INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 1010–1017

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Chemical utilization of hydrogen from fluctuating energy sources — Catalytic transfer hydrogenation from charged Liquid Organic Hydrogen Carrier systems

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ARTICLE INFO

Article history:
Received 26 July 2015
Received in revised form
16 September 2015
Accepted 6 October 2015
Available online 7 November 2015

Keywords:
Hydrogen storage
Liquid Organic Hydrogen Carrier
Dibenzyltoluene
Hydrogenation
Dehydrogenation
Transfer hydrogenation

ABSTRACT

Liquid Organic Hydrogen Carrier (LOHC) systems offer a very attractive way for storing and distributing hydrogen from electrolysis using excess energies from solar or wind power plants. In this contribution, an alternative, high-value utilization of such hydrogen is proposed namely its use in steady-state chemical hydrogenation processes. We here demonstrate that the hydrogen-rich form of the LOHC system dibenzyltoluene/perhydro-dibenzyltoluene can be directly applied as sole source of hydrogen in the hydrogenation of toluene, a model reaction for large-scale technical hydrogenations. Equilibrium experiments using perhydro-dibenzyltoluene and toluene in a ratio of 1:3 (thus in a stoichiometric ratio with respect to H_2) yield conversions above 60%, corresponding to an equilibrium constant significantly higher than 1 under the applied conditions (270 °C).

Introduction

As the production of electricity from wind and sun is highly intermittent in character, storage technologies are required to adapt production to demand. For energy systems with high shares of fluctuating renewable electricity, it is necessary to develop high-value applications for energy equivalents that are produced at times with very little demand (e.g. during sunny and/or windy weekends). Apart from electric (e.g.

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http://dx.doi.org/10.1016/j.ijhydene.2015.10.013

batteries, capacitors, redox-flow systems) and mechanical storage options (e.g. pumped hydro, fly wheels) the conversion of excess electricity into hydrogen by water electrolysis is considered as most attractive [1–3]. Besides energetic use of the produced hydrogen, the latter can be used as feedstock in catalytic hydrogenation reactions. However, this economically very interesting way of hydrogen utilization often requires transport of hydrogen from the place of renewable electricity production to a chemical production site.

In this context, chemical hydrogen storage and transport systems are highly interesting. These should allow storing large amounts of hydrogen and release of pure hydrogen on demand. For both requirements the application of Liquid Organic Hydrogen Carrier (LOHC) systems is very attractive. LOHC systems consist of a pair of high-boiling, liquid organic molecules – a hydrogen-lean compound and a hydrogen-rich compound – that can be reversibly transformed into each other by catalytic hydrogenation and dehydrogenation reactions [4–7].

Historically, the pair toluene/cyclohexane has been proposed as LOHC system [8–10], however, the low boiling points of this system and the toxicological profile of toluene are not ideal [11]. In contrast, high-boiling aromatic and heteroaromatic compounds allow dehydrogenation in the liquid phase with easy condensation of evaporated parts of the hydrogen carrier. A system that gained greater attention by the scientific community is N-ethyl-carbazole/perhydro-N-ethyl-carbazole (NEC/H12-NEC) introduced in 2004 by the company Air Products and Chemicals [12,13]. However, despite its unquestionable attractiveness for low temperature hydrogen release [14], this system has a number of important drawbacks, namely the limited technical availability of NEC from coal tar distillation, the solid nature of the fully dehydrogenated NEC at room temperature (mp: 68 °C), and the limited thermal stability of NEC [15].

Recently, the use of well-established, industrially widely used heat transfer oils as LOHC systems has been proposed [16]. In particular, mixtures of isomeric benzyltoluenes and dibenzyltoluenes that are industrially applied on large scale (typical tradenames are Marlotherm©, Farolin© or Diphyl©) show excellent performance in reversible hydrogenation/dehydrogenation cycles. These systems are characterized by very good technical availability (in very high and well-specified purities), high hydrogen capacities without solidification (mp: <−30 °C), very high thermal stability (application range for long-term heat transfer applications is up to 350 °C), and full toxicological and ecotoxicological assessment of their hydrogen-lean forms [17,18]. The hydrogenation of the commercial isomeric mixture of dibenzyltoluenes has been found to proceed readily using commercial Ru on alumina catalysts [12] (see Scheme 1).

