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Article

Hydrogen Loading and Release Potential of the LOHC System Benzyltoluene/Perhydro Benzyltoluene over S−Pt/TiO_2 Catalyst

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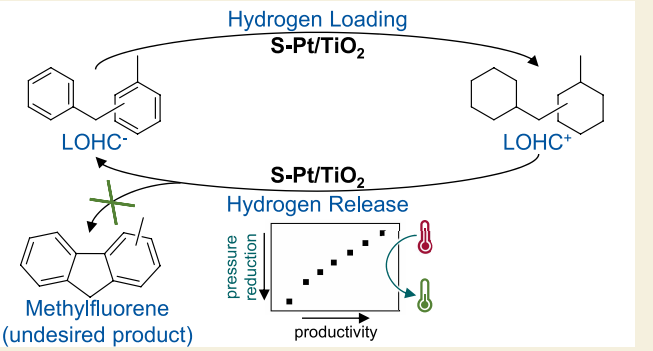
ABSTRACT: Platinum on oxide catalysts are established for the loading and unloading of liquid organic hydrogen carriers (LOHCs). These catalysts have been optimized so far to provide high reaction rates and consequently high power densities in the loading and unloading reactor units. However, high temperatures are required for catalytic dehydrogenation (hydrogen release), which can result in low energy efficiency. Another challenge is to avoid the formation of the undesired side product methylfluorene. In this work, the optimized S−Pt/TiO_2 catalyst was successfully applied in the hydrogenation and dehydrogenation of the commercially attractive LOHC system benzyltoluene/perhydro benzyltoluene (H0-BT/H12-BT). Methylfluorene was not detected using S−Pt/TiO_2, while utilizing the S−Pt/Al_2O_3 state-of-the-art catalyst caused methylfluorene formation. The S−Pt/TiO_2 catalyst combines the prevention of this side reaction with a competitive hydrogen release rate. Hence, the application of S−Pt/TiO_2 in the LOHC cycle was further studied. It was shown that the catalytic hydrogen release can be accelerated by increasing the temperature, but low reaction temperatures are desired to increase the energy efficiency of the process by enabling heat integration between the hydrogen release and waste heat generation from energetic hydrogen use cases. Accordingly, the potential for low-temperature hydrogen release at reduced pressure was demonstrated by a systematic investigation of pressure influence. With pressure reduction, the hydrogen release productivity continuously increased. Finally, the hydrogenation and dehydrogenation productivity obtained in this work was compared to results reported in the literature to demonstrate the implementation potential of the optimized S−Pt/TiO_2 catalyst.



KEYWORDS: *liquid organic hydrogen carriers, heterogeneous catalysts, dehydrogenation, methylfluorene, reaction pressure, hydrogenation, productivity*

INTRODUCTION

Using green hydrogen as an energy carrier enables to establish a sustainable energy system based on renewable energy sources, while ensuring a constant supply according to the energy demand.[1−6] For a successful application of this technology, sufficient amounts of H_2 must be stored and transported under limited space, while guaranteeing safety and usability.[7] Among the alternatives, liquid organic hydrogen carriers (LOHCs) meet these requirements. In LOHCs, hydrogen is bound to the carrier in a catalytic hydrogenation step to form loaded LOHC$^+$. Then, the LOHC$^+$ can be handled via the existing infrastructure for liquid fuels and does not suffer from self-discharge. As soon as hydrogen is required, it is released by catalytic dehydrogenation of the loaded LOHC$^+$, while the unloaded carrier LOHC$^-$ is further reused in another hydrogen storage cycle.[1,2,6−10] Suitable LOHC systems include cyclic hydrocarbons such as dibenzyltoluene (H0-DBT)/perhydro dibenzyltoluene (H18-DBT), benzyltoluene (H0-BT)/perhydro benzyltoluene (H12-BT), diphenylmethane (DPM)/dicyclohexylmethane, or benzophenone (BP)/dicyclohexylmethanol.[1,3,11,12] The use of the DBT- and BT-based systems is highly attractive, as these are well-established heat transfer oils and show beneficial thermal stability as well as availability on a technical scale.[1,3] In general, 57 kg H_2 can be stored per 1 m^3 of H18-DBT, while the

