

LOHC: kinetics of toluene hydrogenation over Pt/Al₂O₃ catalyst in a trickle bed reactor

Vincenzo RUSSO^{*1}, Muhammad Usama DAUD¹, Alessandro ESPOSITO¹, Federica COSENZA¹, Riccardo TESSER¹,
Martino DI SERIO¹

¹ Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy.

* v.russo@unina.it

Significance and Relevance

The main novelty of the paper was the kinetic investigation of toluene hydrogenation to methylcyclohexane using 5wt.% Pt/Al₂O₃ catalyst, packed in a trickle bed reactor. The catalyst shown good activity, stability, and total selectivity to the desired product, representing a good candidate for LOHC technology. Kinetic information was retrieved on the collected data, having hints on the reaction mechanism, showing that the reaction follows an Eley-Rideal model.

Preferred and 2nd choice for the topic: H₂ storage and transportation, green H₂ production, hydrogen vectors, Fundamental advances in understanding catalysis.

Preferred presentation: Oral only

Introduction and Motivations

Hydrogen is considered nowadays a clean energy vector. However, to date, one of the factors delaying its adoption as a fuel is the lack of adequate storage and transport systems. Conventionally, hydrogen storage is done by high-pressure compression or cryogenic liquefaction, but both techniques include safety issues, low storage density, evaporative losses and relatively high costs.

A promising alternative to counteract the problems associated with these techniques is the use of Liquid Organic Hydrogen Carriers (LOHC), which are organic compounds that can store and release hydrogen through a cycle of chemical reactions of hydrogenation and dehydrogenation¹. These reactions require to be promoted by suitable catalytic systems, usually represented by transition metals (e.g., Ni, Ru, Pd or Pt) fixed in the form of a fine powder on a porous support (e.g., Al₂O₃).

The present work is concerned with studying the continuous hydrogenation reaction of toluene, thus used as a carrier molecule, to give methylcyclohexane, catalysed by platinum supported on alumina (Pt/Al₂O₃). Considering the three-phase gas-liquid-solid system, the reaction was conducted in a trickle bed reactor (TBR) and, by appropriately varying the operating conditions, several tests were carried out to retrieve kinetic information on the chemical reaction. Flow chemistry principles were exploited to increase the performance of the process, with the advantages of better control of reaction conditions, rapid analysis and reduced diffusion limitations.

Materials and Methods

In the present study, high-purity toluene (99.5%) and n-heptane (≥99%) were purchased from Merck, along with a commercial catalyst, 5wt.% Pt-Al₂O₃ in powdered form (40μm average radius). Catalyst pre-reduction was conducted in a glass-bed reactor at 130°C under a hydrogen flow rate of 0.05L/min for 3 hours to activate the metallic phase.

Kinetic experiments were conducted in a 10 cm trickle bed reactor with a 0.635 cm inner diameter, loaded with 104.3mg of catalyst ($\rho_B=0.02\text{g/cm}^3$). The reactor was heated up at the desired temperature level with via electrical resistance. Azura P 4.1S HPLC pump was used to pump the liquid solution to the reactor, while two gas flowmeters regulators were adopted to feed nitrogen and hydrogen to the reactor, at a defined volumetric ratio. A gas-liquid separation unit was put in series to the trickle bed reactor, enabling the collection of liquid samples. The liquid phase was analyzed via GC-FID analysis (Perkin Elmer Clarus 500) using Elite 5 column ($ID=0.32\text{mm}$ $L=30\text{m}$, film thickness=0.25μm, composition of the stationary phase: 5% diphenyl/95% dimethylpolysiloxane). Each sample, diluted with heptane, was injected with a 1 μL syringe at 250 °C. The chromatographic run involved an initial step at $T=90$ °C held for two minutes, followed by two temperature ramps: 2 °C/min up to 120 °C (held for one minute) and a rapid increase to 200 °C at 40 °C/min.

