Modelling of Sol-Gel Synthesis of Functionalized Silica Materials in a Microreactor

Yuliia Miroshnychenko, Yuriy Beznosyk

Department of Cybernetics of Chemical Technology Processes, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", UKRAINE, Kyiv, Peremogy avenue 37, E-mail: yu_beznosyk@ukr.net

Abstract* – *In this paper, the optimal parameters of the process of silica surface functionalization in the microreactor were studied based on the developed mathematical model: the residence time distribution, the flow velocity, the concentration profile. Detailed investigation of fluid dynamics in the microvolume reactor channel was solved using CFD models.

Key words – silica surface functionalization, sol-gel technology, microreactor, CFD-modelling, adsorbent.

I. Introduction

The process of silica surface functionalization is the effective approach to receive new materials with predetermined parameters. Useful properties of such materials allow successfully use them as highly selective adsorbents that are able to extract different compounds depending on the grafted functional group. The basic method for the synthesis of functionalized structures is the sol-gel technology. Today it is known attempts to realize this process in the laboratory [1, 2]. But in this case there are many limits based on the organization and controlling of chemical transformations. So in this paper we consider the possibility of carrying out the reaction of sol-gel synthesis in the microreactor.

Microreactors offer several opportunities to optimize the reaction systems due to high specific interfacial area improving heat and mass transfer, the smaller working volumes, continuous mode of operation, efficient operation, low wastage of chemicals and intrinsic safety [3]. Potential advantages of microstructured reactors (MSR) give the background to discuss the realization of the functionalization process using the microreactor. The solution of a wide range of issues related to the real experiment is achieved by modeling the test object with the help of special methods and tools.

Detailed simulation studies conducted in different operation conditions provide important insights to the reaction behavior in a microsystem environment. Comparison of performances in theoretical and practical experiments has been presented in the literature for different types of reactions, which suggests the adequacy of computing and credibility of the calculated data when integrated process in a laboratory or industrial scale.

Several definitions of methods and designing the principles of the theoretical study of microreaction systems can be found in the literature. For example, the evaluation of two different fluids molecular mixing within the microfluidic channels with grooved surface was carried out in [4] by the solving of incompressible Navier-Stokes and convection-diffusion equations at the steady state using a CFD (computational fluid dynamics) functions of the COMSOL Multiphysics (version 3.1).

In order to analyze the complex phenomena in reactive multiphase systems, in the work [5] was proposed a film-near model as well as a micromixing model in the bulk phase. Here was used the Euler-Lagrange approach implemented in the open-source CFD-package "OpenFOAM".

Vaccaro S. and Ciabelli P. [6] presented the comparison between countercurrent and concurrent flow patterns of endothermic and exothermic reactant streams in the combustion channel. The model was consisted of the material, energy and momentum balances equations for the system under examination and contained the constitutive equations for physical-chemistry properties of the reactants species and kinetic expressions for the reactions. The model solutions were carried out by the FEM software (COMSOL Multiphysics).

Borovinskaya E. S. [7] developed a complex Kinetic program for the kinetic modeling of processes in the microreactor in case the limiting stage is the reaction kinetics. In the thesis [7] was presented the mathematical model of the phenylacetonitrile alkylation process and the modified methods of the kinetic parameters interval estimating.

As for sol-gel process, Chokkalingam [8] presented a droplet-based microfluidic scheme to perform fast chemical reactions and demonstrated this scheme explicitly for the production of mesoporous silica particles and platinum doped silica particles from a sol-gel synthesis route for heterogeneous catalysis. However, there was experimental investigation without using any modelling tools.

According to the investigations described above, the development of the adequate mathematical model of the process and its implementation in the professional software package allow us to describe the conversion of reactants at a real experiment. Based on modelling data it is possible to formulate clear guidelines for the directed synthesis of functionalized materials.

Here we report on the application of the microreactor for synthesis of functionalized silica materials on the grounds of theoretical experiments.