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storage capacity of H12-BT is 54 kg H_2 per 1 m^3.[11,12] However, H18-DBT suffers from a high dynamic viscosity (790 mPa s at 15 °C) leading to challenges in its applicability. On the contrary, the dynamic viscosity of H12-BT is low (8 mPa s at 15 °C) and makes it a highly attractive LOHC system.[13−16] For the hydrogenation (loading) and dehydrogenation (unloading) of LOHC systems based on cyclic hydrocarbons, platinum nanoparticles supported on aluminum or titanium oxides have been reported as suitable catalysts.[11,12,15,17−20] However, low-coordinated sites on the Pt-nanoparticles as well as surface functionalities of the support can catalyze undesired side reactions such as cracking, cyclization, and polymerization.[21] These can be suppressed by selective sulfur poising of low-coordinated sites of platinum.[12,15,17,21] Using S−Pt/Al_2O_3 in cycles of loading and unloading of BT, the amount of cracking products obtained was less than 0.1% and the formation of side products with high boiling points was reduced as well.[15] Nevertheless, the undesired side product methylfluorene (MF) was detected.[11,15] Potentially, fluorene species results from an oxidative cyclization of H0-BT which is itself formed during the hydrogen release from H12-BT.[11,15] Further dehydrogenation of the desired dehydrogenation product H0-BT forming fluorene species can occur due to a nucleophilic attack of the main ring on a proton present in the catalytic reaction system similar to the formation of fluorenic derivates from diphenylmethane.[22] In this case, bond formation between the benzyl- and the toluene-ring occurs via an intermediate with delocalized positive charge on the main ring leading to the cyclization product methylfluorene and one equivalent H_2.[22] Under the conditions for dehydrogenation reaction, fluorene species could as well be formed by a radical mechanism via homolytic cleavage of a C−H bond and, afterward, bond formation between the two rings of H0-BT.[22,23] Another possible option for the mechanism of methylfluorene formation is the oxidative dehydrogenation via oxygen activation.[24] Here, oxygen which is present in the reaction system is first activated, for example, by adsorption on acid sites of the catalyst. The activated oxygen could then react with hydrogen from H0-BT via a six-membered cyclic transition state forming one mol of hydrogen peroxide for each methylfluorene formed. Furthermore, hydrogen peroxide itself can react with H0-BT forming methylfluorene and two equivalents of water. This type of mechanism is similar to the mechanistic steps reported for the oxidative dehydrogenation of alkylbenzenes on Lewis acid sites.[24] The side reaction forming MF seems to be irreversible, and hence, fluorene derivates accumulate over the performed storage cycles.[15] For example, Rüde et al. showed that the amount of methylfluorene increased over two cycles (8 h hydrogenation, 40 h dehydrogenation) from 0.05 to 0.27%.[15] Fluorene derivatives do not restrict the ability of the liquid to store hydrogen as they act as LOHCs themselves. However, they can negatively influence properties like the melting point or the dynamic viscosity of the LOHC system and can slow down the dehydrogenation process.[11,15,25] Moreover, the existence of methylfluorene can lead to coke formation and deactivation of the catalyst.[11,15,22] This undesired formation of fluorene species is not only a problem for the utilization of the BT-based LOHC system but similarly occurs for systems like DPM or BP, respectively.[11,12]

Besides side product formation, another hurdle for large-scale application of the LOHC technology presents the high energy demand.[13] To increase the overall efficiency, the dehydrogenation unit can be heated by waste heat from other processes.[26−29] Ideally, the heat is provided by a subsequent hydrogen utilization step like exothermal fuel cell operation.[28−31] However, for typical proton-exchange membrane (PEM) fuel cells, the operation temperature is limited to below 200 °C.[30] Thus, for waste heat integration with these devices, sufficient hydrogen release must be enabled below this temperature limit. In addition, dehydrogenation at lower temperatures leads to lower energy demand for preheating, reduced heat losses, and enhanced operational dynamics of the dehydrogenation unit.[28,30,31] To realize dehydrogenation at lower temperatures with a technically relevant conversion of more than 80%, overcoming the thermodynamic limitation is required. According to Le Chatelier's principle, this can be enabled by removing the product hydrogen from the reaction system.[30,32,33] For this purpose, dilution with an inert gas or reduction of the total pressure reduces the hydrogen partial pressure in the system.[30,32] In literature, it was shown that a reduced total pressure of 500 mbar at 180 °C during dehydrogenation of the LOHC perhydro-N-ethyl-carbazole leads to 60% of the productivity obtained at 200 °C and ambient pressure.[29] For H18-DBT, the hydrogen release rate was increased by a combination of dehydrogenation with electrochemical hydrogen compression (EHC), which reduced the pressure in the dehydrogenation unit.[32] Integration of the dehydrogenation and EHC with heating by waste heat results in a beneficial combination as not only the pressure is reduced but also high-value compressed and purified hydrogen is obtained.[32] However, systematic investigations of the pressure influence on the dehydrogenation of H12-BT are lacking, and hence, further studies are required for a successful implementation of the dehydrogenation step at reduced pressure.

As mentioned above, applying BT as the LOHC over sulfur-doped platinum on oxide catalysts is highly promising and has gained a lot of interest in recent years. Nevertheless, two main challenges remain: limited recyclability of the carrier in case of side product formation and the high energy demand for hydrogen release.[28,30] In this work, we present possibilities to avoid the formation of undesired fluorene species as well as the need for high temperatures during the dehydrogenation step. For this purpose, loading and unloading of the favorable LOHC system H0-BT/H12-BT was performed over the S−Pt/TiO_2 catalyst (0.1 wt % S, 0.3 wt % Pt). In this study, the influence of pressure and the side product formation during hydrogen release from H12-BT are investigated over a wide range of reaction conditions. The applied S−Pt/TiO_2 catalyst was previously optimized for the dehydrogenation of H18-DBT by members of our working group (Chen et al.[17]) but had not been tested in the dehydrogenation of the favorable H12-BT or hydrogenation reactions. First, to confirm the S−Pt/TiO_2 catalyst reproducibility, the obtained samples were characterized using various techniques (i.e. XRD, N_2 physisorption, and ICP-OES). Next, the prepared catalyst was tested in the dehydrogenation of H12-BT, and its activity as well as the formation of fluorene species was compared to the results obtained with the commercial benchmark catalyst (S−Pt/Al_2O_3). Furthermore, this work addresses the high energy demand of hydrogen release as the second main challenge for the large-scale application of the LOHC technology besides side product formation. For this purpose, the opportunity to decrease the dehydrogenation temperature

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by pressure reduction was explored by a systematic examination of the influence of the pressure on hydrogen release. In contrast to previous studies of dehydrogenation at reduced pressure, a rather simple setup was employed to ensure an examination of the relation between the dehydrogenation rate and reduced pressure while excluding other influences. Additionally, the performance of S−Pt/TiO_2 in the hydrogenation of H0-BT was evaluated to confirm the suitability of the catalyst for the whole LOHC cycle. Finally, the potential of the prepared catalyst for application with the highly promising LOHC system H0-BT/H12-BT is presented by a comparison of the obtained productivity for hydrogen loading and hydrogen release to literature-reported results using other platinum-based catalysts in hydrogenation and dehydrogenation of BT.

