

Batch-to-continuous transposition of three-phase reactions involved in hydrogen storage in liquid organic carriers

Carine Julcour^{1*}, Anne-Marie Billet¹, Sofiane Bekhti¹, Priyanka Gairola¹, Duncan Edel¹

¹ Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

**Corresponding author: carine.julcour@inp-toulouse.fr*

Highlights

- Ni/Al₂O₃ catalyst active for both hydrogenation/dehydrogenation of carbazoles under mild conditions
- Kinetic modelling of the reactions
- Stable catalyst performance in sequential hydrogenation/dehydrogenation cycles
- Continuous hydrogenation of the H₂-lean carbazoles in flooded bed under isothermal conditions

1. Introduction

In the context of the growing demand for carbon free energy, green hydrogen is recognized as a clean fuel and a way to mitigate the intermittency of solar or wind energy sources by providing large capacity and long-term storage capabilities. However, current solutions for its transport and distribution over long distances - high pressure compression (> 300 bar) or cryogenic liquefaction (at -253°C) - raise concerns about safety and boil-off, and thus require high-tech tanks^[1]. Since the 2010s, liquid Organic Hydrogen Carriers (or LOHC) have emerged as a promising alternative to address these challenges, since they provide a safer and easily manageable solution, with a storage at ambient conditions using conventional fuel tanks^[1,2]. Most of the research effort to date has focused on the identification or design of suitable LOHC candidates or on catalyst developments for high recyclability, improved H₂ capacity and reduced costs. However, very little work has addressed the design of three-phase reactors to improve phase contacting and heat transfer management in the hydrogenation (HYD)/dehydrogenation (DH) reactions involved. In addition, the possibility of using the same catalyst for both reactions, thus eliminating the need for liquid/catalyst separation, has been hardly explored.

2. Methods

A mixture of carbazole-based LOHCs, namely n-ethyl and n-propyl carbazoles, was chosen due to their lower energy requirement for dehydrogenation^[3] and their substantial hydrogen storage capacity. The eutectic mixture of these LOHCs also possesses a melting point close to room temperature^[4]. To moderate the heat release and enhance species diffusivity, the mixture was diluted to a 1:4 weight ratio with an inert solvent (dodecane isomer mixture). The activity of various available catalysts was evaluated for both HYD and DH in a batch autoclave reactor working under controlled temperature and pressure and equipped with a gas inducing turbine, a condenser and gauged gas vessels including T/P probes to instantaneously record hydrogen uptake or release. In addition, reaction intermediates were quantified by gas chromatography to monitor the consecutive reaction steps. Mild operating conditions were selected to align with industrial application requirements: $100 \leq T \leq 170^\circ\text{C}$ and $5 \leq P_{\text{H}_2} \leq 30$ bar for the HYD step, and $T < 200^\circ\text{C}$ and $P_{\text{H}_2} \sim 2$ bar for the DH step. The same reactor was used to evaluate the catalyst and LOHC stability in successive HYD/DH cycles.

From the kinetic modelling of LOHC hydrogenation, relevant conditions for operating this exothermic reaction in a fixed bed reactor were identified. An experimental campaign was carried out in a jacketed packed bed column (1 inch diameter, about 1.2 m high) operating in gas-liquid concurrent upflow and its performance was compared with those of the batch stirred reactor and downflow configuration.

3. Results and discussion

The Ni/Al₂O₃ catalyst developed by Johnson-Matthey Plc. has shown high activity with respect to other commercially available extrudates containing noble metals (Ru, Pd or Pt), with quantitative HYD/DH yields obtained after a few hours with a catalyst to LOHC ratio of 20 wt.%. Moreover, after the first

recycling, the catalyst activity proved to be stable over four more consecutive HYD/DH cycles operated with the same LOHC and catalyst loadings. An amount of H₂ equivalent to more than 50% of the liquid mixture capacity could be stored and released within 5 h under the investigated conditions. The kinetic investigation showed the overall HYD rate to be first order with respect to the catalyst weight, the double bond concentration and the hydrogen pressure in the investigated range. The apparent activity energy was found around -40 kJ/mol. On the other hand, the overall DH rate could be related to the amount of stored hydrogen moles, and the Arrhenius plot gave an apparent activation energy of ca. 170 kJ/mol. The time-concentration profiles of the main reaction intermediates (H4-, H8- in addition to H0- and H12-carbazoles) were mainly consistent with a consecutive reaction scheme, but parallel reaction routes might occur at low temperature and high pressure.

