PAPER

View Article Online
View Journal | View Issue Cite this: *Energy Environ. Sci.*, 2015, 8, 641Efficient hydrogen release from perhydro-*N*-ethylcarbazole using catalyst-coated metallic structures produced by selective electron beam melting†W. Peters,^a M. Eypasch,^b T. Frank,^b J. Schwerdtfeger,^c C. Körner,^c A. Bösmann^a and P. Wasserscheid^{*a}

A particularly suitable reactor concept for the continuous dehydrogenation of perhydro-*N*-ethylcarbazole in the context of hydrogen and energy storage applications is described. The concept addresses the fact that dehydrogenation is a highly endothermic gas evolution reaction. Thus, for efficient dehydrogenation a significant amount of reaction heat has to be provided to a reactor that is essentially full of gas. This particular challenge is addressed in our study by the use of a catalyst-coated (Pt on alumina), structured metal reactor obtained by selective electron beam melting. The so-obtained reactor was tested both as a single tube set-up and as a Hydrogen Release Unit (HRU) with ten parallel reactors. In stationary operation, the HRU realized a hydrogen release capacity of 1.75 kW_{therm} (960 W_{el} in a subsequent fuel cell) with up to 1.12 g_{H₂} min⁻¹ g_{Pt}⁻¹ and a power density of 4.32 kW_{el} L⁻¹ of HRU reactor.

Received 2nd November 2014
Accepted 15th December 2014

DOI: 10.1039/c4ee03461a

www.rsc.org/ees

Broader context

The conversion of our current energy system to a hydrogen-based one requires effective ways to store hydrogen in large amounts over long periods of time using existing infrastructures. Liquid Organic Hydrogen Carrier systems, such as *e.g.* perhydro-*N*-ethyl carbazole (H12-NEC)/*N*-ethyl carbazole (NEC), have the potential to substitute step-by-step liquid fossil fuels as they have attractive energy densities and diesel-like handling. Hydrogen release from H₂-rich LOHC systems allows the on-demand utilization of regenerative energy equivalents at any time and at any place. However, the hydrogen release from H₂-rich LOHC systems is challenging due to the endothermic nature of the dehydrogenation reaction combined with the large volume expansion of the reaction mixture. Our contribution shows that 3-D-structured metallic reactors produced *via* selective electron beam melting and coated with Pt on alumina represent very suitable and efficient dehydrogenation reactors for this catalytic dehydrogenation reaction. Using such reactors, we could demonstrate a power density of up to 4.32 kW_{el} L⁻¹ in the dehydrogenation reaction (assuming a fuel cell efficiency of 55%). The system stability and reproducibility of the dehydrogenation results were found to be excellent over 48 h time-on-stream.

1. Introduction

While today's energy system is largely based on the consumption of fossil fuels, there are many good reasons to promote a step-wise transition to electricity production from renewable sources, such as wind and solar power. Important arguments are the limited availability of fossil fuels on the long run and the foreseeable consequences of an anthropogenic climate change.

The key challenge for the massive integration of renewable energy into our energy system is its intermittent character. The production output of *e.g.* wind turbines and solar PV units is primarily determined by meteorological parameters with strong seasonal, day-time and weather dependent fluctuations. Countries with a large share of wind and solar energy, such as *e.g.* Germany, already experience the problem of energy overproduction on very windy or sunny days while their large wind and sun power installations do hardly contribute to electricity production during unfavorable weather conditions. Consequently, a stable and reliable energy supply by renewable energies requires storage technologies that enable balancing of energy over- and underproductions. A significant part of such future energy storage systems should enable lossless storage of large amounts of energy over long time periods in order to allow seasonal or day-time buffering. Based on today's technologies such a task cannot be accomplished reasonably by mechanical

^aDepartment of Chemical and Biological Engineering, University of Erlangen-Nuremberg, Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: peter.wasserscheid@fau.de; Tel: +49-9131-8527420

^bBMW Group Forschung und Technik, Hanauer Straße 46, 80992 München, Germany

^cDepartment of Materials Science, University of Erlangen-Nuremberg, Martensstrasse 5, 91058 Erlangen, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ee03461a

and electrochemical methods alone but requires chemical energy storage technologies.

Hydrogen produced by water electrolysis is considered as a suitable energy carrier due to its high gravimetric energy density (120 MJ kg^{-1}). The generation of electricity, heat or mechanical power from hydrogen involves oxidation of the latter in a fuel cell or combustion engine producing water thus closing the material balance of this carbon-free energy storing cycle.

A major drawback of using hydrogen as an energy carrier is its low volumetric storage density. Under ambient conditions (1 bar, 25°C), one litre of hydrogen contains only 0.003 kW h of thermal energy. Even as a compressed gaseous form (CGH₂, typically at 700 bar pressure) or as liquefied cryogenic hydrogen (LH₂, typically at -253°C), the volumetric storage density of elemental hydrogen is still low, with energy contents of 1.3 and 2.4 kW h L^{-1} , respectively. In addition, H₂ compression and cooling cost some energy and both forms of hydrogen handling require special infrastructures such as compressor stations, pipelines, pressure-resistant containers or cryogenic tank systems. Furthermore, it is difficult to imagine that the handling of large amounts of elemental hydrogen by a broad and untrained public at very high pressures or very low temperatures will work out without applying sophisticated and expensive safety technologies.

