Catalytic plate reactor utilizing laser induced nanofoams as catalyst support for the continuous dehydrogenation of perhydro benzyltoluene.

Phillip Nathrath[1], Tamara Hein[1], Jannis Müller-Ebhardt[2], Eike Hübner[3], Peter Wasserscheid[1], Patrick Schühle[1]*

1 Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, DE-91058, Germany; 2 Kelvion PHE GmbH, Karl-Schiller-Straße 1-3, DE-31157 Sarstedt, Germany; 3 Fraunhofer Heinrich Hertz Institute HHI, Fiber Optical Sensor Systems, Am Stollen 19 H, DE-38640 Goslar, Germany

**Corresponding author: patrick.schuehle@fau.de*

Highlights

- Laser texturing as innovative manufacturing method for durable aluminum oxide catalyst nanofoams
- Successful dehydrogenation with laser induced nanofoams (LINF) plate catalysts
- Competitive activity of LINF compared to washcoated catalysts in a catalytic plate reactor
- Low by-product formation of the LINF plate catalyst

1. Introduction

Hydrogen will play a crucial role for a future sustainable energy system. To utilize this energy vector effectively proper storage solutions have to be found. One option is the reversible chemical bonding to a liquid organic hydrogen carrier (LOHC) molecule. Decentralized and efficient hydrogen release from LOHC compounds imposes certain requirements on the reactor, such as good heat transfer characteristics, easy scalability, and small construction volume. Wall coated or catalytic plate reactors (CPR) are viable options to check these requirements.[1] An inherent challenge linked to the CPR concept is the manufacturing of mechanically durable plate catalysts. State-of-the-art washcoating techniques are used to produce metal oxide layers on top of metallic substrates. Laser texturing of the metal substrates themselves emerges as a convincing alternative to reach catalytic active surfaces.[2] By using pulsed femto-/nanosecond lasers the surface of the metal substrate is directly converted into a porous metal oxide foam. This foam exhibit an excellent adherence and can be exploited as catalyst supports.[3] In this work, alumina based laser induced nanofoams (LINF) are produced from aluminum plates and used as catalysts supports in the highly endothermic dehydrogenation of perhydro benzyltoluene (see Figure 1). This reaction is particularly relevant for the future application of LOHCs. The LINF catalysts are compared with traditional washcoated catalyst in terms of dehydrogenation activity and catalyst stability.

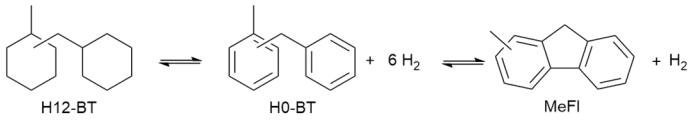

Figure 1. Reaction scheme for the dehydrogenation of perhydro benzyltoluene (H12-BT) to benzyltoluene (H0-BT) and subsequent formation of the by-product methylfluorene (MeFl).

2. Methods

For the preparation of the LINF supports an AMPHOS high-power laser system and the following settings have been used on a AlMg3 substrate: center wavelength of 1030 nm, pulse length of 750, Gaussian beam spot diameter of approximately 140 µm ($1/e^2$) and a scanning speed of 10 mm s^{-1}. The average optical laser output power of 36 W leads to a pulse energy of 36 µJ and a laser fluence of 0.234 J cm^{-2} at a repetition rate of 1 MHz. The resulting structure motive is a thick and white LINF of aluminum oxide, strongly bound on the original plate surface (see Figure 2 (a)). After laser texturing the plates

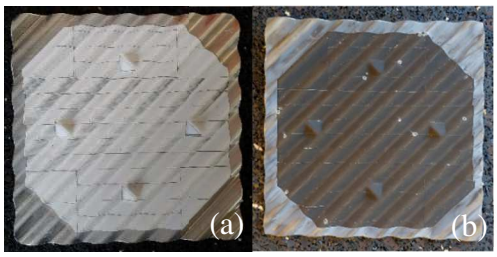

Figure 2. Laser textured AlMg3 substrate with white LINF (a) and LINF plate catalyst after platinum impregnation and reduction (b).

are impregnated with platinum sulfite acid solution in a wet impregnation step and subsequently reduced for 4 h at 440 °C under hydrogen atmosphere. The final Pt-S/LINF catalyst plate is shown in Figure *2* (b). To evaluate the catalytic performance of the plates, continuous dehydrogenation experiments are carried out at varying reaction parameters in a CPR with two facing corrugated catalyst plates in use (one slit). The laser textured plates are compared to reference wash coated plates with similar platinum content.