The kinetic modelling of HYD provided means for batch-to-continuous transposition in which the G-L upflow fixed bed reactor could be operated under near-isothermal conditions with quantitative substrate conversions. To this end, the catalyst bed was diluted to 1:1 by weight with alumina support, and the following conditions were investigated: $100 \leq T \leq 150^\circ\text{C}$, $5 \leq P_{\text{H}_2} \leq 20$ bar, 0.4 kg/h as reference liquid flow rate and over-stoichiometric flow rate of H₂. The measured outlet yield followed the predictions of an ideal plug flow reactor model without external mass transfer limitations, except at the highest temperature where such resistance became significant. This behaviour was consistent with the minor effect of gas flow rate observed in the studied operating condition range. Moreover, as illustrated in Fig. 1, the various species concentration profiles as a function of the hydrogenation yield were almost the same as in the batch stirred reactor. Conversely, the G-L downflow configuration could only be operated up to 120°C to prevent hot spot occurrence. Under stable operation, it gave rise to significant temperature gradients along the bed (up to 20°C) and a much lower formation of intermediates due to poor wall heat exchange, flow heterogeneities and partial catalyst wetting inside the trickle bed.

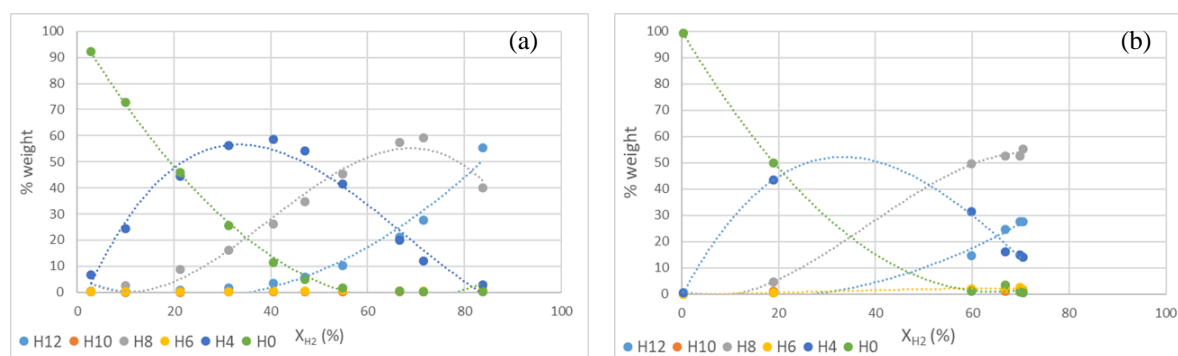


Figure 1. Reaction intermediate profiles vs. overall hydrogenation yield at $T=150^\circ\text{C}$ & $P_{\text{H}_2} = 5\text{-}6$ bar: (a) batch stirred reactor and (b) continuous G-L upflow fixed bed reactor

4. Conclusions

Ni/Al₂O₃ catalyst was shown to be active below 200°C for both hydrogenation and dehydrogenation of carbazole LOHCs and stable over multiple cycles. Apparent rate law expressions were established, that enabled the prediction of hydrogenation yield and hydrogen release over an extended range of conditions. Batch-to-continuous transposition was successfully achieved using a fixed bed reactor operated in upflow mode. In particular, quasi-isothermal conditions could be achieved, in contrast to trickle bed configuration.

References

- [1] Z. Abdin, C. Tang, Y. Liu, K. Catchpole, *iScience* 24 (2021) 102966
- [2] V. Meille, I. Pitault, *Reactions* 2 (2021) 94-101
- [3] M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, *Int. J. Hydrogen Energy* 44 (2019) 6631-6654
- [4] K. Stark, P. Keil, S. Schug, K. Müller, P. Wasserscheid, W. Arlt, *J. Chem. Eng. Data* 61 (2016) 1441-1448

Keywords

Hydrogen storage, carbazoles, hydrogenation-dehydrogenation cycles, multiphase catalytic reactors

Acknowledgments: the authors thank Johnson-Matthey Plc for providing the nickel on alumina catalyst, European Union and Occitanie Region for project funding through the key challenge “hydrogène vert” (FEDER REACT H2VERT)