EXPERIMENTAL SECTION

Safety Warnings

For the conduction of high-pressure experiments using hydrogen, rigorous safety precautions must be taken and appropriate equipment must be used.

Materials

Titania pellets (anatase) as well as an aqueous solution of $H_3Pt(SO_3)_2OH$ (15.3 wt % Pt) were purchased from abcr GmbH. The benchmark catalyst S−Pt/Al_2O_3 (EleMax D101) was provided by Clariant Produkte Deutschland. H0-BT (Marlotherm LH) was supplied by Eastman Chemical Company. H12-BT (99.88% hydrogenated) was provided by Helmholtz Institute Erlangen-Nürnberg for Renewable Energy. Tetradecane (purity ≥99.0%) was sourced from Sigma-Aldrich. Dichloromethane (purity ≥99.9%) was obtained from Honeywell. All chemicals were used without further purification.

Catalyst Preparation and Characterization

The S−Pt/TiO_2 catalyst was synthesized via a wet impregnation method as reported by Chen et al.[17] (details on the preparation of S−Pt/TiO_2 are provided in the Supporting Information). The benchmark catalyst S−Pt/Al_2O_3 was received in pellet form, and the pellets were ground in a ball mill (Fritsch Pulverisette 23 Mini Mill). The obtained powder was reduced analogously to the prepared S−Pt/TiO_2 catalyst (400 °C, 4 h, 10 °C min^{-1}). The prepared catalyst samples were characterized using N_2 physisorption, powder X-ray diffraction (XRD), CO pulse chemisorption measurements, and inductively coupled plasma optical emission spectroscopy (ICP-OES). Further information on the used characterization methods is given in the Supporting Information.

Dehydrogenation Experiments

Dehydrogenation experiments of perhydro benzyltoluene (H12-BT) were performed in a 250 mL four-neck round-bottom flask (details on the used experimental setup are provided in the Supporting Information). For each experiment, H12-BT as well as the catalyst powder were added into the flask, and afterward, all open necks of the setup were sealed by septa. Next, the heating as well as stirring and, if required, the pump for pressure reduction were started. During the reaction, samples of the reaction mixture were taken through a septum on the side neck using a syringe with a steel cannula. Afterward, the liquid was separated from the obtained samples by filtration using syringe filters (Chromafil Xtra PTFE-45/24). After the reaction, the setup was cooled down. Thereafter, stirring was stopped.

Hydrogenation Experiments

Hydrogenation experiments of benzyltoluene (H0-BT) were carried out in a stainless-steel pressure reactor (Parr Micro Benchtop reactor 4590, 50 mL) coupled to a gas buret (further information on the utilized setup is given in the Supporting Information). The reaction was performed at a constant pressure of 30 bar. For each experiment, H0-BT and the catalyst powder were placed in the reactor. Afterward, the reactor system was closed and flushed with hydrogen three times. Next, the reactor was pressurized with 30 bar H_2, and the gas buret was pressurized with approximately 100 bar H_2. Afterward, the reactor was heated to the desired temperature under stirring (500 rpm). The reaction time was started when the desired reaction temperature was reached. After the reaction, the reactor was cooled down. Thereafter, the stirring was stopped, and the system was depressurized. The reaction mixture was taken out, and the catalyst was separated from the liquid phase by filtration using syringe filters (Chromafil Xtra PTFE-45/24).

Liquid Phase Analysis

For a quantitative evaluation, the degree of hydrogenation (DOH) or degree of dehydrogenation (DOD) of the liquid phase was calculated using eq 1 as commonly used in the literature.[14,17]

$$\mathrm{DOD}(t) = 1 - \mathrm{DOH}(t) = \frac{\int_{t_0}^{t} n_{\mathrm{H_2,reaction}}(t)\,dt}{n_{\mathrm{H_2,max}}} \tag{1}$$

In general, the maximum amount of hydrogen $n_{H_2,\,max}$ that can be released from the LOHC in the dehydrogenation or loaded onto the LOHC in the hydrogenation depends on the chosen carrier molecule. The corresponding calculations for the DBT- and BT-based systems are given in eqs 2 and 3, respectively.

$$n_{\mathrm{H_2,max}} = 9 n_{\mathrm{H18-DBT}} \tag{2}$$

$$n_{\mathrm{H_2,max}} = 6 n_{\mathrm{H12-BT}} \tag{3}$$

The liquid composition of the reaction mixture was analyzed using gas chromatography (GC) and mass spectrometry (MS), and thus, the DOD was calculated via the molar fraction x of each BT species HX-BT with X hydrogen atoms bound to the molecule compared to H0-BT (eq 4).

$$\mathrm{DOD_{BT}} = \sum \frac{12 - \mathrm{X}}{12} \times x(\mathrm{HX-BT}) \tag{4}$$

The DOD correlates with the refractive index (RI) and, hence, can be determined by refractometry as well.[34] Further details on the liquid phase analyses as well as the DOD determination by GC-MS and refractometry are provided in the Supporting Information.

