Green Hydrogen Storage in LOHCs via Catalytic Hydrogenation: In-depth Compound Analysis and Kinetic Study of Commercial Dibenzyltoluene Mixture

Xiaolong Ji[1,2], Casimir Maudet[2], Fabienne Fache[3], Essyllt Louarn[1], Valérie Meille[1]*, Isabelle Pitault[2]*

1 IRCELYON; 2 LAGEPP; 3 ICBMS, Université Claude Bernard Lyon 1, 69100, Villeurbanne, France

Corresponding author: valerie.meille@ircelyon.univ-lyon1.fr; isabelle.pitault@univ-lyon1.fr

Highlights
- Establishment of intrinsic L-H kinetic model of green H_2 storage in dibenzyltoluene.
- Efficient low-temperature hydrogenation explored for H_2 storage with Pt/C and Pt/Al$_2$O$_3$ catalysts.
- Individual modeling for most isomers in commercial dibenzyltoluene showed different behaviors.
- Modeling of mass transfer limitation and catalyst deactivation.

1. Introduction

The storage and transport of green hydrogen is one of the major challenges in hydrogen processes. Hydrogen produced with renewable energy can be efficiently stored in LOHCs (Liquid Organic Hydrogen Carriers) through a catalytic hydrogenation of the LOHC compounds, and the release of hydrogen is typically reached via the dehydrogenation of their H_2-rich form. The mixture of dibenzyltoluene (H0-DBT) isomers could be valued for its high storage capacity (6.2 wt-%) and large liquid phase temperature range (-34 ~ 386 °C). H0-DBT hydrogenation was found to be a 3-step consecutive reaction with side-side-middle (SSM) preference producing H6-DBT and H12-DBT as intermediates [1]. However, a deeper understanding of isomers in the mixture and their kinetics of H_2 storage were not present in the literature which are crucial for reactor and process design. In this study, the identification of Hx-DBT isomers was achieved with the help of GC/MS and targeted organic synthesis coupled with kinetic modeling. Kinetic studies have been carried out using commercial Pt/Al$_2$O$_3$ and Pt/C catalysts under different conditions including temperature, pressure and catalyst particle size etc. Kinetic models taking into consideration mass transfer limitations, aromatic ring adsorption, catalyst deactivation and poisoning have been established for each Hx-DBT family and most Hx-DBT isomers.

2. Methods

Isomer analysis of H0-DBT (Jarytherm® Arkema) was carried out using the equipment and methods demonstrated in our published work [2]. Commercial powder catalysts Pt/Al$_2$O$_3$ and Pt/C were separated into two groups with a 50 μm sieve. Kinetic experiments were carried out in a 300 mL stainless-steel batch reactor equipped with a hydrogen container with pressure monitoring. Different Pt/DBT ratio (0.0075 – 0.03 mol-%) were tested in the temperature range of 85 – 250 °C (in isotherm mode or with temperature changes) under 20 – 50 bar of H_2 with a stirring speed of 800 – 1200 rpm. The reaction was monitored by (i) liquid phase sampling, which was analyzed by 2 GC systems equipped with different columns (HeavyWax and DB-35), allowing the establishment of mass balances over Hx-DBT and possible side products and (ii) recording the pressure drop in the hydrogen container upstream of the reactor every second. The set-up was modeled accounting the transfer limitations between the phases and in the porous solid particles. Parameter estimation was performed using non-linear optimization routines minimizing the difference between the simulated and experimental (i) compound quantities at a given time and (ii) the pressure profiles, in Python.

3. Results and discussion

All isomers present in the Jarytherm® mixture (75 wt-% of dibenzyltoluene and 25 wt-% of benzylbenzyltoluene) were successfully identified. Attribution was confirmed by the synthesis of