A very promising concept that avoids new infrastructures and utilizes existing infrastructures is chemical energy storage, *i.e.* the reversible chemical conversion of hydrogen in the form of hydrogen-rich chemicals. Fig. 1 shows the general concept of binding hydrogen from renewable sources to a hydrogen-lean molecule, for example, of the Liquid Organic Hydrogen Carrier (LOHC) system *N*-ethyl carbazole (NEC)/perhydro-*N*-ethyl carbazole (H12-NEC).

The liquid nature of both the hydrogen-rich and the hydrogen-lean form of the hydrogen storage system facilitates storage and transport in the existing infrastructure for liquid fuels. Note that the melting point of pure NEC is 68°C but mixtures with partly dehydrogenated species are liquids at

ambient temperature. Moreover, it is particularly interesting to use liquids as hydrogen-lean molecules as this allows for a closed material cycle without binding or releasing other substances from the atmosphere than water and oxygen (in contrast to systems that use *e.g.* N₂ or CO₂ as hydrogen-lean molecules of the chemical energy storage system). The rationale behind LOHC energy storage systems is that energy is stored during energy-rich times (high solar intensity, strong wind, and cheap energy) by LOHC hydrogenation while hydrogen is released at times and places which are energy deficient by catalytic dehydrogenation.^{1,2}

The hydrogen storage capacity of the LOHC system NEC/H12-NEC is 5.8 wt% if full dehydrogenation is considered and 5.2 wt% if the reaction should result in a liquid, hydrogen-lean mixture. The exothermal, catalytic hydrogenation of NEC to H12-NEC (upper part of Fig. 1) is typically promoted by Ru-catalysts and releases 50 kJ per mol H₂ reaction heat.^{3–6} The endothermic dehydrogenation (lower part of Fig. 1) requires for thermodynamic reasons the same amount of heat at a higher level of reaction temperature.^{7,8}

In this contribution, we focus on a novel reactor concept to release hydrogen from H12-NEC in a most efficient and productive way. Before going into the details of our study, we will summarize shortly the state-of-the-art knowledge with respect to this particular reaction.

A number of studies have been carried out in recent decades demonstrating that H12-NEC can be dehydrogenated using Pt and Pd based catalysts.^{9–12} Alumina, silica and carbon have been used as porous supports.^{6,11,13} So far, kinetic studies have been mostly restricted to batch experiments.^{5,8,10,13–15} In these studies, it has been found that the reaction from H12-NEC to NEC proceeds stepwise over the main intermediates H8-NEC and H4-NEC.^{16,17} The activation energy of the dehydrogenation reaction has been reported to be in the range of $118\text{--}127 \text{ kJ mol H}_2^{-1}$.¹⁶ Detailed mechanistic insight into the dehydrogenation reaction of H12-NEC has been recently gained by surface science studies on different Pd and Pt model catalysts.^{11,12,18,19}

2. Dehydrogenation reactor concepts

From a reaction engineering point of view, the dehydrogenation of H₂-rich LOHCs is complicated by the very large volume of hydrogen gas generated in the reactor ($>650 \text{ mL H}_2$ per mL H12-NEC converted to H0-NEC) and by the need to transport the significant reaction heat to the catalytic sites. In this context, Wild *et al.* and Toseland *et al.* suggested a microwick reactor and a microtube^{5,18} while Cooper *et al.* proposed the application of a microreactor.^{9,20,21} For easy removal of the product gas from the catalytic surface, Hodoshima *et al.* and Karyia *et al.* reported a concept where the dehydrogenation catalyst is covered with a thin liquid LOHC film or is applied under dynamic wet/dry conditions.^{22,23} Later the group of Kariya applied a spray-pulse reactor for LOHC dehydrogenation.²⁴ Hydrogen evolution rates of up to 7.6 g H_2 per g catalyst and min were reported with such devices in the cyclohexane dehydrogenation at 350°C using a Pt/Al₂O₃ catalyst.^{25,26} Recently, Shukla *et al.* reviewed the different tested reactor concepts for LOHC dehydrogenation

Fig. 1 Storage and transport of renewable energy equivalents in the form of hydrogen-rich liquid chemicals based on reversible hydrogenation/dehydrogenation cycles.

and stated correctly that there is only little information available on the application of monolithic reactors which, nevertheless, are characterized with a number of very attractive features for this hydrogen release reaction.²⁷ In general, structured reactors, such as monolithic or foam reactors, exhibit the important advantage over catalytic fixed beds that their structure provides high heat conductivity and thus allows good heat input for endothermic reactions.^{28–33} The range of applicable structured reactors, both with respect to the material (*e.g.* SiC, Cu, aluminium, and aluminium oxide) and the structure (*e.g.* mesh structures, foams, and honeycombs), is huge and this variability is often considered as a great advantage.^{34–36} The high porosity of some monoliths provides a very low pressure drop which is very important for reactions with significant volume expansion, such as *e.g.* the dehydrogenation of hydrogen-rich LOHCs.^{37,38}

A novel concept for the manufacturing of structured metallic reactor systems is the use of additive manufacturing (AM), especially in the form of powder bed based processes like selective electron beam melting (SEBM).^{39–42} In this manufacturing process, the structured reactor is built up layer-by-layer. The reactor wall and the inner 3D-structure (monolithic, foam like or cellular) are processed simultaneously, resulting in an interconnected reactor structure. Furthermore, it is possible to determine orientation, geometry and size of every strut of a cellular structure. The control over geometric properties translates into control over the physical properties (*e.g.* mechanical, flow or heat conductivity properties).^{37,43–45}

SEBM is a relatively new technology that utilizes an electron beam for the local melting of the metal powder in the powder bed. This has a number of potential advantages over laser based technologies. As beam control does not rely on mirrors and lenses, but electro-magnetic fields, very high deflection speeds can be realized. In principle, any electrically conductive powder can be used as a building material for the SEBM process, however, the process is most mature for titanium alloys and specifically Ti-6Al-4V.