II. Numerical model

The flow in the microchannel is laminar and given by the Navier-Stokes equations at steady state:

$$\rho(u\cdot\nabla)u=\nabla\cdot\left[-pI+\mu(\nabla u+(\nabla u)^T)-\frac{2}{3}\mu(\nabla\cdot u)I\right] \quad (1)$$

And the continuity equations:

$$\nabla\cdot(\rho u)=0, \quad (2)$$

where ρ is the solution's density, kg/m^3; u – the velocity vector, m/s; μ – dynamic viscosity of the fluid, Pa·s; p – pressure, Pa; T – the absolute temperature, K; I denote the identity matrix.

The Transport of Diluted Species interface was used to set up and solve the appropriate stationary mass-balance equations:

$$-\nabla\cdot(-D\nabla c+cu)=0. \quad (3)$$

In this equation, D denotes the molecular diffusion coefficient (m^2/s) and c represents the concentration (mol/m^3). In our model, the solving of Eq. (3) was studied for three different values of D – $1\cdot10^{-9}$ m^2/s, $1\cdot10^{-10}$ m^2/s, and $1\cdot10^{-11}$ m^2/s.

To include changes of concentration it was used a correction term in the viscosity that depends quadratically on the concentration:

$$\mu = \mu_0 (1 + \alpha c^2). \quad (4)$$

Here α is a constant of dimension (m^6/mol^2).

An influence of concentration on viscosity is usually observed in solutions after the forming of oligomer particles. In this case the flow and mass transport equations have to be solved simultaneously.

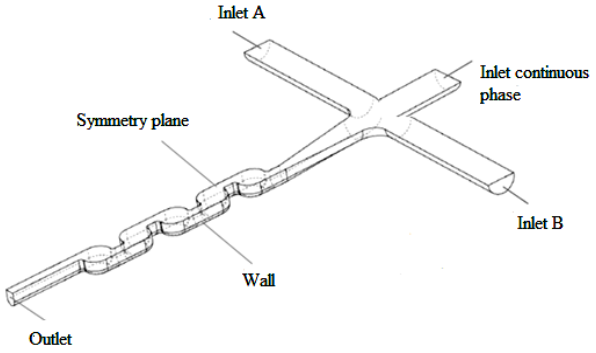

Fig. 1. Model domain boundaries.

The boundary conditions (fig. 1):

- At the inlets and outlets, pressure conditions are applied along with vanishing viscous stress:

$$p = p_0$$
$$n \cdot \mu(\nabla u + (\nabla u)^T) = 0 \quad (5)$$

- At the symmetry plane, using the symmetry boundary condition is set the velocity component in the normal direction of the surface to zero:

$$n \cdot u = 0$$
$$t \cdot \mu(\nabla u + (\nabla u)^T) n = 0 \quad (6)$$

- At the walls, no slip conditions are stated that the velocity is zero:

$$(u, v, w) = (0,0,0) \quad (7)$$

- At the inlets, the concentration boundary condition is used with the following values:

$$c = c_A - \text{inlet A},$$
$$c = c_B - \text{inlet B}, \quad (8)$$
$$c = c_0 - \text{continuous phase},$$

where A – the three-functional silane ($(C_2H_5O)_3Si(CH_2)3NH_2$) in a mixture of methanol and water; B – solution of the silica precursor tetramethoxysilane (TMOS, $Si(OCH_3)_4$); continuous phase – perfluorodecalin oil (PFD, $C_{10}F_{18}$) with 20 wt.% fluorinated surfactant.

