Microreactor Platforms for HomogeneousHydrogenations and Photocatalytic Reactions

Pavlorková, Jana
2014

MICROREACTOR PLATFORMS FOR HOMOGENEOUS HYDROGENATIONS AND PHOTOCATALYTIC REACTIONS

***J. Pavlorková*[a], *J. Kristal*[a], *M. Drhová*[a], *S. Hejda*[b], *P.Klusoň*[a]**

[a] Institute of Chemical Process Fundamentals of the ASCR v. v. i., Rozvojová 2/135, Prague, Czech Republic. E-mail: pavlorkova@icpf.cas.cz

[b] Faculty of Environment - J. E. Purkyně University, Ústí nad Labem, Czech Republic

Microstructured reactor systems are slowly tapping into the subconscious of wide industrial processes that require getting products of a predefined quality and purity. Fulfilment of these requirements can be achieved by using the continuous microreactor flow systems which offer a big variety of benefits. The main feature is their high active surface to the reaction volume ratio. Thanks to this fact, a precise maintaining and controlling of reaction conditions is ensured as well as high heat, mass and momentum transfers so that a by-products creation is overcome and there is no need for additional processes such as separation, cleaning etc. There are several microreactor platforms contains commercially available, in this contribution we present two microreactor systems – a microfluidic flow reactor system (Fig. 1) and a thin liquid layer photocatalytic microreactor system.

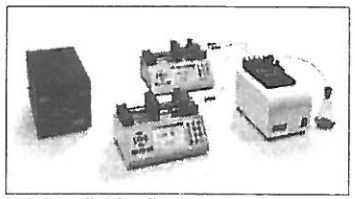

Fig. 1: Microfluidic flow reactor assembly

A glass microfluidic flow reactor system is used for the synthesis of fine-chemicals. The main part of this system is represented by a set of microreactor chips (Fig. 2). As a model reaction a homogeneous asymmetric hydrogenation of methyl acetoacetate to methyl hydroxybutyrate was selected. A homogeneous chiral organometallic catalytic complex Ru-BINAP was used as the most active and selective catalytic form for this purpose. Homogeneous catalysis allows chemical reactions to be performed under milder conditions (lower temperature, lower pressure) and higher selectivity. The multiple bond reduction by gaseous hydrogen in a presence of catalyst is a well-known reaction. Less common, but already used, is the possibility of using organic molecules as the hydrogen donors, which is known as the catalytic transfer hydrogenation. For the model reaction 2-propanol was selected for playing this role.

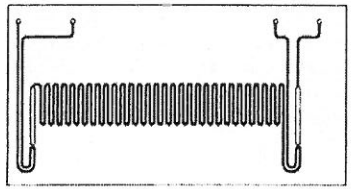

Fig. 2: Microfluidic flow chip

By combining the microreactor technology, organometallic catalytic complexes and transfer hydrogenation one can obtain the highly pure products, high enantiomeric excess and high reaction yield. A catalyst immobilization is necessary for the easier catalyst separation and consequent recirculation. For asymmetric homogeneous catalytic hydrogenations the use of ionic liquids is tested so that a reversibly diphasic system is created [1, 2]. This system offers an efficient mixing of reaction compounds and later easier separation of the metal catalyst from products. Obtained results were compared with the references to the literature.

The second part of the microreactor platform is represented by a thin liquid layer photocatalytic microreactor system (Fig. 3). Thin reaction microchannel (Fig. 4) ensures efficient irradiation of the reaction mixture.

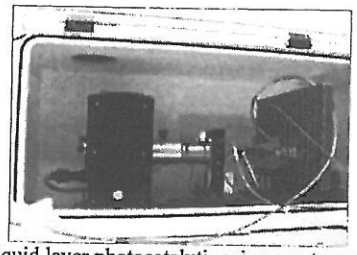

Fig. 3: Thin liquid layer photocatalytic microreactor assembly

Research was focused on a model reaction – photochemical degradation of 4-chlorophenol, which, by the way, is widely used as an herbicide, fungicide or insecticide and it is listed among top priority pollutants. The degradation occurred via photochemical process by the irradiation in a combination with a photosensitizer. UV/VIS light was generated by a high pressure mercury lamp. In this reaction phthalocyanine acts as the photocatalyst generating singlet oxygen [3,4].

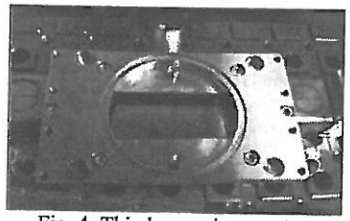

Fig. 4: Thin layer microreactor

Two types of solvents were tested - distilled water and deuterium oxide. Obtained experimental results were compared as is shown in the Fig. 5. The photodegradation of 4-chlorophenol ($c = 1x10^{-3}$ mol/L) was more than two times faster when using deuterium oxide as a solvent in a comparison with distilled water. The experiments with deuterium oxide were two times repeated, whereas the experiments with distilled water were three times repeated so that a proper experimental reproducibility was gained as well.

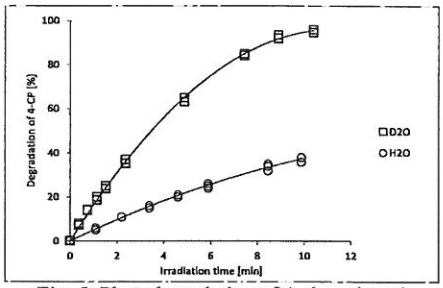

Fig. 5: Photodegradation of 4-clorophenol

Results in a thin liquid layer photocatalytic microreactor were also compared with the previous experiments in a conventional batch reactor (cuvette tests) and showed more than two times higher efficiency.

From our results it is clearly understandable that the use of microstructured reactor systems leads to the proper setup of reaction conditions, process optimization, high degradation yield and high experimental reproducibility.

References

[1] K. Minsker, L. Renken, A. Renken, Microstructured reactors for catalytic reactions. Elsevier, 2005.

[2] A. Wolfson, I. Vankelecom, P. A. Jacobs, The role of additional solvents in transfition metal complex catalyzed asymmetric reductions in ionic liquid containing system, Elsevier, 2005.

[3] M. Oelgemöller. Highlights of Photochemical Reactions in Microflow Reactors, Australia, Wiley, 2012.

[4] K. Ozoemena, N. Kuznetsova, T. Nyokong. Photosensitized transformation of 4-chlorophenol in the presence of aggreageted and non-eggregated metallophthalocyanines, South Africa, Elsevier, 2001.