Using structured reactors, such as monoliths, foams or cellular structures for catalysis involves in most cases the coating of a catalytic active layer onto the reactor through deposition processes like chemical vapour deposition,^{46–48} atomic or electrophoretic particle deposition,^{49,50} and spray^{51–54} or dipcoating.^{55–57} Typical thicknesses of catalytic active layers on monoliths range from a few microns up to 500 μm .^{51,58} In dip- or spray-coating processes, a dispersion or a suspension of ceramic or carbon powder is used in the coating process.^{28,29,57} Many publications apply coatings of ceramic films using the gel-dipping process.^{55,59} Schwarz *et al.* used a low pressure spray coating technique resulting in very adhesive and homogeneous coatings.⁵³ Extensive work on the coating of different monoliths with different ceramic coatings was reported by Groppi *et al.*^{60–63}

This contribution reports on the development of a hot gas-heated dehydrogenation unit for H12-NEC with a capacity of *ca.* 1 kW_{el} in a subsequent fuel cell (*ca.* 2 kW_{therm} with respect to the lower heating value of H_2). By the use of catalytic coated structured metal reactors based on SEBM-manufactured structures,

the volumetric hydrogen production rate and thus the volumetric power output are optimized.

3. Experimental

SEBM reactor tube manufacturing

The reactor tubes were produced using an Arcam S12 system (Arcam AB, Sweden). The system essentially consists of a control unit, a high voltage unit, an electron beam column and a vacuum chamber in which the actual structure building takes place. We applied in the SEBM process gas atomized Ti-6Al-4V powder with a particle size of 45 μm –105 μm . In order to improve the process stability, protective gas at low pressure (He-atmosphere, 2×10^{-3} mbar) was used during building. For every layer, the process consists of four distinct steps: (1) powder is spread out in the building area by a rake system in layers of about 100 μm thickness; (2) the powder is preheated using a defocused electron beam to slightly sinter the powder for electrical conductivity and a certain mechanical stability; (3) the powder is locally molten by a focused e-beam according to the desired part geometry; (4) the building platform is lowered by one layer thickness and the process is repeated until the part is finished. When the total building process is completed, the obtained part is surrounded by a shell of sintered metal powder, which has to be removed by “sand” blasting with the same metal powder as used in the building process to ensure the recyclability of the powder.

For the Ti-6Al-4V monoliths produced in this work, the building temperature was 550–600 $^{\circ}\text{C}$. The energy supplied to the powder during the preheating step was lowered to strongly reduce sintering of the metal powder during the process. This bears the danger of destabilizing the process through insufficient charge transport away from the building area which can lead to charging of the metallic powder. However, the lower temperature was necessary as initial trials showed that otherwise the sintered powder could not be removed completely from the inside of the reactor tubes. The complete powder removal

Fig. 2 Top left: subunit cubic diamond crystal structure; top right: different diamond cell sizes manufactured *via* the SEBM-process; bottom: powder removal at three different stages, measured *via* computational tomography at the cross-section of a single reactor.

was further assisted by introducing a 6 mm channel in the center of the cellular structure and by the large inlet and outlet diameters of the reactor tube.

The need for powder removal also defines the lower limit of possible cell sizes in the cellular structure. Fig. 2 shows a graduated SEBM structure for optimized gas removal from the reactor as well as three cross-sections of the reactor by X-ray tomography to document different stages of powder removal from the reactor.

For our study, a cellular structure based on the cubic diamond geometry was chosen.^{48,64} The unit cell is shown in Fig. 2. The cell size was chosen to be 4.95 mm for the final reactors and the structure was oriented with the [100] direction pointing in the flow direction. Deflection speeds for the beam during melting were in the range of 10^2 mm s^{-1} and 10^4 mm s^{-1} during preheating. The cellular structure was built with a beam current at 2 mA and a residence time on each spot of about 3.5 ms. This ensured thin struts in the range of 0.5 mm diameter.

SEBM reactor machining and coating

After removal of metal powder from the reactor, the tube surface was trimmed by machining prior to the application of screw threads and sealing surfaces (Fig. 3). Aluminium and copper sealings have been applied to verify the pressure tightness. The pressure test was performed at about 55 bar and the pressure loss was found to be less than 1.5 bar h^{-1} . For coating with the catalytic active layer, a commercial boehmite powder and Disperal (Z500100E, Sasol Germany GmbH) were dispersed in diluted nitric acid solution at a pH of 2. After stirring for about 1 h at ambient temperature, a commercial catalyst powder (5% Pt/Alumina, Sigma Aldrich 205974/MKBH3784) was added.

The obtained suspension containing 7.5 wt% of $\text{AlO}(\text{OH})$ and 7.5 wt% of catalyst powder was stirred for another hour. The coating was performed by filling the reactor tube with the suspension, which remained inside the reactor for about 30 s.