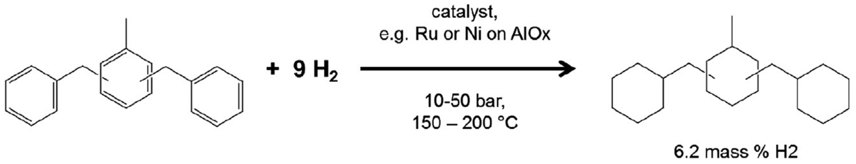
Here, we describe a novel application of the liquid, hydrogen-charged carrier perhydro-dibenzyltoluene, namely its direct application as sole source of hydrogen and solvent in industrially relevant hydrogenation reactions. The here proposed technology does not target the laboratories of synthetic organic chemists where hydrogen is best provided from cylinders with compressed hydrogen. Our aim is to replace hydrogen from fossil sources in industrial, larger-scale continuous hydrogenation processes by “green” hydrogen from water electrolysis based on renewable energy equivalents. Thus the storable, hydrogen-rich LOHC compound is used as a hydrogen buffer system to link intermittent hydrogen production from wind and sun energy with steady-state industrial hydrogenation. We anticipate, that the here proposed technology is most interesting for medium-sized industrial sites that do not operate their own methane reformer due to unfavorable economy of scale but still need significant amounts of hydrogen, e.g. for specialty or fine chemicals production, activation of catalysts or the treatment of materials. The here proposed technology offers a very attractive short-cut compared to the sequence of catalytic LOHC dehydrogenation, hydrogen compression and high pressure hydrogenation, as shown in Scheme 2.

As a very favorable feature of this approach, direct compensation of the heats of reaction of LOHC dehydrogenation and target molecule hydrogenation takes place. Thus, the here proposed concept avoids complex heat transfer installations in both the classical LOHC dehydrogenation (endothermal) and feedstock hydrogenation reactors (exothermal) [19–22]. In future applications of the technology we anticipate the LOHC medium to be used as solvent for the desired transfer hydrogenation reaction thus shifting hydrogenation equilibria due to a large excess of the hydrogen carrier.

