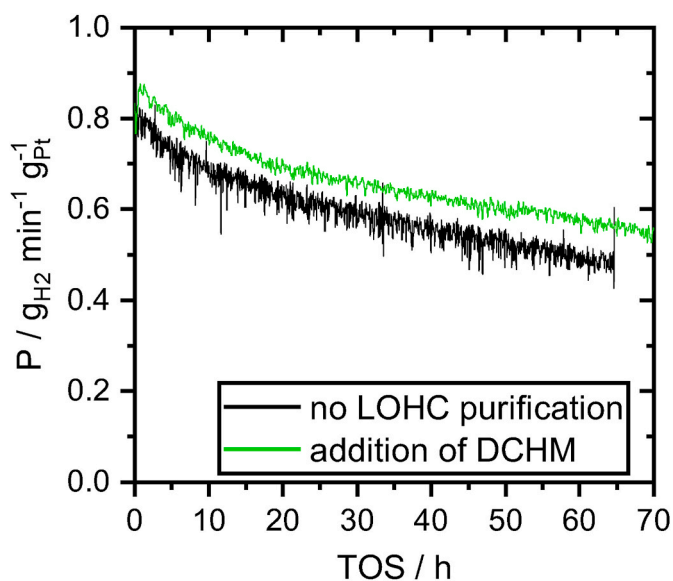


Fig. 6. Effect of the addition of DCHM to purified LOHC on the dehydrogenation process in the pellet string reactor for the use of a preformed catalyst ( $T = 284 \text{ }^\circ\text{C}$ ,  $p = 2.5 \text{ bara}$ ,  $\dot{m}_{\text{H12-BT}} = 0.3 \text{ g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/ $\text{Al}_2\text{O}_3$ ,  $m_{\text{cat}} = 0.6 \text{ g}$ ).

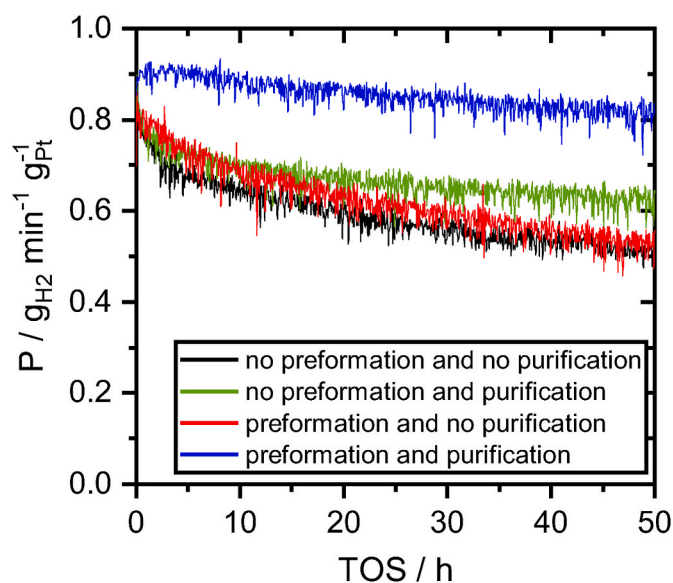


Fig. 7. Influence of the combination of catalyst preformation and LOHC purification (blue) on the stability of the dehydrogenation of H12-BT in comparison to individual measures of catalyst or LOHC pretreatment, and in comparison to the stability test using the untreated catalyst and LOHC as benchmark ( $T = 284 \text{ }^\circ\text{C}$ ,  $p = 2.5 \text{ bara}$ ,  $\dot{m}_{\text{H12-BT}} = 0.3 \text{ g} \cdot \text{min}^{-1}$ , catalyst 0.3 wt-% Pt/ $\text{Al}_2\text{O}_3$ ,  $m_{\text{cat}} = 0.6 \text{ g}$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

## 4. Conclusion

In summary, the use of a pellet string reactor enabled in this study a very detailed description of influencing factors on the stability of a commercial LOHC dehydrogenation catalyst (Clariant, Elemax D101) under realistic operation conditions. With its significantly higher ratio of LOHC volume throughput to catalyst mass, the pellet string reactor allowed us to mimic in 1h time-on-stream (TOS) deactivation effects resulting from impurities that would take place in a technical dehydrogenation reactor over 10–60 h operation time. Thus, the 50–65 h TOS realized in this work simulate real operation times of up to 4000 h TOS in technical dehydrogenation reactors. The influence of coking was suppressed by the low achieved DoDH to focus on the influence of impurities on catalyst stability.