Since the effect of the withdrawal velocity on the coating thickness is well-known, a low percolation velocity was chosen.⁵⁵ Subsequent to the coating, the reactor was dried in a ventilated oven at 280°C for 15 minutes. For higher coating thicknesses, the procedure was repeated. The reactor was calcined in air at 500°C for 6 h to stabilize the coating. The finally coated mass was 3.5 g per reactor. Thus, coating thicknesses of more than 200 microns were realized.

Single dehydrogenation test reactor

The dehydrogenation of H12-NEC was conducted in a single reactor tube. The reactor tube was mounted in a ventilated oven (Fig. 4). The reactions were carried out under continuous H12-NEC flow using a HPLC pump with flow rates ranging from $0.5\text{--}4 \text{ mL min}^{-1}$ at temperatures between 220°C and 260°C and at ambient pressures. H12-NEC was purchased from Hydrogenious Technologies GmbH (<http://www.hydrogenious.net>).

Hydrogen Release Unit (HRU) consisting of ten parallel reactors and test set-up

Furthermore, a tenfold, parallel reactor setup has been developed to realize higher hydrogen evolution in a multi-reactor set-up. To demonstrate heat integration with a high temperature hydrogen combustion unit (e.g. a hydrogen burner or a solid oxide fuel cell), the HRU was designed for hot air heating (up to 450°C ; 200 NL min^{-1} volumetric flow rate). Technical details of the applied test set-up are given in the ESI.[†] The total volume of the applied HRU (Fig. 5) is 4 liters while the total reactor volume of the ten reactors is only 250 mL. The pre-heated H12-NEC is fed into the ten reactors through the unit bottom. The dehydrogenated products as well as the released hydrogen leave the reactor at the top where in the reactor head gas/liquid separation takes place. Subsequently, the hydrogen flow rate is measured *via* a hydrogen mass flow meter and the H_2 is fed into a fuel cell for electricity production.

Inlet and outlet temperatures of the hot air flow are monitored and controlled as well as its volumetric flow rate. Other

Fig. 3 Single reactor tube manufacturing; left: blueprint; center: unmachined reactor tube after the SEBM process; right: machined reactor: screw threads and sealing surfaces manufacturing using conventional methods.

Fig. 4 Set-up for catalytic tests of a single SEBM reactor; left: single reactor tube with fittings at reactor head and bottom after machining; right: single reactor tube test setup in a heated oven with multiple temperature measurements and H_2 -flow rate detection *via* a hydrogen mass flow meter.

Fig. 5 Hydrogen release unit (HRU) consisting of ten parallel reactors mounted in the vertical direction. Left: schematic view showing the reactors in the hot air box – hot air enters the box from the left to ensure counter-current heat transfer; right: photograph of the open HRU unit with ten SEBM-manufactured and catalytically functionalized reactor tubes. The unit is surrounded by a box to guide the hot air flow.

important parameters that are monitored and controlled in the experiment are the inlet and outlet temperatures of the LOHC flow at the HRU, the reaction temperature inside the reactor tubes (six different measurement points in six different reactor tubes), the hydrogen exit flow and the system pressure. The system pressure of the whole test-rig is 1.6 bar absolute pressure in all experiments reported here. By adjusting the hot air temperature and the volumetric flow rate, we measured three different isotherms of 230, 250 and 260 °C for variable H12-NEC flow rates between 10 and 40 mL min⁻¹. The goal is to monitor hydrogen production rates and catalyst productivities under different reaction conditions to identify suitable operation points of the HRU.

4. Results and discussion

Single reactor tube H12-NEC dehydrogenation results

Single reactor tube experiments have been performed at three different temperatures with varying H12-NEC flow rates. The resulting hydrogen flow rates and the calculated hydrogen yields (the amount of hydrogen released/total releasable hydrogen in the LOHC system) are presented in Fig. 6.

Fig. 6 Hydrogen release rates and hydrogen yields as a function of reaction temperature and H12-NEC flow rates obtained from single reactor tube experiments.

As expected, the reaction rate is higher at higher temperature which is both due to a higher driving force for the endothermic reversible dehydrogenation reaction and due to the higher reaction rate constant at higher temperature. From a kinetic perspective, the first hydrogenation step, from H12-NEC to H8-NEC, is known to proceed easiest, while the further dehydrogenation steps to NEC proceed slower.

Table 1 summarizes the single tube results with respect to temperature and hydrogen flow rate deviation. Due to the good heat transfer of the lab setup, the temperature deviation remained below 3%. A minor issue was the observed hydrogen flow rate fluctuation of up to 5.4% within a stationary measurement. Nevertheless a high catalyst activity of 1.27 g_{H₂} min⁻¹ g_{Pt}⁻¹ (260 °C, H12-NEC flow rate: 4 mL min⁻¹) could be reached. Considering the volume of the platinum coated reactor as a reference, a volumetric activity of 4.32 kW_{el} per liter was achieved.

HRU H12-NEC dehydrogenation results

Applying the HRU (ten parallel reactors) for H12-NEC dehydrogenation, it has been found that it takes about 45 minutes to reach the steady state in the whole set-up. After that time, however, stationarity was excellent. Fig. 7 shows the four main variables of the experiment, namely system pressure, LOHC-inlet temperature, reaction temperature and hydrogen flow rate exemplified for the time interval between 67.5 and 76 min time-on-stream.

Pressure deviations over this time range were less than 0.05 bar (3%). Deviation of the LOHC-inlet and reaction temperatures was less than 2 °C (1%), while deviations in hydrogen release were less than 100 mL H₂/min (1.5%). The spread in temperature of the six different measuring points in 6 different reactors was within 10 °C (4%). Therefore in total we can assume that the experiments in the HRU were operated under a steady state with only minor fluctuations.