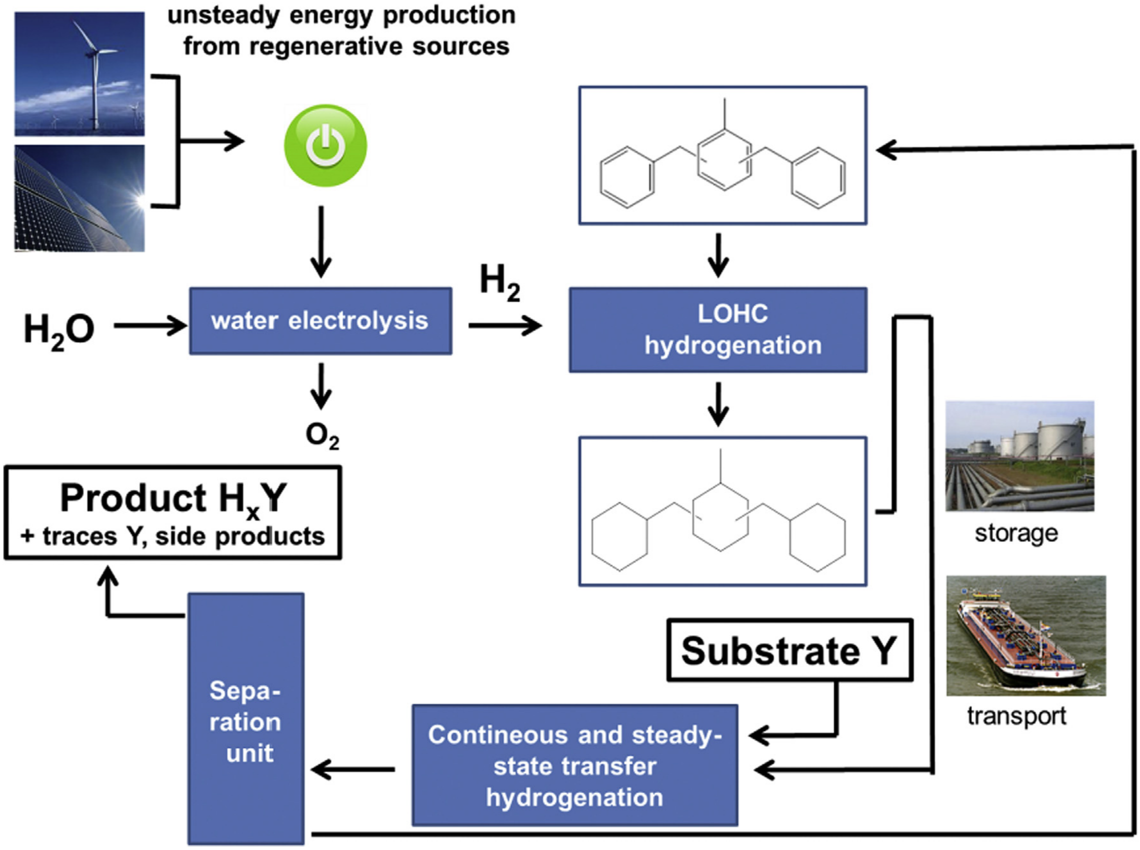
We are fully aware that the selection of potential substrates to be hydrogenated by the here proposed transfer hydrogenation is not fully unrestricted. As separation of hydrogenated substrate and un-charged LOHC material (followed by re-hydrogenation of the uncharged LOHC) is an important step of the overall process, we expect the technology to be particularly useful for hydrogenation reactions in which substrates and products show a significant boiling point difference with the applied perhydro-dibenzyltoluene/dibenzyltoluene transfer hydrogenation system.

In overview, the potential advantages of transfer hydrogenation based on LOHC systems include the following aspects:

- Potential direct link of unsteady green hydrogen production (via electrolysis from unsteady renewable energy



Scheme 1 – Catalytic hydrogenation of isomeric mixtures of dibenzyltoluenes to obtain the transfer hydrogenation agent perhydro-dibenzyltoluene.



Scheme 2 – Transfer hydrogenation using LOHC systems as source of hydrogen and solvent enabling the use of unsteadily produced hydrogen from renewables in steady-state hydrogenation processes of the chemical industry.

sources) to steady-state continuous industrial hydrogenation processes due to the hydrogen storage function of the diesel-like hydrogen carrier;

- Potential for almost thermoneutral hydrogenation processes as the exothermicity of the substrate hydrogenation and the endothermicity of the LOHC-dehydrogenation are in balance;
- Potential for low pressure hydrogenation processes in which only very little "free" hydrogen (H_2 in the gas phase of the reactor) is present;
- Potential for new hydrogenation mechanisms (direct C–H-cleavage/C–H-formation processes) and – linked to that – potential for novel hydrogenation selectivities for well-established reactions.

Catalytic transfer hydrogenation (CTH) per se is not a new concept and has been intensively studied in the past years [23,24]. Heterogeneous palladium catalysts used to be considered as the most active catalysts [20] and have been widely used for CTH reactions [25–27]. Also other metals, e.g. ruthenium [28] or raney nickel [29] proved to be applicable for direct hydrogen transfer. Various organic substances, in particular secondary alcohols [30–32] and cyclohexene [23] have been applied as source of hydrogen for functional groups reduction or the hydrogenation of unsaturated compounds. However, to the best knowledge of the authors of this paper, transfer hydrogenation from a hydrogen storage material, i.e. a material designed for storing hydrogen under a technical scenario, has not been reported yet.