From the DOD or DOH, productivity for a given reaction range a to b can be calculated (eq 5) to provide a base for quantitative comparison of reactions with different amounts of the active species platinum and different reaction times.[20,28,35,36]

$$P_{\mathrm{a-b}}(t) = \frac{\Delta m_{\mathrm{H_{2,a-b}}}}{m_{\mathrm{Pt}} \times (t_{\mathrm{b}} - t_{\mathrm{a}})} = \frac{n_{\mathrm{H_2,max}} \times (\mathrm{DOH_b} - \mathrm{DOH_a}) \times M_{\mathrm{H_2}}}{m_{\mathrm{Pt}} \times (t_{\mathrm{b}} - t_{\mathrm{a}})} \tag{5}$$

Negative values of productivity are obtained for dehydrogenation, while positive values occur for hydrogenation. Note that it is important to attribute productivity values to a certain range a-b as the kinetics of hydrogenation and dehydrogenation batch-mode experiments are strongly dependent on the distance from the thermodynamic equilibrium under the given conditions, and thus, the productivity is usually not constant over the whole reaction. Further information on the calculation of productivity as discussed in this work is provided in the Supporting Information.

RESULTS AND DISCUSSION

Performance of the Prepared Catalyst in Hydrogen Release from H12-BT

In previous work, the catalyst system S−Pt/TiO_2 (0.1 wt % S, 0.3 wt % Pt) had been optimized for the dehydrogenation of H18-DBT.[17] In this work, the reported catalyst was first reproduced and it was applied for the hydrogenation and dehydrogenation of the more favorable LOHC system H0-BT/

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H12-BT. Successful reproducibility of the catalyst was confirmed by the obtained physicochemical properties which are in accordance with the results reported by Chen et al.[17] (details of the catalyst characterization results are provided in the Supporting Information, Figure S3 and Table S1). Catalytic performance of the prepared S−Pt/TiO_2 in the dehydrogenation of H12-BT was studied at reaction temperatures between 220 and 270 °C (Figure 1; further information on the hydrogenation procedure is given in the Supporting Information).

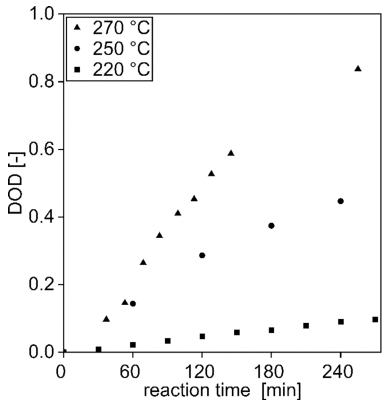

Figure 1. Degree of dehydrogenation (DOD) over reaction time in the dehydrogenation of H12-BT using S−Pt/TiO_2 (0.1 wt % S, 0.3 wt % Pt) as a catalyst at different temperatures; experimental conditions: 30 g of H12-BT, 0.1 mol % Pt to substrate, 400 rpm, ambient pressure.

The desired dehydrogenation reaction over the optimized S−Pt/TiO_2 catalyst proceeded at all of the reaction temperatures employed. However, the dehydrogenation rate is strongly influenced by the reaction temperature. For example, at 270 °C, a degree of dehydrogenation (DOD) of 0.41 was already achieved after 100 min, while only a DOD of 0.36 was reached after 180 min at 250 °C. Besides, the reaction at 220 °C led to a DOD of 0.07 after 180 min, which increased up to 0.10 after 270 min. Thus, an increase in the reaction rate with increasing reaction temperature was observed as expected from both kinetics and thermodynamics.[30,32,33]

As the used S−Pt/TiO_2 catalyst has been optimized for H18-DBT dehydrogenation, the obtained H12-BT dehydrogenation results are further compared with its performance in H18-DBT dehydrogenation. As reported by Chen et al.,[17,37] the dehydrogenation of H18-DBT was investigated at 270 °C using S−Pt/TiO_2. To allow fair comparison, the experiments herein were performed at the same reaction conditions except the inert gas pressure (270 °C, 400 rpm, 0.10 mol % Pt to substrate corresponding to 0.10 wt % Pt to H12-BT and 0.07 wt % Pt to H18-DBT), although the physicochemical properties of HX-BT and HX-DBT (e.g., viscosity, boiling point, hydrogen partial pressure at given total pressure) differ, and hence, this can influence the obtained results. However, the order of magnitude of the catalyst's activity in both LOHC systems can be compared as far as the reactions are performed at similar conditions. In the dehydrogenation of H18-DBT, a DOD of about 0.18 was obtained after 60 min and increased to about 0.25 after 90 min.[17,37] A productivity ($P_{0-90\ min}$) of −0.26 g_{H2} g_{Pt}^{-1} min^{-1} was obtained when H18-DBT was used (details for calculation of productivity are given in the experimental section, and further information on the comparison of productivity is given in the Supporting Information).[17,37] In contrast, the dehydrogenation of H12-BT reached a DOD of 0.26 after 69 min and 0.34 after 83 min. Besides, a productivity ($P_{0-83\ min}$) of −0.26 g_{H2} g_{Pt}^{-1} min^{-1} was obtained with H12-BT. The obtained results prove that the optimized S−Pt/TiO_2 catalyst system for the dehydrogenation of H18-DBT is suitable for H12-BT with a similar hydrogen release productivity for both LOHC systems at similar reaction conditions. Therefore, further tests on the favorable BT-based LOHC system were conducted by using the S−Pt/TiO_2 catalyst.