Table 2 shows the results of a LOHC-flow rate variation at 230, 250 and 260 °C. From the obtained data, we calculated

Table 1 Experimental data of continuous H12-NEC dehydrogenation experiments in a single tube SEBM reactor

Temperature		LOHC	Hydrogen		Catalyst
Nominal, °C	Deviation (%)	Flow rate, mL min ⁻¹	Yield (%)	Deviation (%)	Productivity, g _{H₂} min ⁻¹ g _{Pt} ⁻¹
230	0.7	1.0	57.6	1.4	0.40
	0.9	1.5	50.2	1.6	0.53
	0.7	2.0	39.7	1.5	0.62
	1.1	3.0	36.5	0.6	0.77
	0.6	4.0	28.3	0.8	0.79
250	0.5	1.0	63.2	4.5	0.44
	1.1	1.5	65.7	5.4	0.69
	0.9	2.0	53.5	2.6	0.75
	1.8	3.0	49.0	2.4	1.03
	1.4	4.0	40.0	3.2	1.12
260	1.2	2.0	57.6	4.2	0.82
	2.4	4.0	45.3	3.1	1.27

Fig. 7 Steady-state operation of the HRU after a start-up time of 45 min. Conditions: reaction temperature: 230 °C; H12-NEC flow rate: 1 mL min⁻¹.

standard deviations for temperature, pressure and hydrogen yield. Deviation within an experiment, as depicted in Fig. 7, is referred to as stationary, whereas the deviation comparing all experiments is labelled reproduction. Deviation calculations are based on at least 1000 measured values or a period of 10 min to 50 min. The standard deviation of the catalyst productivity is equivalent to the one of the hydrogen yield. The indicated hydrogen yield is the fraction of the released hydrogen over the overall stored hydrogen in the LOHC.

Due to the crystallization of NEC (m.p. of pure NEC is 68 °C) at very high hydrogen yields, the system pressure rose up to 3.4 bar for some operation points (indicated with “*” in Table 2). This results in a relatively high pressure deviation of up to 41%. However, as shown in Table 2, there is a rather marginal effect of this pressure fluctuation on the hydrogen yield (as the equilibrium is far away) and therefore on the catalyst productivity. The average standard deviation of the hydrogen yield of all measurements is 6.9% and the maximum is 18.2%. This

discrepancy results in particular from the use of different batches of H12-NEC with slightly different levels of impurities, such as *e.g.* H12-carbazole.

From the data shown in Table 2, the thermal and potential electric power of the HRU under investigation can be determined according to eqn (1).

$$P_{\text{therm}} = \rho \times \dot{V}_{\text{H}_2} \times \text{LHV}_{\text{H}_2} \quad (1)$$

Calculating with the Lower Heat Value (LHV) of hydrogen of 120 MJ kg⁻¹ and the volumetric density (ρ) of hydrogen of 0.0899 kg m⁻³ under standard conditions, the flow rate of 9.8 NL min⁻¹ (as obtained in the HRU experiments at 250 °C, see Table 2) results in 1.75 kW thermal power or 960 W electric power (using a fuel cell with 55% efficiency). The results listed in Table 2 are further illustrated in Fig. 8 where the hydrogen

Fig. 8 Hydrogen release rates and hydrogen yields as a function of reaction temperature and H12-NEC flow rate as obtained in H12-NEC dehydrogenation experiments using the HRU; depicted fits do not represent kinetic models but aim to illustrate general tendencies based on the average H₂-flow rate values at each temperature and H12-NEC flow rate.

Table 2 Continuous H12-NEC dehydrogenation experiments in the HRU. Temperature, pressure and hydrogen flow rate deviations refer to data of reproduction experiments. Stationarity deviation refers to deviation within a stationary operation point; values indicated with “*” were obtained in experiments in which the pressure rose to higher values due to NEC crystallization

Temperature			LOHC	Pressure		Hydrogen		H ₂ -Deviation		Catalyst
Nominal, °C	Actual, °C	Deviation, °C	Flow rate, min ⁻¹	Actual, bar	Deviation (%)	Flow rate, NmL min ⁻¹	Yield (%)	Stationarity (%)	Reproduction (%)	Productivity, g _{H₂} min ⁻¹ g _{pt} ⁻¹
230	230	0.3	10	1.60	0.0	2918	48.2	6.8	6.6	0.33
	231	0.3	20	1.60	3.6	5700	47.1	1.4	1.2	0.65
	229	0.9	30	1.70	4.1	8712	48.0	2.1	12.3	0.99
	230	0.7	40	2.40*	36.9	9313	38.5	0.8	9.0	1.06
250	251	0.6	10	1.60	0.9	4757	78.7	3.7	1.3	0.54
	253	1.0	15	2.80*	33.7	5271	58.1	1.1	8.0	0.60
	247	1.0	20	2.10*	40.8	7100	58.7	1.4	18.2	0.81
	247	0.4	30	1.70	9.8	9789	54.0	2.3	6.1	1.12
260	260	0.3	10	2.60*	5.7	4762	78.7	—	0.8	0.54
	261	0.3	15	1.67	5.7	6609	72.9	1.4	5.5	0.75

Fig. 9 System stability for continuous H12-NEC dehydrogenation using the HRU within 48 hour time-on-stream. (A): First results (within the first 10 hours of the experiment) – (B) reproduction (within the last 10 hours of the experiment).

flow rates and the hydrogen yields of the HRU are plotted over the LOHC flow rate.