In this contribution, we focus on the transfer hydrogenation from perhydro-dibenzyltoluene to toluene. Toluene has been selected as a model compound for the industrially highly relevant hydrogenation of monoaromatic compounds, e.g. in the context of the technical production of adipinic acid or caprolactam [33]. Of course, many other substrates would be also applicable and interesting to be studied using this technology, such as e.g. the hydrogenation of alkynes, alkenes, functionalized aromatic compounds, ketones, acids etc. However, we decided to investigate first toluene hydrogenation as it offers – in addition to a pure feasibility study – conclusions on the driving force of dibenzyltoluene dehydrogenation in comparison to toluene hydrogenation. Such study is of general importance to strengthen the thermodynamic foundations of the LOHC system dibenzyltoluene/perhydrodibenzyltoluene.

Results

Transfer hydrogenation of toluene with perhydro-dibenzyltoluene – influence of temperature

The first set of experiments aimed for determining the reaction conditions under which effective transfer hydrogenation of toluene with perhydro-dibenzyltoluene takes place. For this purpose we first carried out a temperature variation. These experiments were carried out using a defined amount of the applied commercial Pd on carbon catalyst (0.2 mol %) and a ratio of perhydro-dibenzyltoluene (H18-LOHC) to the toluene substrate corresponding to a 3:1 excess in transferable hydrogen. The results are shown in Fig. 1 and Table 1.

Remarkably, already at a temperature as low as 210 °C clear transfer hydrogenation activity is observed over 4 h reaction time. At such a low temperature the thermal release of hydrogen from perhydro-dibenzyltoluene with the applied Pd-catalyst would be very low (below 5% hydrogen release after 4 h). As expected, the degree of toluene conversion increases strongly with temperature up to 270 °C. At this temperature, toluene hydrogenation to methylcyclohexane proceeds within 2 h to a toluene conversion of above 95%. There is no further increase in toluene hydrogenation indicating that the obtained value of 96.5% toluene conversion represents the equilibrium state of the transfer hydrogenation under the applied conditions. Interestingly, at higher temperatures of 290 °C and 300 °C toluene conversion does not accelerate in comparison to 270 °C. We interpret this finding as a very strong indication for mass transfer limitation of the transfer hydrogenation process above 270 °C degree.

Transfer hydrogenation of toluene with perhydro-dibenzyltoluene – ratio of hydrogen transfer agent to substrate

Fig. 2 shows the results of a variation of the LOHC to substrate ration at 270 °C using the same Pd-catalyst as in Fig. 1. Experiments with a molar ratio of LOHC to toluene between 3:1 and 1:1 (corresponding to a molar ratio of available and consumable hydrogen of 9:1 to 3:1) have been carried out. It is obvious and not surprising that a greater excess of hydrogen offered in form of the LOHC hydrogen transfer liquid accelerates the reaction significantly. It was surprising, however, to see that even under conditions with relatively small excess hydrogen the reaction proceeds smoothly and reaches within 4 h reaction time a toluene conversion of 60%. All results are summarized in Table 2.

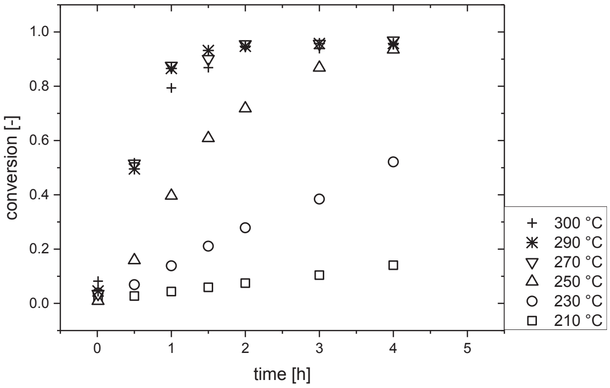


Fig. 1 – Transfer hydrogenation of toluene with perhydro-dibenzyltoluene using a commercial Pd on carbon catalyst – Temperature variation. Reaction conditions: n(toluene):n(Pd) = 500; H18-LOHC, n(H18-LOHC):n(toluene) = 3:1 (9:1 with respect to hydrogen).