Comparison of the Optimized Catalyst to the Benchmark Catalyst

To gain further insights into the performance of the prepared catalyst S−Pt/TiO_2 in the dehydrogenation of H12-BT, the catalyst was compared to the commercial benchmark catalyst S−Pt/Al_2O_3 (0.1 wt % S, 0.3 wt % Pt). For this purpose, the DOD over the reaction course as well as the molar amount of the undesired side product methylfluorene were analyzed. The results obtained with both catalysts in dehydrogenation at 250 °C are illustrated in Figure 2.

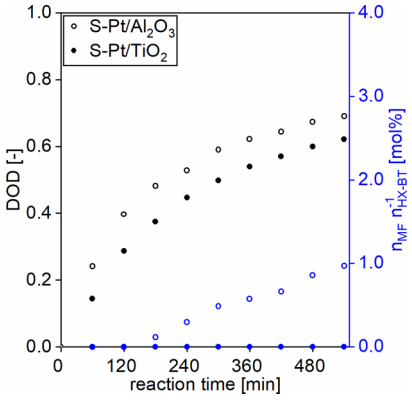

Figure 2. Degree of dehydrogenation (DOD) and molar amount of methylfluorene (MF) over reaction time in the dehydrogenation of H12-BT using the S−Pt/Al_2O_3 benchmark catalyst (0.1 wt % S, 0.3 wt % Pt) and the prepared S−Pt/TiO_2 catalyst (0.1 wt % S, 0.3 wt % Pt); experimental conditions: 250 °C, 30 g of H12-BT, 0.1 mol % Pt to substrate, 400 rpm, ambient pressure.

Using the S−Pt/Al_2O_3 benchmark catalyst, the DODs over the reaction course of 540 min were consistently about 0.1 higher than the results obtained in the reaction with S−Pt/TiO_2. Besides, the reaction over the S−Pt/Al_2O_3 catalyst led to slightly higher productivity ($P_{0.24-0.53}$) of −0.10 g_{H2} g_{Pt}^{-1} min^{-1} compared to S−Pt/TiO_2 with $P_{0.14-0.50}$ of −0.09 g_{H2} g_{Pt}^{-1} min^{-1}. Remarkably, the side product methylfluorene was identified as expected for the dehydrogenation reaction over the S−Pt/Al_2O_3 catalyst, while methylfluorene was found below the detection limit of our analysis of the liquid phase product obtained with our S−Pt/TiO_2 catalyst. With the S−Pt/Al_2O_3 benchmark catalyst, the first traceable amount of methylfluorene to benzyltoluene species (0.12 mol %) was measured after 180 min at a DOD of 0.48. After 540 min, the amount of methylfluorene increased to 0.97 mol % which is a relevant quantity given the negative influence of methylfluorene on physiochemical properties and the further coke formation.[11,15] A highly remarkable note is that no fluorene derivatives were found in the liquid product for all of the

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reactions performed using our S−Pt/TiO_2 catalyst even at a reaction temperature of 270 °C.

Based on the obtained results, methylfluorene is most probably formed via oxidative cyclization of H0-BT.[11,15] Hence, during the dehydrogenation of H12-BT, H0-BT must be formed by the dehydrogenation reaction before this side reaction can occur. Therefore, the influence of H0-BT on the methylfluorene formation was studied by using not only H12-BT but a mixture of H12-BT and H0-BT as starting material in the dehydrogenation over S−Pt/Al_2O_3 (detailed comparison of these dehydrogenation runs is provided in the Supporting Information, Figure S4). Accordingly, when H0-BT was present from the beginning of the reaction, the first traceable amount of methylfluorene was already measured after 120 min. These results indicate that the methylfluorene formation depends indeed on the H0-BT content in the reaction mixture. Besides, these preliminary results indicate that the functionality of the used catalyst is more decisive for methylfluorene formation than the possible alteration of the catalyst during the reaction time. Apparently, the cyclization of H0-BT seems to be suppressed over the titania-supported catalyst instead of the analogous catalyst with alumina as the support. In the literature, different possible mechanisms for methylfluorene formation from H0-BT such as initiation by oxygen activation, nucleophilic attack of the main ring of H0-BT, or a radical mechanism are discussed.[22−24] However, to prove or disprove if these hypothetical mechanisms are occurring in our system and provide exclusive mechanistic evidence, extensive experimental tests and advanced characterization methods are required. Moreover, in situ techniques are required to identify the significant functionalities of the catalyst leading to methylfluorene formation. In general, the significant difference in methylfluorene formation between the two catalytic systems could be caused by steric effects as well as the electronic properties, the different pore structure of the supports, or the higher acidity of alumina compared to titania. Besides, alumina was reported as an active catalyst for oxidative dehydrogenation of alkylbenzenes on Lewis acid sites.[24] Thus, the side reaction forming fluorene species could also depend on the nature as well as the number of acid sites of the employed oxide support. Overall, under the current experimental conditions, the prepared S−Pt/TiO_2 catalyst showed beneficial properties as it offers a competitive rate of hydrogen release from H12-BT, while completely suppressing the formation of the most relevant side product methylfluorene.