Model of the symmetry plane and cell walls with the no flux condition:

$$(-D\nabla c + cu) \cdot n = 0 -$$
$$\text{at the symmetry plane and walls}, \quad (9)$$
$$(-D\nabla c) \cdot n = 0 - \text{at the outlet}.$$

III. Results and discussion

T-microreactor was selected to implement the sol-gel synthesis of functionalized materials and the slug flow generation was produced in the microchannel. The geometry of the microchannel was chosen on the basis of quantum-chemical calculations of molecules parameters and the size of structural units [9, 10]. The mixing zone was presented in zigzag form to achieve better stirring of the components (fig. 1). During the merging and mixing of droplets inside the microfluidic device, none of the reactive mixture gets in contact with the microfluidic channels which avoid any precipitation or sticking to channel walls.

The theoretical experiment was performed by using CFD-modelling. The CFD models include all reactor hydrodynamic effects, heat transfer, mass transfer, and the reduced set of controlling heterogeneous and homogeneous reactions [11, 12, 13]. Meshing was performed by the default triangular and tetrahedral meshing algorithm with a mesh size of 0.001mm.

To comparison the influence of the diffusion coefficient on the mixing it was performed modelling for three different values of D – $1 \cdot 10^{-9}$ m^2/s (fig. 2), $1 \cdot 10^{-10}$ m^2/s (fig. 3), and $1 \cdot 10^{-11}$ m^2/s (fig. 4). Concentration distribution for the species on figs. 2 and 3 is virtually identical and indicates reduction of the target component in the output stream. So, based on modelling result the optimal value of D equals $1 \cdot 10^{-9}$ m^2/s that corresponds to the value of the diffusion coefficient for liquid-liquid processes.

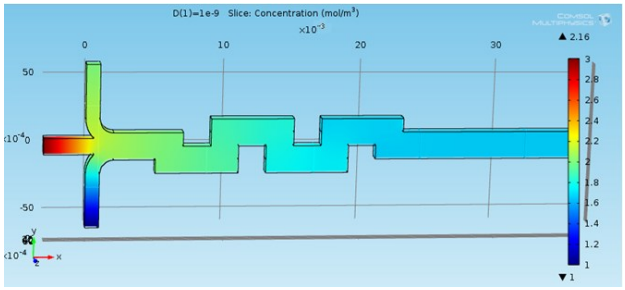

Fig. 2. Concentration distribution for a species with diffusivity $1 \cdot 10^{-9}$ m^2/s

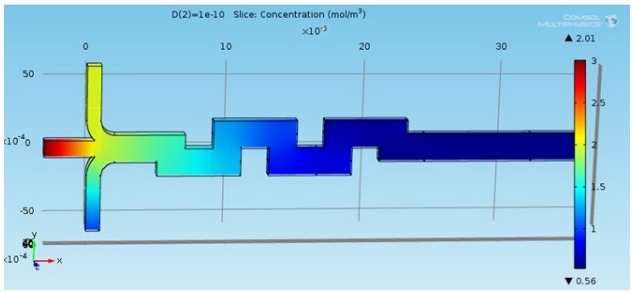

Fig. 3. Concentration distribution for a species with diffusivity $1 \cdot 10^{-10}$ m^2/s

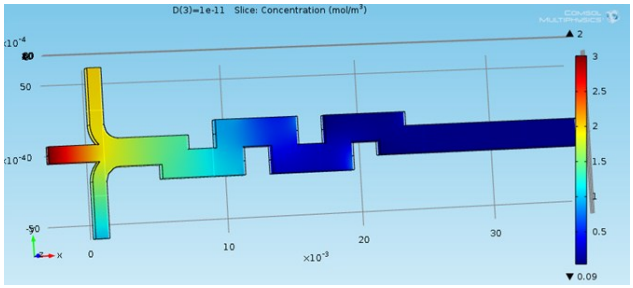

Fig. 4. Concentration distribution for a species with diffusivity $1 \cdot 10^{-11}$ m^2/s

The final mixing on the molecular scale, where the reaction takes place, occurs only by molecular diffusion. Based on the diffusion coefficient value the mixing time in microchannels of the rectangular form with a hydraulic diameter of 0.2 mm is defined as [14]

$$t_D = A' \frac{(l/2)^2}{D} = \frac{1}{3} \frac{(2 \cdot 10^{-4}/2)^2}{10^{-9}} = 3.3[s], \qquad (10)$$

where l – the thickness of the aggregate (in the case of single-channel microreactors without any complex internal structures, the characteristic dimension can be assumed to be equal to its diameter, $l=d_h=2 \cdot 10^{-4}$ m); A – the form factor.