Results and Discussion

Figure 1A shows the trend of toluene conversion to methylcyclohexane as a function of the liquid flow rate for the 3 different temperatures, highlighting the influence of temperature and flow rate on the process. An inverse proportionality between the conversion degree and the volumetric flow rate, indicating negligible fluid-solid mass transfer limitations. Moreover, there a strong effect of temperature was measured: passing from 80 to 100 °C there is a significant conversion difference and, in addition, at the highest temperature, diffusion phenomena probably begin to occur, as only a minor influence of the volumetric flowrate was measured. It must be noted that in every experiment selectivity was always 100% towards methylcyclohexane, and the catalyst was stable for 50h of time on stream.

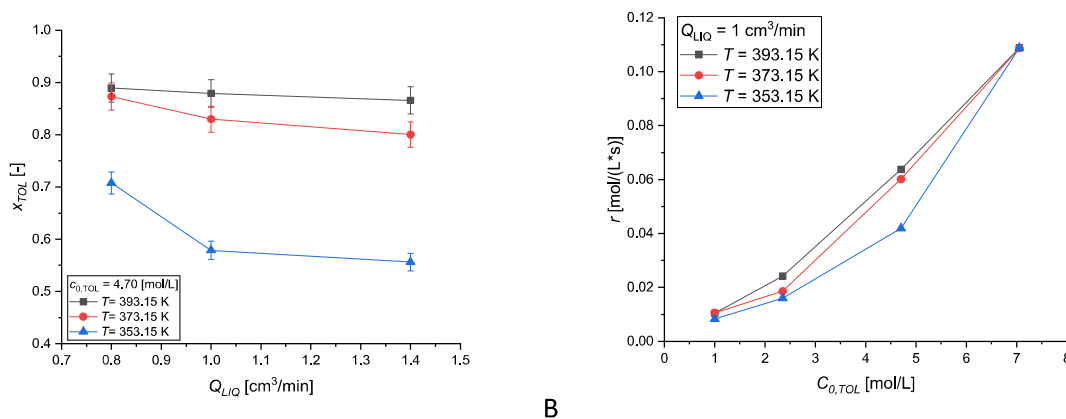


Figure 1 A. Evolution of the toluene steady-state conversion at different liquid flow-rate and at different temperatures, imposing $C_{0,TOL}=4.7$ mol/L, $Q_G=5$ cm³/min and N₂/H₂=4:1 vol/vol. B. Evolution of the observed reaction rate as a function of the feed toluene concentration, at different temperatures, imposing $Q_L=1$ cm³/min, $Q_G=5$ cm³/min and N₂/H₂=4:1 vol/vol.

The hydrogenation reaction rate dependence with the feed toluene concentration was studied at different temperatures (Figure 1B). At each temperature, the reaction rate increases with the concentration of the reactant in the feed, revealing a shift of the reaction order when increasing the temperature. In particular, a first order behavior can be observed at the highest temperature value, while at lower temperatures, the apparent order is lower than one. These peculiar trends could be explained by assuming surface reaction mechanism (e.g., Langmuir-Hinshelwood, Eley-Rideal). In particular, an Eley-Rideal mechanism for the hydrogenation reaction is hypothesized, assuming that hydrogen reacts from the bulk of the liquid phase, at a constant hydrogen concentration, the reaction rate is given as in Eq. 1 in both explicit and simplified form.

$$r = \frac{k C_{TOL}}{1 + K_{TOL} C_{TOL}} \quad (1)$$

As physical adsorption is an exothermic process, it is reasonable to hypothesize that at high temperatures, $K_{TOL} C_{TOL} \ll \alpha$, leading to a first order reaction rate, $r = k C_{TOL}$. Conversely, at lower temperatures, $K_{TOL} C_{TOL} \gg \alpha$, thus the apparent reaction order shifts from 1 to zero. At intermediate temperatures, it is plausible that the apparent order is between 0 and 1.

In conclusion, the present study allowed to retrieve important information on the reaction kinetics, useful for a future scale-up with the related design of dedicated chemical plants.

References

1. M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, *International Journal of Hydrogen Energy* **2019**, *44*(13), 6631-54.