Table 1 – Conversion of toluene (%) using a commercial Pd on carbon catalyst – temperature variation.

Reaction time (h)	Temperature (°C)					
	210	230	250	270	290	300
1	0	14	40	88	87	79
2	7	28	72	95	95	94
3	10	38	87	96	96	94
4	14	52	94	96	96	95

Stoichiometric transfer hydrogenation experiments and thermodynamic insight derived thereof

From a practical point of view, it would be desired to perform the transfer hydrogenation reaction at a minimal excess of perhydro-dibenzyltoluene that still allows a certain, desired substrate conversion and product yield. Due to the high structural similarity of toluene and dibenzyltoluene the driving force for the transfer hydrogenation reactions (i.e. the Gibbs free energy of reaction) is presumably rather small. One would therefore expect an equilibrium constant close to unity for stoichiometric hydrogen conditions and consequently a maximum conversion due to the reaction equilibrium of about 50%.

To explore this experimentally, we applied in our next set of experiments a molar ratio of perhydro-dibenzyltoluene to toluene of 1–3. With this stoichiometry the amount of available hydrogen equals the amount of consumable hydrogen. The reactions were allowed to proceed for much longer till equilibrium conditions were reached. Interestingly, as shown in Fig. 3, the well reproducible results of these experiments yielded toluene conversions of about 62% at 270 °C. In all experiments, methylcyclohexane was found as the sole product

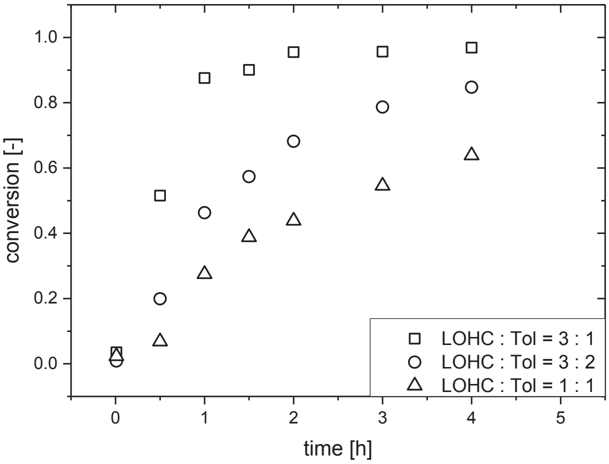


Fig. 2 – Transfer hydrogenation of toluene with perhydro-dibenzyltoluene using a commercial Pd on carbon catalyst – Variation of ratio of hydrogen transfer agent to substrate. Reaction conditions: T = 270 °C; n(toluene):n(Pd) = 400; n(H18-LOHC):n(toluene) from 3:1 to 1: 1 (9:1 to 3:1 with respect to hydrogen).

Table 2 – Conversion of toluene (%) using a commercial Pd on carbon catalyst – variation of ratio of hydrogen transfer agent to substrate.

Reaction time (h)	Ratio of LOHC:Toluene		
	3:1	3:2	1:1
1	88	46	28
2	95	68	44
3	96	79	55
4	97	85	64

and no partially hydrogenated cyclic compounds were identified.

Note in this context that reaction equilibria leading to maximum conversions in the order of about 50% are very sensitive to small differences in the thermodynamic driving force. A conversion of 62% for a stoichiometric mixture would be the result of an equilibrium constant expressed in concentrations of 7.1. Calculating backwards from the equilibrium constant to the Gibbs free energy of the transfer hydrogenation reaction results in a value of only −1.0 kJ/mol-H_2 at the applied reaction conditions. Taking effects of non-ideal behavior into account by using the UNIFAC model [34] a similar value of −1.2 kJ/mol-H_2 is obtained.

