Catalyst Support Effects and Development of a Compact Continuous Catalytic Reactor with Solid Foam Internals for the Hydrogenation of Terpenes

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Highlights

- Pd /nanocarbons present high activities for the total hydrogenation of myrcene and squalene.
- Acidic pretreatment of the supports plays a crucial role in the catalyst activity.
- A compact continuous foam milli-reactor is optimized for the hydrogenation of neat terpenes.

The major uses for terpenes are in the flavour and fragrance industries, as a solvent, and in the manufacture of polymers and adhesives. Most of the terpenes are obtained as co-products of the paper or food processing industries. Recently, metabolic engineering has been successfully used to produce these valuable compounds in microbial hosts which enables their production on a larger scale [1] and for some of them opens the way for a potential use as a bio-fuel. Some applications of terpenes (e.g. cosmetics and fuel) require fully hydrogenated terpenes obtained with a complex network of exothermic catalytic reactions [2]. In the first part of this study, the development of new Pd catalysts supported on innovative carbon supports is presented. Several carbon supports were investigated including a screening of their pretreatments in order to identify the best catalytic material in comparison to reference Pd/Al_2O_3 and Ni/SiO_2-Al_2O_3 commercial catalysts. Myrcene was used as a model substrate because of the presence of conjugated double bonds that could lead to thermally activated by-products. Unsaturated all-*trans* squalene ($C_{30}H_{50}$) has also been studied as a strategic substrate. Squalane ($C_{30}H_{62}$), obtained by full hydrogenation of squalene, is a key ingredient in the cosmetic, neutraceutical and pharmaceutical industries. For both substrates, hydrogenation can be the subject of external and internal mass and heat transfer issues leading potentially to a decrease in selectivity, productivity and safety. Thus, the second part of this work is focused on the development of an intensified continuous reactor involving highly porous metallic foams. These internals, known for their low pressure loss and enhanced transfer capacities [3], are suitable to promote the highest apparent activity of the best identified catalysts in neat or concentrated media without alteration of the selectivity and/or safety.

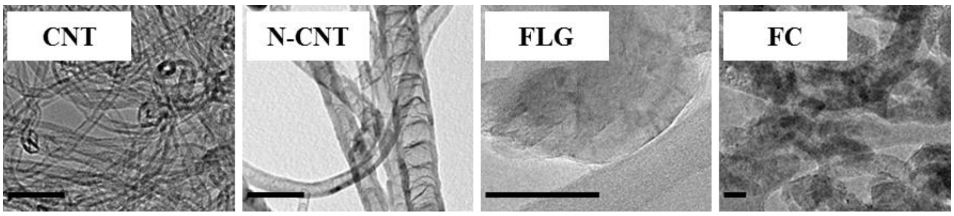

Figure 1. TEM pictures of the carbonaceous supports investigated in this work (scale bar ⇔ 50 nm)

Four kinds of carbon materials were studied (Figure 1): carbon nanotubes (CNTs), nitrogen-doped carbon nanotubes (N-CNTs), filamentous carbon (FC) and few layer graphene (FLG). 4 pretreatments are also compared: no pretreatment (-), oxidation with nitric acid (-COOH); high temperature annealing (-HT) and a combination of nitric acid oxidation followed by high temperature annealing (-COOH-HT). All the catalysts are well characterized (TEM, SEM, XRD, BET, ICP, TGA, etc.) and present a Pd loading between 1-2 wt.% with mainly 2 nm well dispersed nanoparticles. The screening was conducted in a mechanically stirred tank reactor of 200 mL at 120°C under H_2 atmosphere at a constant pressure of 20 bar with a 1M substrate solution in heptane. Reaction course monitoring was done by following the H_2 consumption in a

reservoir. When necessary, product distribution profiles were also followed as the function of time with GC analysis (DB17 column). Continuous experiments are conducted in a home-made stainless steel tubular reactor (4 mm inner diameter) made of several 10cm long segments in order to investigate some mass and heat transport effects with mutual variation in superficial velocity and reactor length at constant contact time. 2 grades of the same metallic foam were investigated (Hollomet Foamet FeCrAl foams, 400µm and 900µm mean cell sizes). A wide parametric study is done in order to characterize and optimize this continuous process.