major components 2,4, 2,5 and 3,4-DBT and the kinetics results. It has been found that there was a 0.005 mol-% poison in the commercial mixture which could nullify a part of the catalyst at the beginning of the reaction. Furthermore, in-depth kinetic studies have been performed using Pt/Al$_2$O$_3$ and Pt/C catalysts at different reaction conditions which showed very different behaviors. Pt/C catalyst was found subject to deep deactivation after about 60 min at temperatures above 200 °C due to an inhibitor formed from H6 and H12-DBT via a side reaction which was not observed on Pt/Al$_2$O$_3$. A deactivation function Φ_D based on inhibitor concentration C_{in} was applied to the kinetic models (Eq. 1). On the other hand, Pt/C showed much better activity than Pt/Al$_2$O$_3$ at temperatures lower than 200 °C. Low temperature hydrogenation was favored by reaction thermodynamics and allowed the total conversion towards H18-DBT with no residue of H12-DBT contrary to high temperature processes reported in the literature [3]. Abrupt changes of slope in the H$_2$ storage curve were observed on both Pt/Al$_2$O$_3$ and Pt/C catalysts as well as in the literature [3] which was successfully explained by a pseudo Langmuir-Hinshelwood model taking different adsorptions of center and side aromatic rings into account. Thiele modulus calculation showed internal transfer limitations at the beginning of the reaction at high temperatures. From the set-up dynamic model, reaction rate of Hx-DBT r_x were established on each H0, H6, H12, H18-DBT family and most isomers, estimating intrinsic hydrogenation rate constants k_i, inhibitor formation rate constant k_{in} (allowing the calculation of C_{in}), center and side aromatic ring adsorption coefficients K_c and K_s, internal transfer efficiency η_i, gas-liquid transfer coefficient k_La and liquid-solid transfer coefficient k_D (Eq. 1). An example of concentration and hydrogen pressure fitting is shown in Figure 1.

$$r_x = \frac{k_x C_{Hx-DBT} C_{H_2}}{1+K_C C_{aro,C}+K_S C_{aro,S}} \Phi_D \quad with \quad \Phi_D = \frac{B+1}{B+\exp\left(AC_{in}\right)} \tag{1}$$
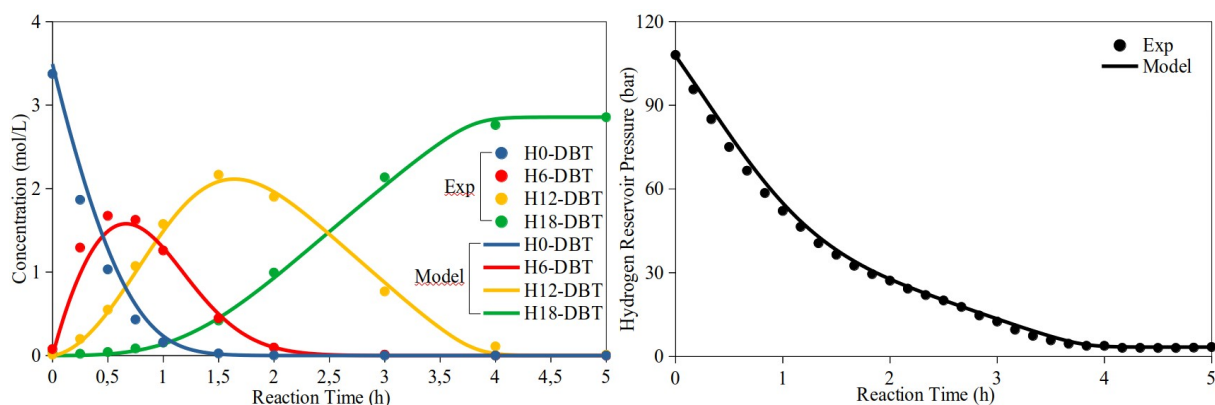

Figure 1. Simulated and experimental values of left) Hx-DBT concentrations and right) H$_2$ storage profile at 150 °C, 30 bar H$_2$ and 1000 rpm with 5 wt-% Pt/C catalyst using a Pt/DBT ratio of 0.0015 mol-%

4. Conclusions

The identification and the hydrogenation kinetic study of Hx-DBT/Hx-BBT isomers allowed to highlight their different behavior and established the foundation of mechanism exploration taking intermediate and product isomers into account. Kinetic modeling of hydrogenation under different conditions exploring intrinsic reaction, transfer limitation, ring adsorptions, catalyst deactivation and poisoning allowed to determine optimal green hydrogen storage operating conditions and the design of hydrogenation reactors on an industrial scale. Poison and deactivation study could also provide potential guidance for the synthesis of new resistant catalysts or suitable process development.

References

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