

INVESTIGATIONS IN THE FOCUS OF REACTION ENGINEERING ON AN INERT MICROREACTOR

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Summary

A novel and unique approach combining photonic crystal fibers (PCFs) and Supported Ionic Liquid Phase (SILP) is studied in this project. Aim of the contribution is the sensing and online-monitoring of chemical reactions in the hollow core of PCFs in-situ. Therefore a preparation technique was developed. As a proof of concept a catalytic ethene hydrogenation was carried out in the fibers.

Keywords

Photonic crystal fibers, supported ionic liquid phase, microreactor

Introduction

Aim of the study is the application of the impregnation SILP technique for the homogeneous immobilization of catalyst inside the hollow channels of photonic crystal fibers (PCF) [1]. The hollow channels in the PCFs allow for the transportation of gaseous or aqueous reactants and simultaneous light-guiding for an in-situ monitoring of chemical reactions via spectroscopy [2].

Different to SILP systems reported in literature, where the Ionic Liquid (IL) is spread over a system of connected pores in porous catalyst supports, in this study a thin IL film needs to be deposited along one hollow channel [1]. Hence closures in the fiber should be avoided and a strong adhesion of the IL to the fiber's surface is necessary, as a convective flow has to be realized inside the channels during application.

Methods

To achieve these prerequisites a three step procedure was elaborated:

- Etching of the fiber to introduce silanol groups
- Surface modification by covalent anchoring of an IL cation
- Catalyst immobilization by employment of the SILP technique

The crucial step is the chemically grafting of a monolayer of [1-methyl-3-[3-(triethoxysilyl)propyl] imidazolium] [bis(trifluoromethanesulfonyl)imide] ([TESIM][Tf₂N]) by a condensation reaction to silanol groups (introduced by etching with a pH 10 buffer solution) at the glass surface.

The condensation reaction was performed at 60 °C. By intensive flushing with solvent, non-reacted IL is removed. Result of this preparation method in a covalently bonded monolayer of the cation of the IL. In the following impregnation step [EMIM][Tf₂N], hosting a Wilkinson catalyst system, was immobilized on the IL-modified glass surface through an catalyst/IL/solvent mixture and evaporation procedure (p = 17.5 kPa, T = 50 °C and ultrasound treatment) [3].

For a better understanding of the grafting process, the chemical bonding of [TESIM][Tf₂N] to the glass surface was studied by means of angle resolved x-ray photoelectron spectroscopy (ARXPS) on planar Suprasil surfaces (basic raw material for PCF drawing). As a proof of concept an ethene hydrogenation was carried out to realize chemical reactions based on the SILP concept in PCFs for the first time.

Additional to calculations of the residence time and the changing pressure inside the channels a characterization of fluid flow behavior within the fibers was carried out for diameters from 30 to 80 μm and fiber length from 10 to 100 cm. Therefore the flow of gas and liquid inside the channels was determined experimentally at varying pressure differences. The experimental results were compared to calculations according a finite element method (using COMSOL Multiphysics) and analytical equations (Hagen-Poiseuille).

Results

In the first preparation step an online-monitored etching experiment of a Mercedes type fiber revealed, that etching reduces the transmission properties. A linear dependency of transmission loss to etching time was observed. To investigate, if enough silanol groups for the surface modification (second step) are created, ARXPS studies on reference substrates were performed. As a result nearly one monolayer of covalently bonded IL could be realized by the condensation reaction (pretreatment at pH 10 for 10 min at 60 °C). This short conditioning in alkaline solution ensures both negligible transmission loss and sufficient silanol groups for the surface modification with IL later on.

Performing the SILP technique, without prior surface modification, results in the formation of droplets and a huge number of enclosures. The described IL-surface modification the SILP leads to a reproducible device for enclosure and droplet free channels. The studies showed that different to the SILP method on porous supports in this case an ultrasound treatment is necessary.

The formation of a catalyst loaded IL film inside the fibers could be proven within the application of SILP-fibers as a microreactor for ethene hydrogenation. Thereby stabilities of more than 80 h time on stream without significant loss in activity showed the stability of the SILP system in PCFs. Variation of the reaction temperature and pressure were performed on the fiber and the results show the expected response of the system.

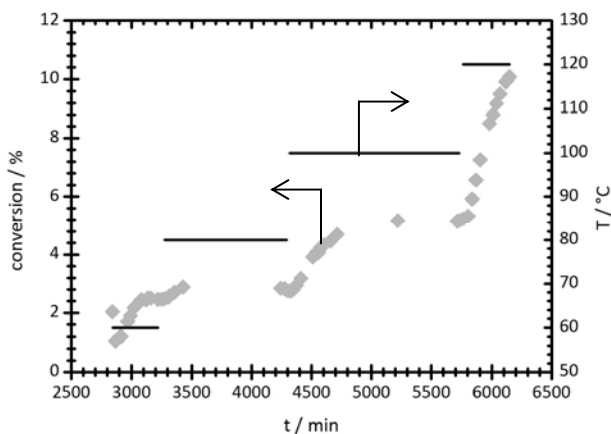


Figure 1: Temperature variation at constant pressure: (4 wt-% $RhCl(PPh_3)_3$ in $[EMIM][Tf_2N]$, ethene: $H_2 = 1:1$ $p_{out} = 0.77$ MPa, $\tau = 1,77$ s, $V = 5,66 \cdot 10^{-9} m^3 s^{-1}$).

The description of the fluid flow in capillary fibers regarding Reynolds and Knudsen number revealed, that in the investigated range the flow is hydrodynamic and laminar ($Kn < 0.1$ and $Re < 2300$). In general the analytical approaches give the same results but underestimate the measured data by 25 to 30%. A correction factor results in a proper fitting for both gas and liquid flow.

The liquid flow in capillary fibers can be described by an incompressible behavior. The gaseous flow follows a good

description for compressible Hagen-Poiseuille in the analytical approach and weakly compressible Navier-Stokes equation in the finite elements simulation. As the compressible gas flow in μm sized capillary fibers can be described via compressible Hagen-Poiseuille an easy characterization of the residence time distribution for the chemical reaction is possible.

The Comsol Multiphysics model was advanced for the description of fluid flow in non cylindrical Mercedes type fibers, which are used for the sensing approach later on. Therefore the model was carried out by two means. First a 3D reconstruction of one single channel of the Mercedes type fiber and secondly replacing the complex flow channel by capillary fiber of equal cross section area. In comparison the capillary model shows higher aberration. The FEM simulation of the real fiber geometry showed similar deviation as for the capillary fibers. Hence the derived correction factor can also be used for other geometries.

Conclusion and Outlook

The studies show the feasibility of the immobilization of IL on surface modified PCFs and the application of these indicate a high potential for sensing and as chemical reactors. The fluid flow in capillary fibers is laminar in the studied region. Introduction of a correction factor was established and results in a proper fitting of measured and calculated data. The oncoming stage concerning the employment of PCFs as microreactors is the utilization in reactions, like hydroformylation reactions, which are interesting for the spectroscopic in-situ analysis and photocatalytic reactions. Moreover, due to the high stability of the film, the application as capillary columns and its performance in gas chromatography will be investigated in more detail.

References

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