ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Meerwein-Ponndorf-Verley reduction of cyclohexanone catalysed by zirconium species-doped silica. Monolithic continuous–flow microreactor vs. batch.

Katarzyna Maresz[1*], Agnieszka Ciemięga[1], Julita Mrowiec-Białoń[1,2]

1 Institute of Chemical Engineering Polish Academy of Sciences, Bałtycka 5, 44-100 Gliwice, Poland; 2 Department of Chemical Engineering and Process Design, Faculty of Chemistry, Silesian University of Technology, Strzody 7, 44-100 Gliwice, Poland

**Corresponding author: k.kisz@iich.gliwice.pl*

Highlights

- The performance of slurry and flow microreactor in MPV reduction was compared.
- Monolithic reactor showed superior performance compared to batch system.
- The rate constants of cyclohexanone reduction were determined.

1. Introduction

The continuous flow reactors have many advantageous over slurry reactors: continuous production, easier process control and automation and operation costs reduction. Monolithic microreactor based technology appeared to be promising for the effective production of pharmaceuticals and fine chemicals. This technology has been successfully applied in chemoselective Merweein-Ponndorf-Verley (MPV) reduction [1]. The MPV reduction proceeds via hydrogen transfer between ketone/aldehyde and alcohol and enables carbonyl-selective hydrogenation of substrates with highly reducible substituents such as nitriles and halogens [2]. The number of heterogeneous catalysts has been used in this reaction, i.e. zeolites, metal oxides or MgAl hydroxides [3, 4]. In this work we continued the studies of innovative miniaturized flow system for reduction of carbonyl compounds as a beneficial alternative to slurry process. Rod-shaped silica monoliths, doped with zirconium complexes were used as a reactive core of the microreactors. The monoliths were synthesized using combined sol-gel, pore templating and phase separation processes. The microreactors exhibit large surface area and extremely high surface to volume ratio. They allow to achieve a significant efficiency and improved selectivity of the reaction. Following our previous promising results [1] herein we present a preliminary kinetic studies of the reduction of cyclohexanone with 2-butanol using zirconium-modified silica materials in flow and batch processes.

2. Methods

Zirconium-functionalized monoliths were synthesized according to procedure described in [1]. The structure of the monolith was determined from nitrogen adsorption, mercury porosimetry and SEM analyses. For physicochemical characterization of the materials FTIR and ICP methods were applied. Monoliths were modified with zirconium precursor to achieve Zr/Si molar ratio equal to 0.14. After functionalisation with active centres, monoliths in the form of rods with diameters of 4.5 mm were used as cores of microreactors. Powdered monolith and zirconium propoxide were employed in batch process as heterogeneous and homogeneous catalysts, respectively. Kinetic experiments were conducted at 95 ^{o}C for substrates molar ratio 1:52.

3. Results and discussion

Monolithic supports, with high surface area of about 330 $m^2 \cdot g^{-1}$, featured bi-modal distribution of mesopores (small with diameters of 2.5 nm and larger ones of 20 nm) and continuous structure of macropores with diameter in the range of 30-50 μm. 10% decrease of specific surface area was recorded after functionalisation of materials. The concentration of zirconium species was confirmed by ICP measurement.
The catalytic experiments performed for batch and flow processes showed a linear correlation between the natural logarithm of cyclohexanone concentration and reaction time (or contact time in case of flow reactor)

indicating the first order of the MPV reaction. Hence, the reaction rate was calculated from the slope of plot of $\ln(C_o/C)$ vs. time.

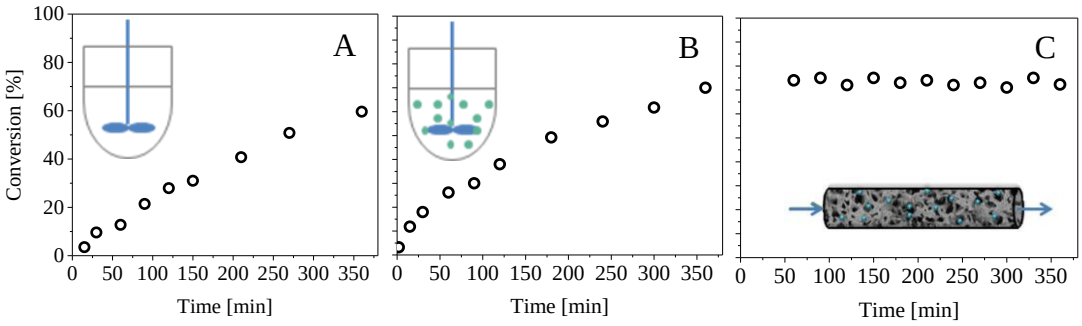

Figure 1. Conversion vs. time in batch reactor with (A) homogeneous and (B) heterogeneous catalyst, and (C) in 4 cm-long continuous-flow microreactor.

MPV experiments were performed in batch reactors using homogeneous catalyst (Fig. 1A) and powdered Zr-doped monolith (Fig. 1B). The results were compared with those obtained in the flow microreactor (Fig. 1C). The amount of zirconium, applied in homo- and hetero- catalyzed batch processes was the same as used previously in monoliths functionalisation. The activity in cyclohexanone reduction of immobilized catalyst showed slightly better performance than homogeneous $Zr(OPr)_4$, and the reaction rate constants were equal to $3.5 \cdot 10^{-3}$ and $2.5 \cdot 10^{-3}$ min^{-1}, respectively. The 75% conversion was achieved in continuous-flow microreactor, operating with flow rate of 0.09 $cm^3 \cdot min^{-1}$ (resistance time: 7 min). Stability of its catalytic properties was demonstrated in 6-hour-long experiment. The value of k_1, calculated from data obtained for various contact time, was $80 \cdot 10^{-3}$ min^{-1}. Comprehensive studies of the MPV reaction kinetics are in progress and they will be presented after abstract acceptation.

4. Conclusions

The rate constants of cyclohexanone reduction, assuming first order of the reaction, were determined. The results clearly demonstrate the superior performance of monolithic continuous-flow microreactor in Meerwein–Ponndorf–Verley reduction of cyclohexanone with 2-butanol over typical batch reactors.

References

[1] A. Koreniuk, K. Maresz, J. Mrowiec-Białoń, Chem. Commun. 64 (2015) 48-51.
[2] M. Boronat, A. Corma, M. Renz, J. Phys. Chem. 110 (2006) 21168-21174.
[3] B. Zhang, F. Xie, J. Yuan, L. Wang, B. Deng, Catal. Commun. 92 (2017) 46-50.
[4] E. Plessers, D.E. De Vos, M.B.J Roeffaers, J. Catal. 340 (2016) 136-143.

Acknowledgments: The support of the National Science Centre (Poland) for the project No. DEC-2017/01/X/ST8/00083 is gratefully acknowledged.

Keywords
Meerwein-Ponndorf-Verley reduction kinetics; monolithic flow microreactor; reaction rate constant.