As expected, H_2 yields decrease with increasing LOHC flow rates due to lower residence times in the reactor, while the catalyst productivity rises due to fast dehydrogenation of H12-NEC to H8-NEC. For high H12-NEC flow rates, productivities of up to $1.12 \text{ g}_{H_2} \text{ min}^{-1} \text{ g}_{Pt}^{-1}$ are obtained.

To check the catalyst stability, system control and reproducibility, several operation points of the HRU were adjusted at the beginning of a 48 hour continuous dehydrogenation experiment (within the first 10 hours) and at the end of the run (within the last 10 hours). Fig. 9 shows the H_2 -flow rate and productivity data for this type of stability test under continuous operating conditions for 48 hour time-on-stream.

In general, the system stability and reproducibility are very high. The average standard deviation of the hydrogen yield is only 1.9% and corresponds to small discrepancies in the reaction temperature and pressure of 1% and 3.9%, respectively. Thus we conclude that continuous operation of the here presented HRU is possible in a quasi-stationary manner over at least 48 hour time-on-stream.

Due to practical limitations of our test rig, it was not possible to further increase the hydrogen yield or catalyst productivity. Main limitations were the operation range of the LOHC pump and the performance of the applied hot air gun. To avoid inhomogeneous heat input, we restricted LOHC flow rates to 30 mL min^{-1} at 250°C and even to 15 mL min^{-1} at 260°C .

5. Conclusions and outlook

The conversion of our current carbon-based energy system to a hydrogen-based one requires effective ways to store hydrogen in large amounts over long periods of time. LOHCs have the potential to substitute step-by-step liquid fossil fuels as they are energy carriers with attractive energy density and diesel-like handling. Hydrogen release from H_2 -rich LOHC systems allows

the on-demand utilization of regenerative energy equivalents at any time and at any place if the charging of the LOHC system was carried out with hydrogen from electrolysis of excess regenerative electricity.

In this contribution, we have demonstrated that 3-D-structured metallic reactors produced *via* selective electron beam melting form very suitable dehydrogenation reactors for perhydro-*N*-ethylcarbazole after appropriate coating with an active layer of Pt on alumina. Tubular SEBM reactors were successfully manufactured with an interconnected 3-D structured cellular network inside the reactor. The optimization of the foam network structure towards optimal heat conductivity and efficient hydrogen gas removal from the catalytic surfaces has been previously published by our collaboration partners in detail elsewhere.⁶⁵

The prepared catalytic SEBM reactor tubes have been tested in continuous dehydrogenation reactions in a single reactor and in a Hydrogen Release Unit (HRU) consisting of ten identical reactors. Summarizing the HRU hydrogen release experiments, we demonstrated a hydrogen generation of $9.8 \text{ NL}_{H_2} \text{ min}^{-1}$ in a total catalytic reactor volume of 250 mL (250°C , 30 mL min^{-1} flow rate of H12-NEC). The corresponding thermal capacity was 1.75 kW which transforms to an electric capacity of 960 W using a fuel cell with 55% efficiency. The single reactor tube experiments demonstrated a power density of up to $4.32 \text{ kW}_{el} \text{ L}^{-1}$.

In the HRU with its ten parallel reactors, this value reduced slightly to $3.84 \text{ kW}_{el} \text{ L}^{-1}$ which is still quite remarkable and promising in the context of future energy storage systems. Based on the total volume of the HRU (including hot gas channels and housing), the realised power density was $0.4 \text{ kW L}_{total \text{ volume}}^{-1}$. The developed HRU set-up showed very stable operation after a start-up phase of 45 min. The system stability and reproducibility of the dehydrogenation results proved to be excellent within 48 h time-on-stream.

Optimization potential in the hydrogen release system and apparatus presented here is obvious. First, the problems of NEC solidification at very high hydrogen release can be circumvented with more recent LOHC systems that are liquids at room temperature in all hydrogen loading states.⁴ Second, a more homogeneous temperature distribution in the tubes has to be realized at high temperatures and high LOHC flow rates. In this study, inhomogeneous temperature distribution prevented experiments under the most productive dehydrogenation conditions. We anticipate that an HRU device of the same dimensions could easily exceed power outputs of $5 \text{ kW}_{el} \text{ L}^{-1}$ if proper heat transfer (*e.g.* by heat transfer oil instead of hot air) allows us to maintain 260°C in the reactor with an H12-NEC flow rate of 40 mL min^{-1} . This is a volumetric power density that would make such HRUs highly attractive in the context of zero-emission range extender concepts for mobile applications.

Acknowledgements

The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) within the Excellence Cluster "Engineering of Advanced Materials" in the framework of the

excellence initiative. The present work was supported by BMW Forschung und Technik GmbH. We thank Christian Schmidt, Michael Zenner, Marco Di-Pierro and Daniel Teichmann for helpful discussions and technical input. The following contributions by members of the Department of Chemical and Biological Engineering of University of Erlangen-Nuremberg are gratefully acknowledged: Irma Schmidt for the CT-measurements; Tobias Horneber, Cornelia Rauh and Antonia Delgado for fruitful discussions about heat transfer and fluid dynamics; Florian Enzenberger and Wilhelm Schwieger for their support with regard to SEBM structure design and catalytic functionalization.