Investigation of the mixing time as a function of microreactor diameters in the range of 0.1–1 mm considering rectangular and cylindrical shapes is depicted on the plot (fig. 5). As shown in fig. 5, the transformation of reactants in the cylindrical microchannel requires less time to achieve the homogeneous flow. Because the gel formation can occurs before the achievement of homogeneity of the solution, in our case it is desirable to slow the hydrolytic polycondensation reaction. That is why we were chosen the rectangular microchannel for the carrying out of the sol-gel synthesis of functionalized silica particles.

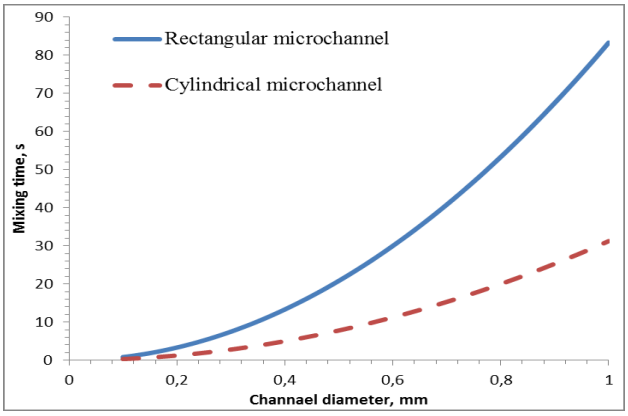

Fig. 5. Diffusion time for liquid phase in rectangular and cylindrical channels

So, the formation of monodisperse silicagel in the simulated microreactor takes about 3.3 s. Concentration profile shows that the homogeneity of the reaction stream in the microchannel is achieved on the length of 0.02 m. Meanwhile, the flow rate at the walls is 0 mm/s and a maximum flow rate (37 mm/s) is observed in the center (fig. 6). The reason is that the process of hydrolysis and polycondensation of three- and tetrafunctionalized silicon compounds occurs quickly and almost always simultaneously.

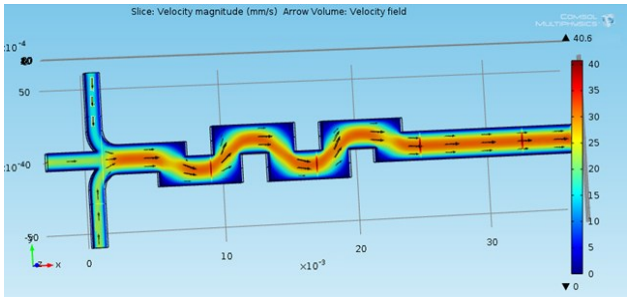

Fig. 6. Flow velocity field

The condensation reaction starts with the deprotonation of silanols by reacting with hydroxyl ions. The condensation of deprotonated silanols combined with the aggregation of the condensed species leads to a continual growth of the formed gel up to a point where the silica particles become too large to be solvated. Since the development of the gel network takes some time, the delay line after the zigzag mixing zone was predicted. The monodisperse silicagel particles formed in the delay line have to be collected outside of the microfluidic device in a beaker containing the same perfluorinated continuous phase. The final steps of the synthesis are aging, washing and drying of the hydrogel with subsequent formation of mesoporous silica xerogel with developed porous structure.