In the light of these numbers, our findings appear highly relevant for the further technical implementation of benzyltoluene-based LOHC technologies. While a catalyst preformation that reduces all Pt surface compounds to elemental Pt and removes water from the hygroscopic alumina support affects only the catalyst stability in the first hours of operation, more significant long-term stability effects originate from impurities that are entered into the reactor together with the LOHC feedstock. Consequently, removing volatiles and oxygen-containing organic compounds from the feedstock by purging and adsorption procedures proved to be very effective to enhance long-term catalyst stability.

Mechanistically, our study indicates very clearly that CO poisoning of the Pt catalyst plays a major role for the observed deactivation processes. This raises the question in which way a CO-poisoned dehydrogenation catalyst can be regenerated or reactivated. Hydrogen treatment under pressure to convert Pt-bound CO to methane or air-bleeding to convert Pt-bound CO to  $\text{CO}_2$  may offer interesting options. In the latter case, however, it has to be assured that no LOHC material remains in the catalyst pores during the air-bleeding step as such compounds would undergo oxidation to form oxygenated organic compounds that could later generate CO under dehydrogenation conditions. In any case, we expect that some of the impurities that have shown in this work to affect catalyst stability in a negative manner stem from the technical production process of benzyltoluene and perhydro benzyltoluene. Such

impurities must be removed only once to qualify the material for its use as hydrogen carrier if appropriate storage conditions prevent their formation during the hydrogen storage application in an effective manner.

### CRedit authorship contribution statement

**F. Rullo:** Writing – original draft, Visualization, Investigation, Formal analysis. **C.-K. Beier:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **J. Henseler:** Writing – review & editing, Data curation. **A. Bösmann:** Writing – review & editing, Validation, Supervision, Conceptualization. **P. Preuster:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. **P. Wasserscheid:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **M. Geißelbrecht:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Conceptualization.

### Data availability

Data for this article are available at zenodo under <https://doi.org/10.5281/zenodo.13927630>. Further data used to support the findings of this study can be made available by the corresponding authors upon request.

### Declaration of interest statement

Peter Wasserscheid is founder and minority share holder of the company Hydrogenious LOHC technologies ([www.hydrogenious.net](http://www.hydrogenious.net)) that offers commercially hydrogen storage systems based on the LOHC technology.

There is no conflict of interest to declare with regard to the specific scientific results reported in this paper.

### Acknowledgements

The authors acknowledge financial support by the Ministry of Economic Affairs, Industry, Climate Action and Energy of the State of North Rhine-Westphalia through the project “HECTOR”.

### References

- [1] Abdin Z, Zafaranloo A, Rafiee A, Mérida W, Lipiński W, Khalilpour KR. Hydrogen as an energy vector. *Renewable and sustainable energy reviews* 2020;120:109620.
- [2] Kovač A, Paranos M, Marcius D. Hydrogen in energy transition: a review. *International journal of hydrogen energy* 2021;46(16):10016–35.
- [3] Lebrouhi B, Djoupo J, Lamrani B, Benabdellaziz K, Kouksou T. Global hydrogen development-A technological and geopolitical overview. *Int J Hydr Energy* 2022; 47(11):7016–48.
- [4] Aakko-Saksa PT, Cook C, Kiviahjo J, Repo T. Liquid organic hydrogen carriers for transportation and storing of renewable energy – review and discussion. *J Power Sources* 2018;396:803–23.
- [5] Preuster P, Papp C, Wasserscheid P. Liquid organic hydrogen carriers (LOHCs): toward a hydrogen-free hydrogen economy. *Acc Chem Res* 2016;50(1):74–85.
- [6] Jorschick H, Geißelbrecht M, Ebl M, Preuster P, Bösmann A, Wasserscheid P. Benzyltoluene/dibenzyltoluene-based mixtures as suitable liquid organic hydrogen carrier systems for low temperature applications. *Int J Hydr Energy* 2020;45(29): 14897–906.
- [7] Jorschick H, Preuster P, Dürr S, Seidel A, Müller K, Bösmann A, Wasserscheid P. Hydrogen storage using a hot pressure swing reactor. *Energy Environ Sci* 2017;10 (7):1652–9.
- [8] Geißelbrecht M, Mrusek S, Müller K, Preuster P, Bösmann A, Wasserscheid P. Highly efficient, low-temperature hydrogen release from perhydro-benzyl toluene using reactive distillation. *Energy & environmental science* 2020;13(9):3119–228.
- [9] Ichikawa M. Organic liquid carriers for hydrogen storage. *Solid-State Hydr Storage* 2008:500–32. Elsevier.
- [10] Kwak Y, Kirk J, Moon S, Ohm T, Lee Y-J, Jang M, Park L-H, Ahn C-i, Jeong H, Sohn H. Hydrogen production from homocyclic liquid organic hydrogen carriers