References

- 1 M. Klell, H. Eichlseder and M. Sartory, *Int. J. Hydrogen Energy*, 2012, **37**, 11531–11540.
- 2 D. Teichmann, W. Arlt, P. Wasserscheid and R. Freymann, *Energy Environ. Sci.*, 2011, **4**, 2767–2773.
- 3 M. Yang, Y. Dong and H. S. Cheng, *Adv. Mater. Res.*, 2014, **953–954**, 981–984.
- 4 X. Ye, Y. An and G. Xu, *J. Alloys Compd.*, 2011, **509**, 152–156.
- 5 F. Sotoodeh and K. J. Smith, *Ind. Eng. Chem. Res.*, 2010, **49**, 1018–1026.
- 6 K. M. Eblagon, D. Rentsch, O. Friedrichs, A. Remhof, A. Zuettel, A. J. Ramirez-Cuesta and S. C. Tsang, *Int. J. Hydrogen Energy*, 2010, **35**, 11609–11621.
- 7 D. Teichmann, K. Stark, K. Müller, G. Zöttl, P. Wasserscheid and W. Arlt, *Energy Environ. Sci.*, 2012, **5**, 9044–9054.
- 8 N. Brückner, K. Obesser, A. Bösmann, D. Teichmann, W. Arlt, J. Dungs and P. Wasserscheid, *ChemSusChem*, 2014, **7**, 229–235.
- 9 A. Bernard Toseland, DOE Hydrogen Programm, 2009.
- 10 F. Sotoodeh, B. J. Huber and K. J. Smith, *Int. J. Hydrogen Energy*, 2012, **37**, 2715–2722.
- 11 M. Sobota, I. Nikiforidis, M. Amende, B. S. Zanón, T. Staudt, O. Höfert, Y. Lykhach, C. Papp, W. Hieringer, M. Laurin, D. Assenbaum, P. Wasserscheid, H.-P. Steinrück, A. Görling and J. Libuda, *Chem.–Eur. J.*, 2011, **17**, 11542–11552.
- 12 M. Amende, S. Schernich, M. Sobota, I. Nikiforidis, W. Hieringer, D. Assenbaum, C. Gleichweit, H.-J. Drescher, C. Papp, H.-P. Steinrück, A. Görling, P. Wasserscheid, M. Laurin and J. Libuda, *Chem.–Eur. J.*, 2013, **19**, 10854–10865.
- 13 F. Sotoodeh and K. J. Smith, *J. Phys. Chem. C*, 2013, **117**, 194–204.
- 14 F. Sotoodeh and K. J. Smith, *J. Catal.*, 2011, **279**, 36–47.
- 15 F. Sotoodeh, B. J. Huber and K. J. Smith, *Appl. Catal., A*, 2012, **419**, 67–72.
- 16 F. Sotoodeh, L. Zhao and K. J. Smith, *Appl. Catal., A*, 2009, **362**, 155–162.
- 17 M. Yang, C. Han, G. Ni, J. Wu and H. Cheng, *Int. J. Hydrogen Energy*, 2012, **37**, 12839–12845.
- 18 M. Amende, C. Gleichweit, K. Werner, S. Schernich, W. Zhao, M. P. A. Lorenz, O. Höfert, C. Papp, M. Koch, P. Wasserscheid, M. Laurin, H.-P. Steinrück and J. Libuda, *ACS Catal.*, 2014, **4**, 657–665.
- 19 M. Amende, C. Gleichweit, S. Schernich, O. Höfert, M. P. A. Lorenz, W. Zhao, M. Koch, K. Obesser, C. Papp, P. Wasserscheid, H.-P. Steinrück and J. Libuda, *J. Phys. Chem. Lett.*, 2014, **5**, 1498–1504.
- 20 G. Pez and B. Toseland, *Air Products Presentation*, 2005.
- 21 J. von Wild, T. Friedrich, A. Cooper, B. Toseland, G. Muraro, W. TeGrotenhuis, Y. Wang, P. Humble and A. Karim, *Proceedings of the WEHC*, 2010.
- 22 S. Hodoshima, H. Arai and Y. Saito, *Int. J. Hydrogen Energy*, 2003, **28**, 197–204.
- 23 N. Kariya, A. Fukuoka and M. Ichikawa, *Appl. Catal., A*, 2002, **233**, 91–102.
- 24 N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, *Appl. Catal., A*, 2003, **247**, 247–259.
- 25 R. B. Biniwale and M. Ichikawa, *Chem. Eng. Sci.*, 2007, **62**, 7370–7377.
- 26 R. B. Biniwale, N. Kariya and M. Ichikawa, *Catal. Lett.*, 2005, **105**, 83–87.
- 27 J. V. Pande, A. Shukla and R. B. Biniwale, *Int. J. Hydrogen Energy*, 2012, **37**, 6756–6763.
- 28 Y. Peng, *Appl. Catal., A*, 2004, **266**, 235–244.
- 29 J. Richardson, Y. Peng and D. Remue, *Appl. Catal., A*, 2000, **204**, 19–32.
- 30 L. Giani, G. Groppi and E. Tronconi, *Ind. Eng. Chem. Res.*, 2005, **44**, 9078–9085.
- 31 L. Giani, G. Groppi and E. Tronconi, *Ind. Eng. Chem. Res.*, 2005, **44**, 4993–5002.
- 32 G. Groppi, L. Giani and E. Tronconi, *Ind. Eng. Chem. Res.*, 2007, **46**, 3955–3958.
- 33 E. Tronconi and G. Groppi, *Chem. Eng. Sci.*, 2000, **55**, 6021–6036.
- 34 F. Kapteijn, T. Nijhuis, J. Heiszwolf and J. Moulijn, *Catal. Today*, 2001, **66**, 133–144.
- 35 M. T. Kreutzer, F. Kapteijn and J. A. Moulijn, *Catal. Today*, 2006, **111**, 111–118.
- 36 T. J. Schildhauer, K. Pangarkar, J. R. van Ommen, J. Nijenhuis, J. A. Moulijn and F. Kapteijn, *Chem. Eng. J.*, 2012, **185**, 250–266.
- 37 A. Inayat, J. Schwerdtfeger, H. Freund, C. Körner, R. F. Singer and W. Schwieger, *Chem. Eng. Sci.*, 2011, **66**, 2758–2763.
- 38 A. Pestryakov, E. Yurchenko and A. Feofilov, *Catal. Today*, 1996, **29**, 67–70.
- 39 J. Bauer, S. Hengsbach, I. Tesari, R. Schwaiger and O. Kraft, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 2453–2458.
- 40 J. Schwerdtfeger, P. Heintz, R. F. Singer and C. Körner, *Phys. Status Solidi B*, 2010, **247**, 269–272.
- 41 J. Schwerdtfeger, F. Wein, G. Leugering, R. F. Singer, C. Körner, M. Stingl and F. Schury, *Adv. Mater.*, 2011, **23**, 2650–2654.
- 42 J. Wieding, A. Jonitz and R. Bader, *Materials*, 2012, **5**, 1336–1347.
- 43 A. Inayat, H. Freund, T. Zeiser and W. Schwieger, *Chem. Eng. Sci.*, 2011, **66**, 1179–1188.
- 44 J. Schwerdtfeger, F. Schury, M. Stingl, F. Wein, R. F. Singer and C. Körner, *Phys. Status Solidi B*, 2012, **249**, 1347–1352.