IV. The possibility of industrial implementation of the investigation

The use of micro- and mini-scale devices offers tremendous prospects for miniaturization of many kinds of chemical plants with the possibility of production sites organization in the desktop scale with the performance of conventional plants. The potential features illustrate that microreactors are promising tools for on-site and on-demand production. Unfortunately, there are no examples of industrial implementation of microdevices in Ukraine. But many well-known chemical and pharmaceutical companies actively implement the new advanced technology for large-scale production, namely [15, 16, 17]:

– Degussa, Germany (propylene oxide, 50 000 t/h);
– Eurodyn G mbH, Germany (nitroglitserin, 16 000 t/h);
– Xi'an Huian Chemical, China (nitroglitserin for medicine, 120 t/h);
– Siemens Axiva, Germany (polyacrylate, 2000 t/h);
– DSM Fine Chemicals, Austria (vitamin D, 100 t/h);
– Synthacon GmbH, Germany (fine chemicals, 200 t/h);
– Sigma Aldrich GmbH, Switzerland (fine chemicals, 20 t/h);
– Clariant, Germany (pigments, 10 t/h);
– Schering, Germany (synthesis of steroids, 15 kg/day).

There are a number of research projects involving joint collaboration between universities and companies in Europe and the Far East where robust MRT systems are being developed for various commercial applications. Some examples of these projects are [18]:

– Strategic Research Project on Modular Micro Chemical Engineering (MicroChemTec, www.microchemtec.de);
– Research Association of Micro Chemical Process Technology (MCPT, www.mcpt.jp/english/elink.html),
– New Eco-efficient Industrial Process Using Microstructured Unit Components (NEPUMUC, www.nepumuc.info);
– Towards Optimised Chemical Processes and New Materials by Combinatorial Science (TOPCOMBI, www.topcombi.org);
– Integrated Multiscale Process Units with Locally Structured Elements (IMPULSE, www.impulse-project.net).

In turn, the miniaturization of flow reactors is a decisive advantage in the synthesis of nano-sized particles. Due to the efficient heat transfer and optimal mixing, the full control of reaction parameters is affected. Ideal mixing in the microreactor technology determines undeniable benefits of the flow synthesis for carrier surface functionalization with active substances. There

are already developed and mastered the receipt and processing of polymer nanoparticles using microreactor units Wingspeed AG (Switzerland) [17]. The main advantage of polymers fabricated in microreactors is the homogeneous particle size distribution. Due to the exact and complete control of parameters of the functionalization reaction in the microreactor (pressure, temperature, stoichiometry, reaction time and flow rate), it is possible to obtain a homogeneous particle size distribution. Thus, new horizons open up both in the basic research of nanomaterials and their mass production.

The data of our calculations may be proposed for such companies as Reachemtrans LLC (Ukraine), Holding Company Menschen Group (Russian), IC "Artalia" (Russia), JSC Sorbent (Russia), United States Environmental Protection Agency EPA (USA), Pall Corporation (USA), AquaNano LLC (USA), Dunwell Group (Chinese National Republic) and others. All of them are engaged in manufacturing of sorbents for water purification. But even a partial implementation of microdevices entails significant financial and technical advantages for these enterprises as well as integrates the technology for producing substances with prescribed properties. Therefore, this study is a complete theoretical experiment that could prove perspectives of practical commissioning of microreaction devices for the synthesis of highly selective sorbents. As a result, innovative sorbents will bring in a serious contribution to the environmental and economic well-being of people generation.

Conclusion

A computational fluid dynamics (CFD) model was developed to simulate the sol-gel synthesis of functionalized silica materials in the microreactor. The process parameters were investigated and recommendations for laboratory chemical synthesis and large-scale production of functionalized sorbents was formulated. It was observed that the time for diffusion in the rectangular microchannel with a hydraulic diameter of 0.2 mm is about 3.3 s. An analytical solution of the flow velocity field and the concentration profile was calculated and presented in this work.

The possibility of industrial implementation of the investigation was studied with an objective to reveal the practical assessment and commercial significance of the study.