Results from combustion calorimetry [35] indicate a difference of enthalpies of hydrogenation for dibenzyltoluene and toluene in the liquid phase of 2.0 ± 1.1 kJ/mol-H_2. Assuming a small entropic contribution to the Gibbs free energy of reaction, which seems reasonable for a transfer hydrogenation reaction, these values are consistent with the Gibbs free energy derived from the reaction equilibrium. At first glance the uncertainty of these combustion calorimetry measurements of ±1.1 seems to be very high. However, it should not be compared to the enthalpy of transfer hydrogenation, but rather to that of hydrogenation (−67.4 kJ/mol-H_2 for the hydrogenation of liquid toluene). From this point of view, the difference between the (de)hydrogenation reactions of toluene and dibenzyltoluene as well are (as expected) rather small. Nevertheless, all results point into the direction that hydrogen release from perhydro-dibenzyltoluene is thermodynamically slightly favored over the dehydrogenation of methylcyclohexane.

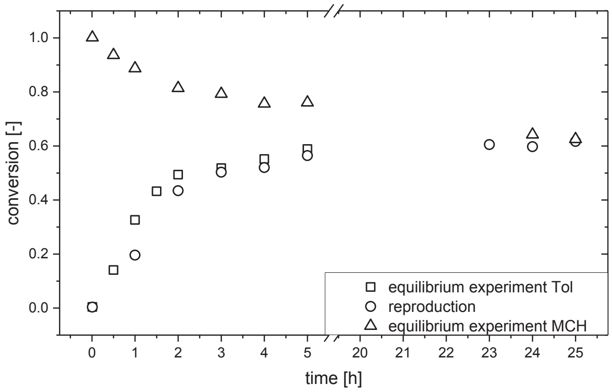


Fig. 3 – Transfer hydrogenation towards equilibrium under stoichiometric hydrogen supply using a commercial Pd on carbon – hydrogenation of toluene with perhydro-dibenzyltoluene (incl. reproduction) and hydrogenation of dibenzyltoluene with methylcyclohexane catalyst. Reaction conditions: T = 270 °C; n(toluene/methylcyclohexane):n(Pd) = 400; n(H18-LOHC/H0-LOHC):n(toluene/methylcyclohexane) = 1:3 (1:1 with respect to hydrogen).

The slight exothermicity of the transfer hydrogenation reaction can also be confirmed when looking at the calculated temperature dependence of equilibrium conversion. In the experiments at temperatures of 270 °C and higher, equilibrium is nearly reached. For these experiments conversion after 4 h is slightly decreasing with increasing temperature as predicted by Le Chatelier's principle for exothermic reactions (see also Fig. 4).

To reach a toluene conversion of 50% at 270 °C about 0.19 mol perhydro-dibenzyltoluene per mol toluene would be required thermodynamically (compared to 0.17 if there was no thermodynamic limitation). To allow for higher toluene conversions either lower temperatures or a higher excess of perhydro-dibenzyltoluene would be required. Due to the weak exothermicity the effect of temperature on equilibrium is rather small. Thus, reduction of temperature for thermodynamic reasons does not justify the negative effect on reaction kinetics. Hence, the ratio of hydrogen donating to accepting compound has to be higher than stoichiometric for full conversion. For the structurally very similar reactants toluene and dibenzyltoluene the number of donating sites has to exceed the number of accepting sites significantly to reach high conversions. A ratio of n(perhydro-dibenzyltoluene) to n(toluene) of 3 (excess of 9 with respect to hydrogen) is required to reach toluene conversions above 95% (as also demonstrated experimentally, see Fig. 2).