- 45 M. Klumpp, A. Inayat, J. Schwerdtfeger, C. Körner, R. F. Singer, H. Freund and W. Schwieger, *Chem. Eng. J.*, 2014, **242**, 364–378.
- 46 R. Ali, E. Alkhateeb, F. Kellner, S. Virtanen and N. Popovska-Leipertz, *Surf. Coat. Technol.*, 2011, **205**, 5454–5463.
- 47 G. Emig, N. Popovska and G. Schoch, *Thin Solid Films*, 1994, **241**, 361–365.
- 48 T. Knorr, P. Heintz, J. Schwerdtfeger, C. Körner, R. F. Singer and B. J. Etzold, *Chem. Eng. J.*, 2012, **181–182**, 725–733.
- 49 P. Rodriguez, B. Caussat, X. Iltis, C. Ablitzer and M. Brothier, *Chem. Eng. J.*, 2012, **211–212**, 68–76.
- 50 K. Maca, H. Hadraba and J. Cihlar, *Ceram. Int.*, 2004, **30**, 843–851.
- 51 T. Olding, M. Sayer and D. Barrow, *Thin Solid Films*, 2001, **398–399**, 581–586.
- 52 S. Ould-Chikh, N. Brodusch, N. Crozet, M. Hemati and L. Rouleau, *Powder Technol.*, 2013, **237**, 255–265.
- 53 T. Schwarz, H. Döring, E. Klemm and S. Schirrmeister, *Chem. Ing. Tech.*, 2010, **82**, 921–928.
- 54 L. Zhao, M. Bram, H. Buchkremer, D. Stover and Z. Li, *J. Membr. Sci.*, 2004, **244**, 107–115.
- 55 C. J. Brinker and A. J. Hurd, *J. Phys. III*, 1994, **4**, 1231–1242.
- 56 E. J. A. Pope, A. Almazan and K. Kratsch, *J. Am. Ceram. Soc.*, 1991, **74**, 1722–1724.
- 57 I. Santacruz, B. Ferrari, M. I. Nieto and R. Moreno, *Adv. Eng. Mater.*, 2003, **5**, 647–650.
- 58 M. Vargová, G. Plesch, U. F. Vogt, M. Zahoran, M. Gorbár and K. Jesenák, *Appl. Surf. Sci.*, 2011, **257**, 4678–4684.
- 59 A. Maione, F. Andre and P. Ruiz, *Appl. Catal., B*, 2007, **75**, 59–70.
- 60 L. Giani, C. Cristiani, G. Groppi and E. Tronconi, *Appl. Catal., B*, 2006, **62**, 121–131.
- 61 M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi and P. Forzatti, *Catal. Today*, 2001, **69**, 307–314.
- 62 C. G. Visconti, E. Tronconi, L. Lietti, G. Groppi, P. Forzatti, C. Cristiani, R. Zennaro and S. Rossini, *Appl. Catal., A*, 2009, **370**, 93–101.
- 63 G. Groppi, W. Ibashi, M. Valentini and P. Forzatti, *Chem. Eng. Sci.*, 2001, **56**, 831–839.
- 64 P. Heintz, A. Rottmair, C. Körner and R. F. Singer, *Adv. Eng. Mater.*, 2007, **9**, 360–364.
- 65 T. Horneber, C. Rauh and A. Delgado, *Chem. Eng. Sci.*, 2014, **117**, 229–238.