**Gas-liquid hydrogenation in continuous flow for process intensification and rapid process optimization**

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**Highlights**

* Catalyst-coated tube reactors provide no mass transfer limitations in hydrogenation
* Compared to packed-bed reactors, the coated tubes show 14-25 times higher throughput
* Quick mass transfer in catalyst-coated tubes provides excellent product selectivity
* Low-cost refractory sensors provide process automation and faster process development

**1. Introduction**

The fine chemicals industry relies on batch reactors which are inefficient in terms of space-time yield and safety. Flow chemistry solves these problems, provides a possibility for process intensification, and allows for production with lower capital requirements. Additionally, flow chemistry offers opportunities for process automation. In the work we present the application of catalyst-coated tube reactors in continuous flow hydrogenation of alkynes, alkanes, imines, and unsaturated aldehydes and their advantages compared to batch and fixed bed reactors in terms of mass transfer and product selectivity.

**2. Methods**

The tube reactors wall-coated with 12 wt% Pt/SiO2, 5 wt% Pd/ZnO, 5 wt% Pd/C catalysts were provided by Stoli Catalysts Ltd [1]. The solid catalysts were obtained by removal of the catalyst coatings. The reactions were performed in a flow system containing an HPLC pump for a substrate solution, mass flow controllers for H2, an oven with the catalyst-coated tube, an Equilibar gas-liquid back-pressure controller downstream followed by a fraction collector. The reaction was operating autonomously using a pre-defined set of steps collecting samples for offline GC analysis controlled with OpenFlowChem automation platform [2].

**3. Results and discussion**

We studied the effect of mass transfer and residence time distribution on semi-hydrogenation reaction of alkyne (2-methyl-3-butyn-2-ol) and full hydrogenation of ethyl cinnamate. The catalyst-coated tube reactors showed no external mass transfer limitations, in contrast to packed beds, and a substantially narrower residence time distribution. The Peclet number in the tube reactor was above 100 indicating an ideal plug-flow behaviour in contrast to the packed-bed (Figure 1A). As a result, the alkyne semi-hydrogenation in packed-bed reactors was a factor of 25 slower less selective (60% vs 95%). The full hydrogenation reaction was 14 times slower in packed-bed compared to catalyst-coated tube. Similarly, the packed-bed reactor filled with a 12 wt% Pt/SiO2 catalyst was inferior to the catalyst-coated tube with the selectivity towards unsaturated alcohol of 20% vs 90% likely due to elimination of mass transfer limitations and excellent control of residence time [3].

The continuous-flow hydrogenation can benefit from process automation. We demonstrated that low-cost (<10$) refractory liquid sensors can be used to accelerate process development and optimisation [4]. An example of dehydrolinanool hydrogenation in Figure 1B shows that the approach provides consistent and reproducible results.

**A**

**B**

**Figure 1.** (A) Effect of the liquid flow rate on the Péclet number obtained in the tube and packed-bed reactors. (B) Dehydrolinalool semi-hydrogenation in a 2.3 wt% Pd/ZnO catalyst-coated tubes at various H₂/substrate feed ratios at 95% H2 absorption.

**4. Conclusions**

The results show that the catalyst-coated tube reactors provide excellent control of hydrogenation reaction conditions without external or internal mass transfer limitations. This results in a substantially higher throughput, a factor of 14-25 and higher selectivity in case of selective hydrogenation reactions. Using online analytics such accelerates the process development.

**References**

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