However, if hydrogen from perhydro-dibenzyltoluene would be transferred to another substance class, e.g. an aliphatic olefin, the excess required could be drastically reduced. For this transfer hydrogenation the thermodynamic driving force would be so high that even with a stoichiometric mixture in hydrogen the reaction equilibrium would be close to total conversion. For example, transfer hydrogenation from perhydro-dibenzyltoluene to 1-octene at 270 °C allows from a thermodynamic point of view for 1-octene conversion above

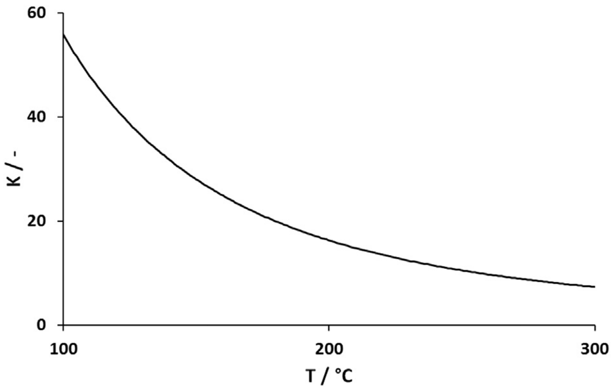


Fig. 4 – Calculated equilibrium constants for the stoichiometric transfer hydrogenation of perhydro-dibenzyltoluene and toluene as a function of temperature.

98% for a mixture of n(1-octene) to n(perhydro-dibenzyltoluene) of 9 (stoichiometric in hydrogen). This numbers confirm impressively the potential efficiency of the LOHC-material perhydro-dibenzyltoluene in relevant transfer hydrogenation reactions.

Transfer hydrogenation of toluene with perhydro-dibenzyltoluene – catalyst variation

Finally, we were interested to find out whether the observed transfer hydrogenation is only possible with the so far applied Pd on carbon catalyst or whether other catalyst systems promote the same kind of reaction. The following set of experiments represents a catalyst screening under strictly comparable reaction conditions of a toluene to metal ratio of 400 at 270 °C in a stoichiometry of n(perhydro-dibenzyltoluene) to n(toluene) of 3:2, that is a ratio of 4.5:1 in hydrogen (see Fig. 5/Table 3).

Conclusion

The here reported results show very interesting technical potential for the use of hydrogen-charged LOHC systems as source of hydrogen in the chemical industry via a direct transfer hydrogen reaction. This utilization of hydrogen-charged LOHC systems would create a direct link between hydrogen production from unsteady renewable sources via electrolysis and its high-added value use in the chemical industry in steady-state hydrogenation processes.

It is obvious that direct LOHC transfer hydrogenation has multiple advantages compared to the two-step catalytic release of hydrogen from the LOHC followed by hydrogenation of the substrate of interest with the released hydrogen. Most striking is the fact that the substrate hydrogenation delivers at least a very substantial part of the heat of dehydrogenation otherwise required for hydrogen release from the LOHC system. Moreover, the heat of substrate hydrogenation is compensated to a large extent by the endothermic dehydrogenation reaction making heat management in the transfer hydrogenation reactor much easier. Note that also hydrogen compression that would otherwise be necessary in the two step process is not necessary in direct LOHC transfer hydrogenation. Based on the fact that the transfer hydrogenation from perhydro-dibenzyltoluene is in most cases a thermoneutral or even a exothermic reaction, the relatively high temperature level of the transfer hydrogenation reaction is not a drawback but an advantage as it allows using the reaction heat for steam production or heating.

