

Summary of doctoral dissertation

Title: Monolithic, silica continuous-flow microreactors with acid centres. Fabrication, properties and application in selected catalytic processes.

Author:: mgr inż. Agnieszka Ciemięga

Thesis supervisor: dr hab. inż. Julita Mrowiec-Białoń

Auxiliary thesis supervisor: dr inż. Katarzyna Maresz

The aim of the work was to elaborate innovative, highly effective continuous-flow microreactors for organic synthesis purposes. Modified silica monoliths were applied as catalytically reactive cores of microreactors. The monoliths were prepared by an aggregate of the sol-gel, surfactant templating and phase separation methods. The materials featured a hierarchical pore structure of i. interconnected flow-through macropores, and ii. mesopores, located in the silica skeleton, with mono- or bi-modal size distribution, providing large specific surface area.

Cylindrical monoliths, with diameter of 4.5 mm and lengths of 1 to 8 cm, with three different morphologies resulting from the use of various synthesis protocols, were obtained. Detailed studies of the structural properties of materials were carried out by means of low-temperature nitrogen adsorption, mercury porosimetry, scanning electron microscopy. Monoliths with large flow-through macropores, in the range of 30-50 μm and a bimodal mesopore size distribution (2.5/20 nm) were characterised by specific surface area of about 300 m^2/g and a total pore volume ca. 4 cm^3/g . When surfactant was not added and the synthesis was performed under mild hydrothermal treatment conditions (lower temperature and/or ammonia concentration i.e. at 80 $^{\circ}\text{C}$ and 40 $^{\circ}\text{C}$, and using 1M and 0.1 M NH_3 solution, respectively; standard conditions were 90 $^{\circ}\text{C}$ and 1M NH_3) monoliths featured smaller macro- and mesopores (i.e. 4-6 μm /15 nm and 1-3 μm /9 nm) but larger specific surface area, up to 575 m^2/g . The flow resistance of liquids was measured and the permeability coefficients were calculated. The values strongly depended on the size of macropores.

The surface of monoliths was modified with various moieties to impart acidic properties. Brönsted acid centres were obtained by functionalization with arenesulfonic groups. The physicochemical properties of materials were determined using spectroscopic and thermogravimetric methods. The highest concentration of centres, 0.97 mmol/g, was reached in the sample of the largest specific surface area. The performance of the microreactors was studied in continuous-flow model esterification reactions of acetic and lactic acids with butanol. Effects of organic group concentration, length of monolith, flowrate of reactants, temperature and molar ratio of the substrates on a conversion and thus microreactor productivity (space-time yield) were determined. Long-term

catalytic stability of the microreactor at 140 °C has been confirmed. It was found that microreactors boost the esterification process and additional important assets are continuous operation with no need for catalyst separation and recycling.

The catalytic and flow-through properties of the "monolith in monolith" microreactor, made by introducing hierarchically structured silica into the channels of typical cordierite monolith were also studied. The modification increased the mechanical strength of the reactor, its size and enhanced reaction capacities, as well. However, that reactor featured enlarged (by 40%) pressure drop than recorded in the monolithic microreactors.

Comparative studies of the monolithic silica microreactors modified with different Lewis sites were performed in the Meerwein-Ponndorf-Verley (MPV) selective reduction of the carbonyl compounds. Lewis acid centres were obtained by monolith's modification using various zirconium, aluminium and titanium precursors. A comprehensive characterization of the physicochemical properties of the catalysts was performed. The effects of different active centres, chemical environment and concentration on the efficiency of the MPV reaction were shown.

Catalytic studies were carried out for a number of ketones and aldehydes. Reaction kinetics was determined and the results were compared with literature data. Microreactors containing zirconium sites surrounded by propoxy ligands, appeared to be the most effective. The facile preparation, regeneration, storage, control of process parameters and high productivity were found to be inherent features of the proposed microreactors.

The properties of monolithic titanosilicates, synthesized by impregnation and co-condensation method were compared. Those prepared by co-condensation were characterised by excellent dispersion of titanium ions over the silica skeleton, required for their high activity in the selective oxidation of organic compounds. Catalytic performance of the microreactors was verified in the selective oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethyl-1,4-benzoquinone, an important intermediate for vitamin E synthesis. Activity of the centres, productivity and structural properties of the microreactors were determined.

It was concluded that a waving, tortuous structure of flow-through channels present in the monoliths, which induce intensive micromixing and enhance external mass transport, plus an easily accessible, large surface area stand behind a very high activity and efficacy of the monolithic microreactors.

The performed studies demonstrate that the continuous-flow microreactors can be

successfully applied in many important chemical processes, and replace batch and packed bed flow reactors in multi-kilogram scale fabrication of fine chemicals, complex intermediates and pharmaceuticals.