Highly effective monolithic flow microreactors for tandem reactions

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Highlights

- Bifunctional core of microreactor was elaborated
- Tandem processes was performed in microreactors
- Mutual influence of active sites was evidenced

1. Introduction

Tandem reactions constitute an important class of transformations in which simple substrates are converted into more complex, value-added products through consecutive reaction steps performed in a one-pot. In these processes, subsequent transformations occur without the addition of new reagents or the isolation of intermediates. Such an approach increases overall efficiency and selectivity, reduces waste generation, and limits energy consumption, which are in the line with the principles of green chemistry and sustainable development. The implementation of tandem transformations often requires application of catalysts with two distinct types of active centres attached to the surface of the support. The coexistence of these sites may generate synergistic effects that enhance the activity and selectivity of individual reaction steps. At the same time, their proximity can also lead to antagonistic interactions, such as mutual deactivation or competitive adsorption. Therefore, the rational design of bifunctional systems requires careful control over the strength, concentration, and spatial distribution of active centres. Continuous-flow microreactor technology provides an attractive platform for such integrated processes. The microreactors offer improved heat and mass transfer, and precise control of reaction parameters, compared to conventional batch systems.

In this work, we combine the advantages of micro-flow processing and heterogeneous multifunctional catalysis by developing two reaction systems based on monolithic microreactors for sequential transformations. The first one employs a single microreactor with a bifunctional catalytic core, which enables tandem conversion in one unit. The second system is based on a cascade of microreactors, each dedicated to a specific reaction step.

2. Methods

Silica monoliths with a hierarchical pore structure were functionalized with active species and applied as catalytic cores in flow microreactors. In the bifunctional approach, the support was modified with amine groups and zirconia. In the second system, the monoliths were functionalized separately with zirconium propoxide and ethylphenylsulphonic groups to obtain monofunctional catalytic units for cascade operation. The physiochemical properties of the materials were characterized using FTIR spectroscopy, scanning electron microscopy, thermogravimetric analysis, and nitrogen sorption measurements. Catalytic performance was evaluated under continuous-flow conditions in tandem processes: deacetalization–Knoevenagel condensation and the Meerwein–Ponndorf–Verley reduction–etherification–alcoholysis reaction sequence.

3. Results and discussion

The deacetalization–Knoevenagel condensation tandem reaction (Figure 1, system 1) of benzaldehyde dimethyl acetal and ethyl cyanoacetate was carried out in a flow-through microreactor equipped with a bifunctional monolithic core. The high surface area of the monolith and applied modification method resulted in well-dispersed and spatially separated zirconia and amine active species. The studies showed that the active centres were effectively dispersed on the surface and exerted minimal negative mutual influence during the tandem process. The bifunctional microreactor exhibited advantages compared to both batch system and cascade-connected monofunctional reactors [1].

The tandem MPV–etherification–alcoholysis transformation of furfural to butyl levulinate was investigated using acid catalysts (Figure 1, system 2). The synthesis of the ester performed in a batch reactor revealed significant unfavourable interplay between the Lewis and Brönsted acid sites. When both catalysts were introduced together into reactor, a pronounced decrease in activity of both zirconium-based (Lewis acid) and sulfonic acid (Brönsted acid) catalysts was observed. This effect was attributed to a negative influence of water created as a side product of butanol dehydratation in the presence of the strong Brönsted acid, as well as protonation of Lewis acid catalyst. Therefore, a tandem process performed in a cascade system of monofunctional microreactors was proposed. This system excludes interactions between catalysts improves selectivity, operational flexibility, and catalyst regeneration. It was shown that this is the most advantageous proposal for the selective synthesis of butyl levulinate under flow conditions.

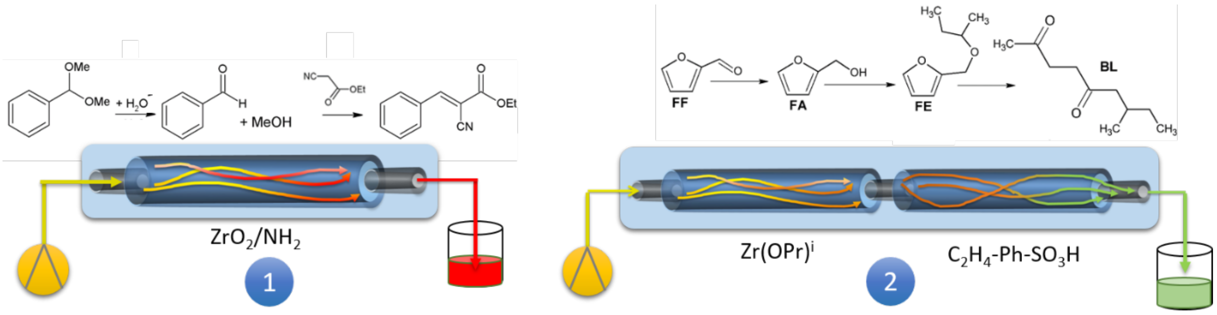

Figure 1. Catalytic systems for tandem processes.

4. Conclusions

The results demonstrate that appropriate catalyst design is crucial for the efficient implementation of tandem catalytic processes under flow conditions. High activity was achieved with minimal unfavourable interactions between active sites in the microreactor where spatially separated acid–base functionalities were integrated within a single monolithic core. On the contrary, systems with acidic functionalities required physical separation of catalytic centres to prevent catalyst deactivation. In this case, the cascade of monofunctional microreactors represents a robust and versatile strategy for the synthesis of butyl levulinate.

References

[1] A. Ciemięga, K. Maresz, J. Mrowiec-Białoń, Sci. Rep. 14 (2024) 25332

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microreactors, tandem reactions, bifunctional catalyst

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