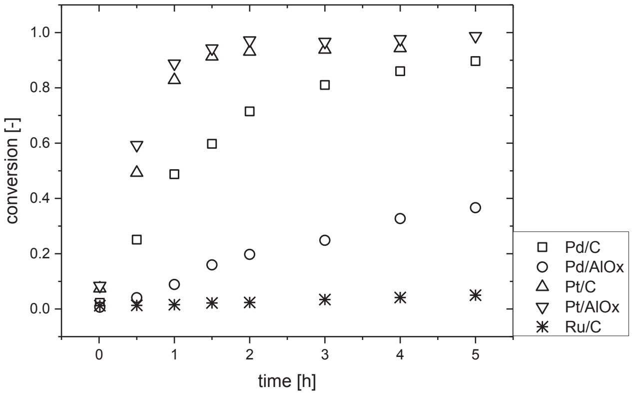


Fig. 5 – Transfer hydrogenation of toluene with perhydro-dibenzyltoluene – Catalyst variation. Reaction conditions: T = 270 °C; n(toluene):n(metal) = 400; n(H18-LOHC):n(toluene) = 2:3 (2:1 in hydrogen).

Table 3 – Conversion of toluene (%) – catalyst variation.

Reaction time (h)	Catalyst				
	Pd/C	Pd/AlOx	Pt/C	Pt/AlOx	Ru/C
1	49	9	83	89	1
2	72	20	93	97	2
3	81	25	94	97	3
4	86	33	94	98	4
5	90	37		99	5

The here investigated transfer hydrogenation from perhydro-dibenzyltoluene to toluene represents only a model reaction for industrial relevant hydrogenations. Nevertheless, very interesting conclusions could be drawn from the here presented work regarding parameter space of the reaction, suitable catalysts and thermodynamic aspects. It is anticipated that economically much more interesting examples can be found in the fine and specialty chemicals industry where hydrogen supply is typically not available on-site from a cheap methane reformer so that the additional advantage of safe and efficient hydrogen logistics via the diesel-like LOHC system results. It is furthermore anticipated that some of these industries can “market” the benefit of using green hydrogen from renewables much better than big refineries or petrochemical sites.

Experimental section

MSH vs. MLH

Materials: Perhydro-dibenzyltoluol (H18-LOHC) was purchase in suitable quality (>98% hydrogenation degree) from *Hydrogenious Technologies GmbH*, Erlangen (www.hydrogenious.net). Alternatively, it can obtained by hydrogenation of dibenzyltoluene (SASOL Deutschland GmbH) in a stirred batch autoclave at 150 °C and 30 bar hydrogen pressure over 12 h using a Ru on AlOx catalyst (0.1 mol% catalyst; 0,5 mass% Ru on support). The applied commercial catalysts for this study are listed in Table 4.

Table 4 – List of commercial catalyst materials applied in this study.

	Type	Producer/Source	Lot No
1	Pd/C (5 wt%)	Sigma Aldrich	MKBS9242V
2	Pd/AlOx (5 wt%)	Heraeus	M 150/10
3	Pt/C (5 wt%)	Sigma Aldrich	BCBF1700V
4	Pt/AlOx (5 wt%)	Sigma Aldrich	MKBS0634V
5	Ru/C (5 wt%)	Sigma Aldrich	MKBQ3189V

Transfer hydrogenation reactions

All experiments were performed by using a 500 mL stainless-steel Parr batch autoclave equipped with a four-blade gas-entrainment stirrer (n = 1000 rpm). To assure an inert atmosphere in the pressure vessel, the reactor was purged with argon three times. The reactor was heated to the desired reaction temperature with an external electrical heating jacket. To determine the progress of the reaction, liquid samples were taken and analyzed by using gas chromatography (Varian 3900 equipped with a CP Sil PONA CB50 m × 0.21 mm capillary column).

Acknowledgments

The authors like to thank Prof. Wolfgang Arlt, FAU, for important advices and fruitful discussions. DG, AB and PW thank the Free State of Bavaria for support of this work in the context with its institutional support for the Helmholtz-Institute Erlangen-Nuremberg for Renewable Energies (www.hi-ern.de). PP and KM thank the Free State of Bavaria for support of their part of this work in the context of the Energie Campus Nuremberg (www.encn.de). PW. thanks in addition the European Research Council for dedicated resources to study the fundamental aspects of LOHC dehydrogenation catalysis under the ERC Advanced Investigator Grant no. 267376.

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