References

[1] Yu. Zub, "Functionalized Organosilicas: Synthesis, Structure and Physicochemical Properties," Diss. of the doctor of chem. Sciences, 603 p., 1996.

[2] Yu. Zub, "Design of Functionalized Polysiloxane Adsorbents and their Environmental Applications, " in ARW NATO, Eds. P. Innocenzi, Yu.L. Zub, V.G. Kessler, pp.1-29, 2008.

[3] W. Ehrfeld, V. Hessel, H. Löwe, "Microreactors. New technology for modern chemistry," Weinheim, Wiley–VCH Verlag GmbH, 651 p., 2000.

[4] Z. Zhang, C. Yim, Min Lim, X. Cao, "Quantitative characterization of micromixing simulation," AIP: Biomicrofluidics. vol. 2(3), 2008.

[5] S. Radl, D. Suzzi, Johannes G. Khinast, "Fast reactions in bubbly flows: Film model and micromixing effects," Ind. Eng. Res, vol. 49(21). pp.10715-10729, 2010.

[6] S.Vaccaro, P. Ciabelli, "Results of modeling of a catalytic micro-reactor," 31st Meeting on Combustion., pp.1-6, 2012.

[7] E.S. Borovinskaya, "Mathematical models and software for research and optimization of liquid-phase reactions in microreactors," Diss. of the cand. of tech. sciences, 190 p., 2008.

[8] V. Chokkalingam, "A droplet-based microfluidic scheme for complex chemical reactions," dissertation, Saarbrücken, 123 p., 2010.

[9] Yu. Miroshnychenko, Yu. Beznocyk, O. Smirnova, Yu. Zub, "Quantum-chemical modeling of functionalized silica surface," Research bulletin of the National Technical University of Ukraine "Kyiv Polytechnic Institute", vol. 3, pp.141-145, 2011.

[10] Yu. Miroshnychenko, Yu. Beznocyk, O. Smirnova, Yu. Zub, "Quantum-chemical modeling of silica surface functionalized with nitrogen, phosphorus, and sulfur-containing groups," Eastern European Journal of Enterprise Technologies, vol. 2/14 (56), pp.49-50, 2012.

[11] B. Yang, T. Yuschak, T. Mazanec, A. Lee Tonkovich, S. Perry, "Multi-scale modeling of microstructured reactors for the oxidative dehydrogenation of ethane to ethylene," Chem. Eng. Journal. 135, pp.147-152, 2008.

[12] M.N. Kashid, A. Renken, L. Kiwi-Minsker, "Gas–liquid and liquid–liquid mass transfer in microstructured reactors," Chem. Eng. Science. 66, pp.3876-3897, 2011.

[13] A.A. Kulkarni, A.K. Gorasia, V.V. Ranade, "Hydrodynamics and liquid phase residence time distribution in mesh microreactor," Chem. Eng. Science vol. 62, pp.7484-7493, 2007.

[14] Madhavanand N. Kashid, A. Renken, L. Kiwi-Minsker, "Microstructured devices for chemical processing," Weinheim : Wiley–VCH Verlag GmbH & Co. KGaA, 358 p., 2015.

[15] K. Schubert, W. Edrfeld, I.H. Rinard, R.S. Wegeng, "Realization and testing of microstructure reactors. Micro heat exchangers and micromixers for industrial applications in chemical engineering," Proceeding of the conference on Process Minituarization: 2nd International Conference on Microreaction Technology, IMRET2, pp.88-95, 1998.

[16] A. Kleemann, "Microreaction technology, lnnovations in Pharmaceutical Technology," pp.72-76, 2001.

[17] R. Yarullin, A. Herbst, "Continuous flow reactor," The Chemical Journal, pp.44-49, 2012.

[18] Patrick L. Mills, David J. Quiram, James F. Ryley, "Microreactor technology and process miniaturization for catalytic reactions – A perspective on recentdevelopments and emerging technologies," Chem. Eng. Science vol. 62, pp.6992-7010, 2007.