

Hydrogen Storage in Dibenzyltoluene via Catalytic Hydrogenation: In-depth Compound Analysis and Kinetic Study

Xiaolong Ji^{1,2}, Casimir Maudet², Fabienne Fache³, Essyllt Louarn¹, 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 complete kinetic model of dibenzyltoluene hydrogenation.
- Efficient low-temperature hydrogenation explored for H₂ storage with Pt/C catalysts.
- Individual modeling of 15 isomers in commercial dibenzyltoluene showed different behaviors.

1. Introduction

The storage and transport of hydrogen is one of the major challenges in hydrogen processes. Hydrogen 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 H₂-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 H₂ 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. Kinetic studies have been carried out using commercial Pt/Al₂O₃ and Pt/C catalysts under different conditions including temperature, pressure and catalyst particle size etc. Kinetic models taking into consideration mass transfer limitations, compound adsorption and catalyst deactivation and poisoning have been established for each Hx-DBT family and all H0-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 Pt/Al₂O₃ catalyst was reduced under H₂ flow at 300 °C for 4 h and Pt/C was used as is without reduction. All catalysts 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 H₂ 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 were successfully identified. Attribution was confirmed by the synthesis of major components 2,4, 2,5 and 3,4-DBT. It has also been found that the commercial mixture has not only 75 wt-% of H0-DBT but also 25 wt-% of benzylbenzyltoluene (H0-BBT). Furthermore, in-depth kinetic studies have been performed using Pt/Al₂O₃ and Pt/C catalysts at different reaction conditions which showed very different behaviors. 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. Abrupt changes of slope in the H₂ storage curve were observed on both Pt/Al₂O₃ and Pt/C catalysts as well as in the literature [3] which was successfully explained by a pseudo Langmuir-Hinshelwood model taking the adsorption of aromatic rings into account. 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/Al₂O₃. An empirical deactivation function [4] was applied to the kinetic models. On the other hand, Pt/C showed much better activity than Pt/Al₂O₃ 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] Effect of particle size displayed internal transfer limitations at the beginning of the reaction at high temperatures which was confirmed by the values of the Thiele modulus. A kinetic model was established on each H0, H6, H12 and H18-DBT family, one of which is shown in Figure 1 as an example, estimating intrinsic hydrogenation rate constants k_i , inhibitor formation rate constant k_{in} , aromatic ring adsorption coefficient K , internal transfer efficiency η_i , gas-liquid transfer coefficient $k_{l,a}$ and liquid-solid transfer coefficient k_D . Kinetic models specific to each H0-DBT isomer were also established which had different reaction rate constants with that of the most abundant isomer 2,4-DBT being the highest.

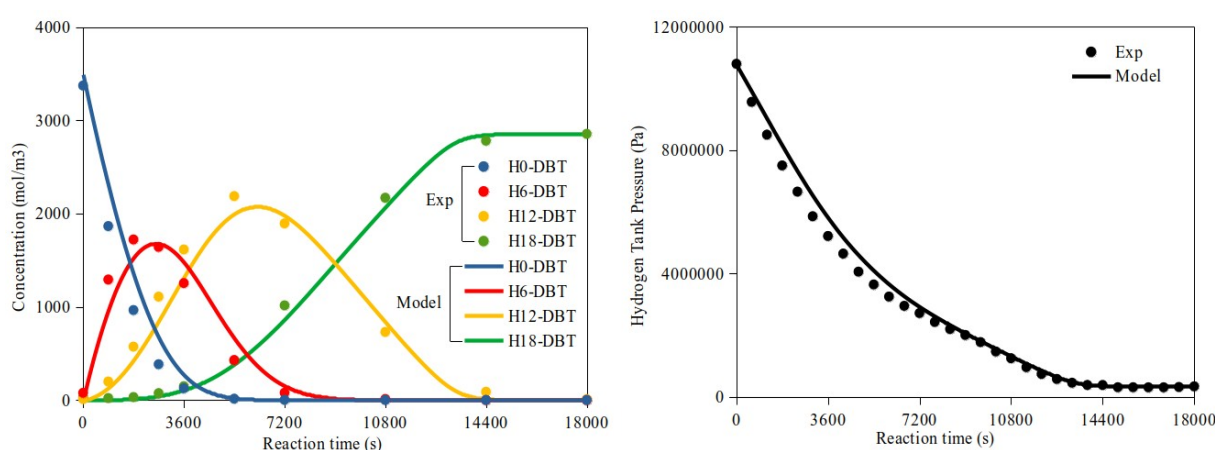


Figure 1. Simulated and experimental values of left) Hx-DBT concentrations and right) H₂ storage profile at 150 °C, 30 bar H₂ and 1000 rpm with 5 wt-% Pt/C catalyst using a Pt/DBT ratio of 0.0015 mol-%

4. Conclusions

The study of H0-DBT/H0-BBT isomers and their hydrogenation allowed to highlight the behavior of the different reactant isomers which also 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 adsorption and catalyst deactivation and poisoning allowed to determine optimal 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. Low-temperature hydrogenation could lower the energy and economic cost of hydrogen storage processes in LOHCs.

References

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Keywords

LOHC; Hydrogen Storage; Kinetics; Catalysis