



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

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

Denise Geburtig^a, Patrick Preuster^a, Andreas Bösmann^a,
Karsten Müller^b, Peter Wasserscheid^{a,c,*}

^a Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, D-91058, Germany

^b Lehrstuhl für Thermische Verfahrenstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, D-91058, Germany

^c Helmholtz-Institute Erlangen-Nürnberg for Renewable Energies, IEK-11, Forschungszentrum Jülich, Nägelsbachstraße 59, 91058 Erlangen, Germany

ARTICLE INFO

Article history:

Received 26 July 2015
Received in revised form
16 September 2015
Accepted 6 October 2015
Available online xxx

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 H₂) yield conversions above 60%, corresponding to an equilibrium constant significantly higher than 1 under the applied conditions (270 °C).

Copyright © 2015, 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/>).

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.

* Corresponding author. Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, D-91058, Germany.

E-mail address: wasserscheid@crt.cbi.uni-erlangen.de (P. Wasserscheid).

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

0360-3199/Copyright © 2015, 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/>).

Please cite this article in press as: Geburtig D, et al., Chemical utilization of hydrogen from fluctuating energy sources – Catalytic transfer hydrogenation from charged Liquid Organic Hydrogen Carrier systems, International Journal of Hydrogen Energy (2015), <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).

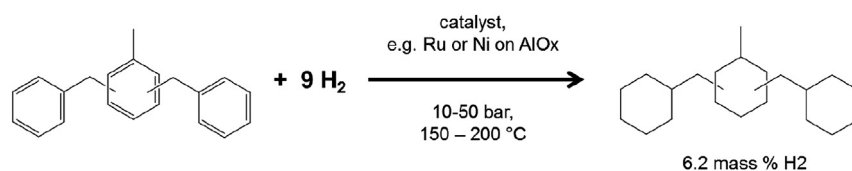
Here, we describe a novel application of the liquid, hydrogen-charged carrier perhydro-dibenzyltoluene, namely its direct application as sole source of hydrogen and solvent in industrially relevant hydrogenation reactions. The here proposed technology does not target the laboratories of synthetic organic 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 (endothermic) and feedstock hydrogenation reactors (exothermic) [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.

Download English Version:

<https://daneshyari.com/en/article/7712632>

Download Persian Version:

<https://daneshyari.com/article/7712632>

[Daneshyari.com](https://daneshyari.com)