- (LOHCs): benchmarking studies and energy-economic analyses. *Energy Conv Manag* 2021;239:114124.
- [11] 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 Fuel* 2022;6(6):1541–53.
  - [12] Auer F, Hupfer A, Bösmann A, Szesni N, Wasserscheid P. Influence of the nanoparticle size on hydrogen release and side product formation in liquid organic hydrogen carrier systems with supported platinum catalysts. *Catal Sci Technol* 2020;10(19):6669–78.
  - [13] Chen X, Gierlich CH, Schötz S, Blaumeiser D, Bauer T, Libuda Jr, Palkovits R. Hydrogen production based on liquid organic hydrogen carriers through sulfur doped platinum catalysts supported on TiO<sub>2</sub>. *ACS Sustain Chem Eng* 2021;9(19): 6561–73.
  - [14] Shi L, Zhou Y, Tan X, Qi S, Smith KJ, Yi C, Yang B. The effects of alumina morphology and Pt electron property on reversible hydrogenation and dehydrogenation of dibenzyltoluene as a liquid organic hydrogen carrier. *Int J Hydrogen Energy* 2022;47(7):4704–15.
  - [15] Bong B, Mebrahtu C, Jurado D, Bösmann A, Wasserscheid P, Palkovits R. Hydrogen loading and release potential of the LOHC system benzyltoluene/perhydro benzyltoluene over S-Pt/TiO<sub>2</sub> catalyst. *ACS Eng Au* 2024;4(4):359–67.
  - [16] Auer F, Blaumeiser D, Bauer T, Bösmann A, Szesni N, Libuda J, Wasserscheid P. Boosting the activity of hydrogen release from liquid organic hydrogen carrier systems by sulfur-additives to Pt on alumina catalysts. *Catal Sci Technol* 2019;9 (13):3537–47.
  - [17] Jo Y, Kim D, Kim TW, Yoon D, Suh Y-W. Highly dispersed Pt–MnOx nanoclusters for the promoted activity of mesoporous Pt–MnOx–Al<sub>2</sub>O<sub>3</sub> in dehydrogenation of perhydro-benzyltoluene. *Appl Catal B: Environ* 2023;334:122848.
  - [18] Jo Y, Kim TW, Oh J, Kim D, Suh Y-W. Mesoporous sulfur-decorated Pt–Al<sub>2</sub>O<sub>3</sub> for dehydrogenation of perhydro benzyltoluene: activity-favorable adsorption of reaction species onto electron-deficient Pt atoms. *J Catal* 2022;413:127–37.
  - [19] Peng Z, Lu H, Zhang S, Cao X, Chen J, Wei B, Sang M, Wang H, Sun Y. *Pt-Sn alloy nanoparticles Supported on Al<sub>2</sub>O<sub>3</sub> for the Dehydrogenation of octadecahydro-dibenzyltoluene*. *ACS applied nano materials* 2023;6(18):16152–60.
  - [20] Lim IS, Jeong Y, Kwak Y, On E-R, Dao QN, Jeong H, Sohn H, Nam SW, Lim T-H, Müller K. Maximizing clean hydrogen release from perhydro-benzyltoluene: energy-efficient scale-up strategies and techno-economic analyses. *Chem Eng J* 2023;478:147296.
  - [21] Dao QN, On E, Ramadhani S, Lee K, Sohn H, Choi SH, Lee SY, Jeong H, Kim Y. Catalytic insights into perhydro-benzyltoluene dehydrogenation: probing surface characteristics revealed by DRIFTS study. *Int J Hydrogen Energy* 2024;56: 1284–93.
  - [22] Wunsch A, Berg T, Pfeifer P. Hydrogen production from the LOHC perhydro-dibenzyl-toluene and purification using a 5 µm PdAg-membrane in a coupled microstructured system. *Materials* 2020;13(2):277.
  - [23] Bartholomew CH. Mechanisms of catalyst deactivation. *Appl Catal Gen* 2001;212 (1–2):17–60.
  - [24] Meng J, Zhou F, Ma H, Yuan X, Wang Y, Zhang J. A review of catalysts for methylcyclohexane dehydrogenation. *Topics Catal* 2021;64:509–20.
  - [25] Alhumaidan F, Tsakiris D, Cresswell D, Garforth A. Hydrogen storage in liquid organic hydride: selectivity of MCH dehydrogenation over monometallic and bimetallic Pt catalysts. *Int J Hydrogen Energy* 2013;38(32):14010–26.
  - [26] Saeyes M, Reyniers M-F, Neurock M, Marin G. *Adsorption of cyclohexadiene, cyclohexene and cyclohexane on Pt (1 1 1)*. *Surface science* 2006;600(16):3121–34.
  - [27] Ouma CNM, Modisha P, Bessarabov D. Insight into the adsorption of a liquid organic hydrogen carrier, perhydro-i-dibenzyltoluene (i= m, o, p), on Pt, Pd and PtPd planar surfaces. *RSC advances* 2018;8(56):31895–904.
  - [28] Morin C, Simon D, Sautet P. Trends in the chemisorption of aromatic molecules on a Pt (111) surface: benzene, naphthalene, and anthracene from first principles calculations. *J Phys Chem B* 2004;108(32):12084–91.
  - [29] Chai MR, Kawakami K. Kinetic model and simulation for catalyst deactivation during dehydrogenation of methylcyclohexane over commercial Pt-, PtRe- and sulfided PtRe-Al<sub>2</sub>O<sub>3</sub> catalysts. *J Chem Technol Biotechnol* 1991;51(3):335–45.
  - [30] Alhumaidan F, Cresswell D, Garforth A. Long-term deactivation of supported Pt catalysts in the dehydrogenation of methylcyclohexane to toluene. *Indus Eng Chem Res* 2010;49(20):9764–70.
  - [31] 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.
  - [32] 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.
  - [33] Sirirjaruphan A, Goodwin Jr JG, Rice RW. Investigation of the initial rapid deactivation of platinum catalysts during the selective oxidation of carbon monoxide. *J Catal* 2004;221(2):288–93.
  - [34] Bitter J, Seshan K, Lercher J. Deactivation and coke accumulation during CO<sub>2</sub>/CH<sub>4</sub> reforming over Pt catalysts. *J Catal* 1999;183(2):336–43.
  - [35] Bartholomew CH. Carbon deposition in steam reforming and methanation. *Catal Rev Sci Eng* 1982;24(1):67–112.
  - [36] Scott D, Lee W, Papa J. The measurement of transport coefficients in gas-solid heterogeneous reactions. *Chem Eng Sci* 1974;29(11):2155–67.