3. Results and discussion

Hydrogenation of myrcene gave substantially different results as the function of catalysts used as well as some complex interplay with external gas-liquid and possible internal mass transfer limitations. All the catalysts were compared regarding two profiles: reaction progress and apparent turn over frequency (based on H_2 consumption rate per mol of Pd). The highest activities are encountered with FC, FLG and MWCNTs supports (Figure 2a). This can be explained by a lower internal limitation (highly mesoporous supports) and by a possible better intrinsic activity due to the particular metal-support interactions. The acidic pretreatment of the carbonaceous supports (except for the basic N-CNTs) was found to be the most beneficial (figure 2b) and its role will be discussed.

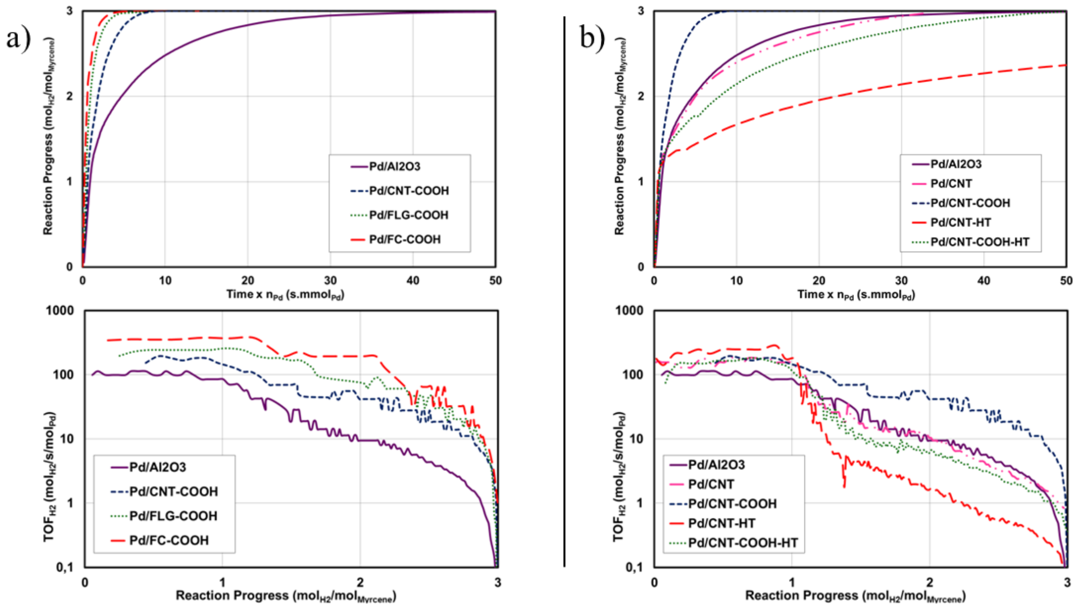

Figure 2. a) Comparison of catalysts in myrcene hydrogenation; b) Comparison of support pretreatment of CNT supports in myrcene hydrogenation. All the tests have been carried out at 20 bar; 120°C; 1M in heptane; 1200rpm.

A coating method of metallic foams with the best catalysts has been developed. Coatings will be characterized in terms of adherence, thickness and homogeneity with a focus on the preservation of the particular catalytic activity encountered in the batch mode. On-going parametric studies concerning the characterization of the continuous reactor, its optimization with neat terpenes will be detailed. Finally, some prospects about scale up options will be evoked.

References

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Keywords

Open cell solid foams; Carbon supports; Terpene hydrogenation; Continuous reactor.