Pressure Influence on the Hydrogen Release

As mentioned before, the dehydrogenation rate can be significantly increased by increasing the reaction temperature, but for a more convenient technical application and a high energy efficiency of the process, a decrease in temperature is desired. One option to increase the thermodynamic driving force for the dehydrogenation and, hence, to reduce the reaction temperature is to reduce the total pressure in the dehydrogenation unit. Therefore, the reaction rate acceleration potential of reduced pressure operations was systematically studied at a reaction temperature of 220 °C. For this purpose, the dehydrogenation without pressure adjustment (as shown before) was compared to reactions at a reduced total pressure between 800 mbar and 300 mbar (Figure 3). The undesired methylfluorene side products were not detected during all these experiments, confirming that side product formation was completely suppressed with the here-applied S−Pt/TiO_2 catalyst.

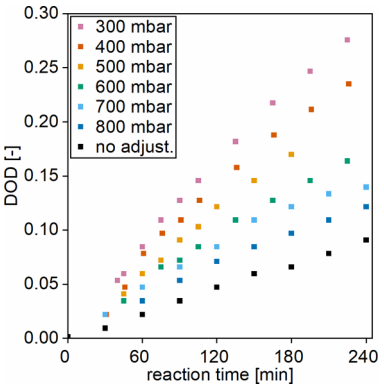

Figure 3. Degree of dehydrogenation (DOD) over reaction time in the dehydrogenation of H12-BT at different total pressures using S−Pt/TiO_2 (0.1 wt % S, 0.3 wt % Pt) as a catalyst; experimental conditions: 220 °C, 30 g of H12-BT, 0.1 mol % Pt to substrate, 400 rpm; pressure of the reaction run "no adjust." is presumably about 1000 mbar.

In general, the reaction rate was found to accelerate significantly with decreasing total pressure, that is, decreasing hydrogen partial pressure in the reaction vessel. While a maximum DOD of 0.09 was reached after 240 min without pressure adjustment at ambient total pressure, the same DOD was obtained after 90 min when the total pressure was reduced to 500 mbar. At a total pressure of 300 mbar, these DOD results were already exceeded after 75 min, as the DOD reached 0.11. Altogether, the initial hydrogen release productivity increased continuously with the reduction of total pressure (Figure 4).

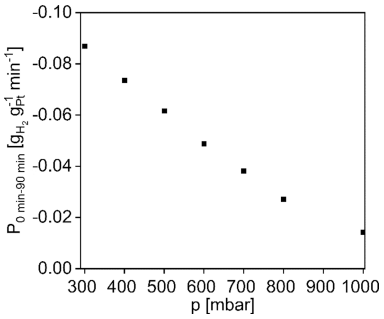

Figure 4. Correlation between the initial hydrogen release productivity ($P_{0-90\ min}$) and the total pressure in the dehydrogenation of H12-BT using S−Pt/TiO_2 (0.1 wt % S, 0.3 wt % Pt) as a catalyst; experimental conditions: 220 °C, 30 g of H12-BT, 0.1 mol % Pt to substrate, 400 rpm, pressure according to reduced total pressure in the reaction vessel, pressure of the reaction run without pressure adjustment is presumable about 1000 mbar.

Overall, the obtained experimental results indicate that pressure reduction can indeed be used to increase hydrogen release productivity and, hence, to obtain relevant DOD in a reasonable time even at temperatures below 250 °C. Thus, the results obtained under the current experimental conditions provide a systematic overview of the total pressure influence on both the DOD and hydrogen release productivity.

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Performance of the S−Pt/TiO_2 Catalyst in Hydrogen Loading of H0-BT

Besides the hydrogen release, the ability of S−Pt/TiO_2 to catalyze the hydrogenation of H0-BT (loading) was studied to ensure the suitability of the prepared catalyst for the whole hydrogen loading and unloading cycle. Using S−Pt/TiO_2 in the hydrogenation of H0-BT at 220 °C (30 bar H_2, 0.020 mol % Pt to H0-BT), a degree of hydrogenation (DOH) of 0.59 was achieved after 30 min of reaction. This corresponds to a productivity ($P_{0-30\ min}$) of 6.14 g_{H2} g_{Pt}^{-1} min^{-1} if the whole reaction time is considered. Note that the experimental procedure for the hydrogenation step also includes a heating period before the start of the reaction time, which can influence the catalytic results (an exemplary heating curve of the hydrogenation reaction is provided in Figure S2). At a lower reaction temperature of 200 °C and otherwise the same reaction conditions, a DOH of 0.44 was reached after 60 min, corresponding to a productivity ($P_{0-60\ min}$) of 2.24 g_{H2} g_{Pt}^{-1} min^{-1}. Furthermore, no side products were detected in the liquid reaction mixture. Overall, these results demonstrate that the optimized S−Pt/TiO_2 catalyst is a very suitable catalyst for the hydrogenation of H0-BT as well as the dehydrogenation of H12-BT.