3. Results and discussion

Figure 3 shows a parameter variation for the dehydrogenation of perhydro benzyltoluene carried out in a CPR with temperatures ranging from 300 – 340 °C and pressures of 2.5 to 5.0 bar_a.

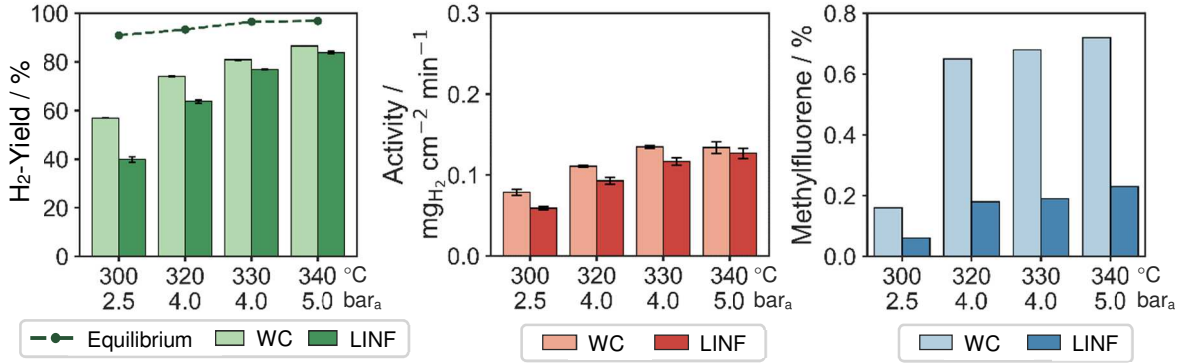

Figure 3. Comparison of the wash coated (WC) and LINF plate catalyst regarding H_2-Yield, activity and methylfluorene (by-product) selectivity in a CPR (feed flow 1 g_{BT} min^{-1}, platinum mass in reactor ~0.5 g).

It can be seen that the hydrogen yield and activities exhibit the same qualitative trend for the washcoat and LINF plates. At low temperatures, the washcoated plates showed up to 17 % higher hydrogen yields. With increasing temperatures and hydrogen yields closer to the reaction equilibrium, the gap between LINF and washcoat catalysts becomes smaller, indicating different reaction kinetics of both catalysts. This might be attributed to differences in the pore structure. The LINF plates have a large proportion of small pores below 5 nm pore diameter, whereas the washcoated catalyst has a mean pore diameter around 12 nm. Overall, both catalysts reached high hydrogen yields above 80 % at 340 °C and 5.0 bar.. As a key marker for the selectivity of the reaction, the content of the primary reaction by-product methylflourene can be taken to account (compare Figure 1).[4] Compared to the washcoated catalyst, the catalytically activated LINF catalyst produces significantly lower amounts of methylfluorene even at similar hydrogen yields and high reaction temperatures. Additionally, LINF plate catalysts have been tested for more than 220 h under reaction conditions with no indication of catalyst deactivation.

4. Conclusions

In this study, we demonstrated the effective production of catalytically active LINF and their application in the continuous dehydrogenation of perhydro benzyltoluene. The laser textured catalyst reached high hydrogen yields with low by-product formation. Furthermore, no catalyst deactivation was found within the over 220 h of operation. Therefore, Pt-S/LINF plate catalyst emerge as a viable option for high performance dehydrogenation application in a catalytic plate reactor.

References

[1] A. Karim, J. Bravo, D. Gorm, T. Conant, A. Datye, Catalysis Today 110 (2005) 86–91.
[2] H. Sun, J. Li, M. Liu, D. Yang, F. Li, Coatings 12 (2022) 1596.
[3] S. Rauh, K. Wöbbeking, M. Li, W. Schade, E.G. Hübner, ChemPhysChem 21 (2020) 1644–1652.
[4] T. Rüde, S. Dürr, P. Preuster, M. Wolf, P. Wasserscheid, Sustainable Energy Fuels 6 (2022) 1541–1553.

Keywords

Dehydrogenation; catalytic plate reactor, laser texturing, plate catalysts.