

# Hydrogen release from perhydrobenzyltoluene: role of the catalyst support

Nataliia MARCHENKO, Mohamad KHARMA, Franck MORFIN, Laurent PICCOLO, Nuno ROCHA BATALHA, <u>Valérie MEILLE</u><sup>\*</sup> IRCELYON, CNRS, UCBL, 69100 Villeurbanne, France. \* valerie.meille@cnrs.fr

#### Significance and Relevance

Perhydro-benzyltoluene (H12-BT) is one of the most popular LOHC. However, its dehydrogenation, to release pure hydrogen, generally produces trace amount of methylfluorene, which leads to coke formation after several cycles (dehydrogenation/hydrogenation). In this contribution, a new  $Pt/TiO_2$  (rutile) catalyst was synthesized and showed a much lower methylfluorene yield during the dehydrogenation of H12-BT at 260°C.

Preferred and 2<sup>nd</sup> choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors / Sustainable and clean energy production and transport Preferred presentation: Oral preferred or short oral

## **Introduction and Motivations**

Among the different methods used to store hydrogen, either for transportation, mobility or intermittent usage, Liquid Organic Hydrogen Carriers seem to have a part to play. Based on the reversibility of the hydrogenation reaction, hydrogen can be stored and released depending on the operating conditions. The LOHC pair perhydrobenzyltoluene/benzyl-toluene (H12-BT/BT) is one of the most studied at the moment, because the molecules are cheap, easily available, and liquid in a wide range of temperature<sup>1</sup>. H12-BT stores 6.2wt-% of hydrogen. To recover hydrogen, a catalytic dehydrogenation is carried out, using platinum-based catalysts. In the present study, the support of Pt was studied, using the diversity of properties that titania can bring through its different phases. The objectives were 1) to have a catalyst at least as active as the standard Pt/Al<sub>2</sub>O<sub>3</sub> and 2) to obtain a better selectivity to BT, avoiding the formation of methylfluorene as a side-product (Figure 1a).

## **Materials and Methods**

The  $0.5wt-\%Pt/TiO_2$  catalysts were prepared by the incipient wetness impregnation method followed by calcination and reduction treatments. Various anatase/rutile phase ratios were obtained starting from different commercial TiO<sub>2</sub> and using different thermal treatments. The resulting materials were named Pt/Ax, x being the percentage of anatase in the titania mixture.

The dehydrogenation reactions were carried out in a stirred glass semi-batch reactor, open to the gas (continuous removing of hydrogen), at a temperature of 260°C. The hydrogen productivity was obtained from the initial slope of H12-BT concentration vs. time (GC-FID analysis) and confirmed by the measurement of hydrogen flowrate (GC-TCD analysis).

## **Results and Discussion**

All prepared 0.5wt-%Pt/TiO<sub>2</sub> powders showed average nanoparticle (NP) sizes from 1.0 to 1.4 nm. They were used in the catalytic dehydrogenation of H12-BT, at a Pt/H12-BT weight ratio of 0.009%. The materials presented different behaviors, confirmed by repeatable testing (Figure 1). The hydrogen productivity is shown in Figure 1b, Pt/A0 and various Pt/Ax (with x between 20 and 90) present higher performance than Pt/Al<sub>2</sub>O<sub>3</sub>. On the other hand, Pt/A100 and Pt/A15 are significantly worse. In Figure 1c, the methylfluorene yield was plotted vs. DoDH (degree of dehydrogenation). At 35% DoDH, methylfluorene reaches 0.35% for the commercial Pt/Al<sub>2</sub>O<sub>3</sub> (99.0% selectivity), whereas it is less than 0.15% for Pt/A0 (> 99.5% selectivity). As methylfluorene is detrimental to the storage performance during repeated cycles<sup>2</sup>, minimizing its production increases the durability of the system.



To explain the results, work is in progress to characterize the acidity of the different materials which could be the source of the side-product formation. It is indeed known that the titania surface acidity depends on the phase, rutile being much less acidic than anatase<sup>3</sup>. The structure sensitivity in the non-scalable Pt particle size regime is also explored using CO-IR spectroscopy. First results show that MF production might be a site-sensitive reaction.

To conclude, it was found that well-dispersed Pt nanoparticles supported on rutile are significantly more active than the  $Pt/Al_2O_3$  reference and lead to much less methylfluorene by-product (-60%). Further work concerns the development of bimetallic Pt-M/rutile which may further help lower the Pt content.



**Figure 1** a) Dehydrogenation of H12-BT. b) Hydrogen productivity of various  $Pt/TiO_2$  catalysts in comparison with  $Pt/Al_2O_3$  during the H12-BT dehydrogenation at 260°C with a Pt/H12-BT ratio of 0.009wt-% - c) Methylfluorene yield as a function of the degree of dehydrogenation.

## References

- 1. P. Modisha, D. Bessarabov, *Current Opinion in Green and Sustainable Chemistry* **2023**, 42, 100820
- 2. T. W. Kim, Y. Jo, K. Jeong, H. Yook, J. W. Han, J. H. Jang, G. B. Han, J. H. Park, Y.-W. Suh, *Journal of Energy Storage*, **2023**, 60, 106676
- 3. H. Li, M. Vrinat, G. Berhault, D. Li, H. Nie, P. Afanasiev, *Materials Research Bulletin*, **2013**, 48, 3374-3382

#### Acknowledgements

This work is a part of the UnLOHCked EU-HORIZON project funded by the Clean Hydrogen Partnership under Grant Agreement 101111964.