- [37] Hipolito A, Rolland M, Boyer C, de Bellefon C. Single pellet string reactor for intensification of catalyst testing in gas/liquid/solid configuration. *Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles* 2010;65(5):689–701.
- [38] Haase S, Weiss M, Langsch R, Bauer T, Lange R. Hydrodynamics and mass transfer in three-phase composite minichannel fixed-bed reactors. *Chem Eng Sci* 2013;94: 224–36.
- [39] Peters W, Seidel A, Herzog S, Bösmann A, Schwieger W, Wasserscheid P. Macrokinetic effects in perhydro-N-ethylcarbazole dehydrogenation and H<sub>2</sub> productivity optimization by using egg-shell catalysts. *Energy Environ Sci* 2015;8 (10):3013–21.
- [40] Willer M, Preuster P, Geißelbrecht M, Wasserscheid P. Continuous dehydrogenation of perhydro benzyltoluene and perhydro dibenzyltoluene in a packed bed vertical tubular reactor–The role of LOHC evaporation. *Int J Hydrogen Energy* 2024;57:1513–23.
- [41] Willer M, Preuster P, Margaretti P, Harting J, Wasserscheid P. Heat transfer to a catalytic multiphase dehydrogenation reactor. *Int J Hydrogen Energy* 2024;80: 1011–20.
- [42] Kadar J, Gackstatter F, Ortner F, Wagner L, Willer M, Preuster P, Wasserscheid P, Geißelbrecht M. Boosting power density of hydrogen release from LOHC systems by an inverted fixed-bed reactor design. *Int J Hydrogen Energy* 2024;59:1376–87.