Potential of S−Pt/TiO_2 Compared to State-of-the-Art Catalyst Systems

The obtained results for the hydrogenation of H0-BT and the dehydrogenation of H12-BT using our optimized S−Pt/TiO_2 catalyst were compared to literature-reported results using platinum catalysts. However, a systematic comparison of different (de)hydrogenation results is still challenging, as different reaction conditions and experimental procedures that influence the obtained results are employed. Furthermore, no standardized evaluation method of the results in the literature has been provided yet. Therefore, in this contribution, an evaluation of productivity for a quantitative comparison is chosen, as the productivity is set to provide a clear relation to the platinum amount used in the reaction and reaction time. Furthermore, evaluation of the obtained results based on productivity also allows us to compare the catalytic performances at different reaction conditions. However, two key factors that can influence productivity must be considered. First, the obtained productivity can also depend on the experimental procedure and the reaction setup employed. Second, the productivity is not constant over the whole reaction course. Therefore, the obtained values depend on the range chosen to calculate productivity (details of the calculation are given in the experimental section; further information on the productivity comparison and the considered studies as well as a broader overview of literature data is provided in Tables S2 and S3). A comparison of the hydrogen release productivity obtained in this work using the optimized catalyst (1) with the benchmark catalyst (2) and the two state-of-the-art catalysts reported in literature (3,4) is provided in Figure 5.

In our experimental dehydrogenation study at 250 °C, a productivity ($P_{0.14-0.50}$) of −0.09 g_{H2} g_{Pt}^{-1} min^{-1} was achieved using the optimized S−Pt/TiO_2 catalyst applied as a powder. At the same reaction conditions, a slightly higher productivity ($P_{0.24-0.53}$) of −0.10 g_{H2} g_{Pt}^{-1} min^{-1} was reached using the commercial benchmark catalyst S−Pt/Al_2O_3 (EleMax D101, Clariant) as powder. Besides, the same commercial catalyst was tested in another study by Geißelbrecht et al. in a catalytic

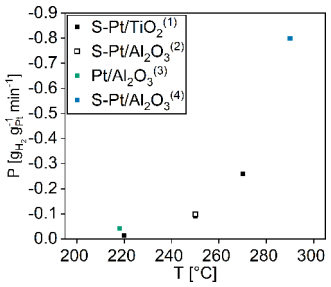

Figure 5. Productivities obtained in the dehydrogenation of H12-BT at temperatures between 218 and 290 °C of different supported platinum catalysts (0.3 wt % Pt), 1: optimized titania-supported catalyst, this work; 2: benchmark catalyst EleMax D101 (Clariant), this work; 3: EleMax D101 (Clariant), derived from experimental results by Geißelbrecht et al.;[28] 4: EleMax-102D (Clariant), derived from experimental results by Rüde et al.;[15] data points for the catalytic experiments reported in the literature were derived based on the values given in the original source as shown in detail in the Supporting Information, Table S2.

fixed-bed reactor (temperature of bed: 218 °C) and a productivity ($P_{0.11-0.33}$) of −0.04 g_{H2} g_{Pt}^{-1} min^{-1} was obtained.[28] For the dehydrogenation at 290 °C and 1 bar hydrogen pressure using the S−Pt/Al_2O_3 commercial catalyst (second generation, EleMax-102D, Clariant), Rüde et al. reported a mean hydrogen release productivity ($P_{0.1-0.5}$) of −0.8 g_{H2} g_{Pt}^{-1} min^{-1}.[15] Comparing the productivity obtained with platinum catalysts in these different dehydrogenation experiments, the expected exponential increase in productivity with higher reaction temperatures is found. These results suggest that the differences between the platinum catalysts (0.3 wt % Pt) are not crucial, but higher reaction temperatures can significantly increase productivity. Furthermore, it is shown that our prepared catalyst S−Pt/TiO_2 has a very similar potential regarding the studied hydrogen productivity compared to the state-of-the-art catalysts, however, with the very important advantage of negligible methylfluorene side product formation.

To evaluate the potential of the S−Pt/TiO_2 catalyst in the H0-BT hydrogenation step, our findings are compared to the experimental results reported by Jorschick et al.[14] and Rüde et al.[15] (Figure 6).

In this work, a productivity ($P_{0-60\ min}$) of 2.24 g_{H2} g_{Pt}^{-1} min^{-1} was obtained during the hydrogenation of BT at 200 °C using our S−Pt/TiO_2 catalyst. On the contrary, a productivity ($P_{0-60\ min}$) of 1.55 g_{H2} g_{Pt}^{-1} min^{-1} during the hydrogenation of H0-BT at the same temperature using the Pt/Al_2O_3 catalyst (5.0 wt % Pt on alumina, 0.017 mol % Pt to H0-BT) originated from the results of Jorschick et al.[14] When the reaction temperature was increased to 220 °C, a productivity ($P_{0-30\ min}$) of 6.14 g_{H2} g_{Pt}^{-1} min^{-1} was recorded for the hydrogenation over our optimized S−Pt/TiO_2 catalyst. At the same reaction temperature, a productivity ($P_{0-30\ min}$) of 4.34 g_{H2} g_{Pt}^{-1} min^{-1} was obtained using the Pt/Al_2O_3 catalyst.[14] It is worth noting that the experimental procedure and especially the method of reactor heating differed in these studies. Additionally, when the productivity for a DOH range between 0.2 and 0.5 is evaluated, Jorschick et al. reported slightly different values $P_{0.2-0.5}$ of 1.59 g_{H2} g_{Pt}^{-1} min^{-1} at 200 °C and $P_{0.2-0.5}$ of 3.87 g_{H2} g_{Pt}^{-1} min^{-1} at 220 °C.[14] For both catalysts, an increase in the hydrogen loading productivity with higher reaction temperatures is found. The hydrogenation at 290 °C with S−Pt/Al_2O_3

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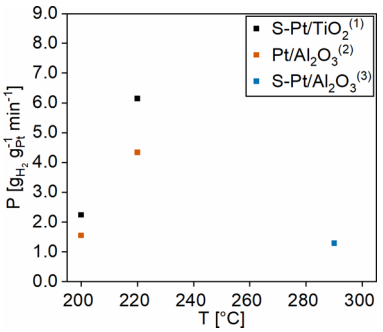

Figure 6. Productivities of various supported platinum catalysts for the H0-BT hydrogenation at 30 bar hydrogen pressure and temperatures between 220 and 290 °C, 1: 0.3 wt % Pt on support, optimized titania-supported catalyst, this work; 2: 5.0 wt % Pt on support, Jorschick et al.;[14] 3: 0.3 wt % Pt on support, EleMax-102D (Clariant), Rüde et al.;[15] data points for the catalytic experiments reported in the literature were derived based on the values given in the original source as shown in detail in the Supporting Information, Table S3.

(0.3 wt % Pt) as studied by Rüde et al. led to a productivity ($P_{0-240\ min}$) of only 1.29 g_{H2} g_{Pt}^{-1} min^{-1}.[15] For the DOH range between 0.5 and 0.9, these authors reported a mean productivity ($P_{0.5-0.9}$) of 4.6 g_{H2} g_{Pt}^{-1} min^{-1}, indicating that the lower value covering their entire reaction time suffers from the fact that the reaction approaches the thermodynamic limitation of hydrogenation at the end of the reaction time.[15] All in all, this comparison shows that the optimized S−Pt/TiO_2 catalyst is a very attractive H0-BT hydrogenation catalyst that seems to outperform its alumina-based counterparts under comparable reaction conditions and at comparable DOHs.

CONCLUSIONS

The S−Pt/TiO_2 catalyst with 0.1 wt % S and 0.3 wt % Pt, which had been optimized for the dehydrogenation of H18-DBT in previous work, was successfully applied in the hydrogenation of H0-BT and in the dehydrogenation of H12-BT. This in turn demonstrates its application potential for the whole storage cycle with the favorable BT-based LOHC system. Most remarkably, the S−Pt/TiO_2 catalyst shows high productivity in the H12-BT dehydrogenation without any detectable formation of methylfluorene species, which are common, and highly undesired side products formed on the established catalysts such as S−Pt/Al_2O_3. Thus, usage of S−Pt/TiO_2 increases the potential for the highly promising technical application of reversible hydrogen storage via H0-BT/H12-BT. Besides, based on the preliminary results obtained, the titania-supported catalyst seems to suppress the cyclization of H0-BT and hinders the formation of fluorene species during the hydrogen release. However, further investigations are required to study the side product formation mechanism and to correlate this remarkable finding to the surface properties of the compared catalyst systems.

The study of the influence of pressure on the dehydrogenation reaction confirmed that the reaction rate can be increased by pressure reduction even at temperatures as low as 220 °C. Evaluation of the hydrogen release productivity over the total pressure of the dehydrogenation unit showed a constant increase in productivity with decreasing pressure from atmospheric pressure to 300 mbar. The obtained linear correlation between reduced pressure and productivity is believed to facilitate optimization of the LOHC technology by running hydrogen release units at lower temperatures and reduced pressures.

Finally, a comparison of the obtained productivities in this study and data reported in the literature is provided for the catalytic hydrogenation of H0-BT and dehydrogenation of H12-BT. This comparison gives some indication of a slightly higher hydrogenation activity of our S−Pt/TiO_2 catalyst compared to the state-of-the-art alumina-based counterparts.

For the dehydrogenation performance, the negligible methylfluorene formation is an outstanding feature of the optimized S−Pt/TiO_2 catalyst that comes without compromising the catalytic productivity. All of these findings make the S−Pt/TiO_2 catalyst a highly attractive catalyst system for hydrogen storage applications using the LOHC system H0-BT/H12-BT.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsengineeringau.4c00003.

Preparation of the S−Pt/TiO_2 catalyst; characterization methods; experimental setup for dehydrogenation; experimental setup for hydrogenation; liquid phase analysis; catalyst characterization results; comparison of productivity; addition of H0-BT to the starting material of dehydrogenation (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

BP,benzophenone; BT,benzyltoluene; DBT,dibenzyltoluene; DOD,degree of dehydrogenation; DOH,degree of hydrogenation; DPM,diphenylmethane; EHC,electrochemical hydrogen compression; GC,gas chromatography; H12-BT,perhydro benzyltoluene; H18-DBT,perhydro dibenzyltoluene; ICP-OES,inductively coupled plasma optical emission spectroscopy; LOHC,liquid organic hydrogen carrier; MF,methylfluorene; MS,mass spectrometry; PEM,proton-exchange membrane; RI,refractive index; XRD,X-ray diffraction.

■ SYMBOLS

m,mass in g; M,molar mass in g mol^{-1}; n,molar amount in mol with index H12-BT for the amount of H12-DBT, H18-DBT for the amount of H18-DBT, $H_{2,max}$ for the maximum amount of hydrogen released from the fully loaded LOHC; $P_{a\text{-}b}$,productivity for a given range a to b in g_{H2} g_{Pt}^{-1} min^{-1}; t,time in min; x,molar fraction, dimensionless

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