

Modelling of Heterogeneous Systems in Microreactors

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Abstract – *In this paper an overview of approaches to the modelling of heterogeneous systems (liquid-liquid) in the microreactor was performed, mathematical models of various chemical reactions in microchannels published in the literature was considered and the comparison of theoretical and practical experiments was executed. Based on the generalized data, it has been proved the feasibility of microstructured reactor application for the process of silica surface functionalization in order to carry out the synthesis of innovative sorption materials. The next stage of this research is to develop a mathematical model of the process and its implementation by means of special software environment.*

Key words – microreactor, microchannel, process of functionalization, silica surface, CFD-modelling, heterogeneous system, miniaturization.

I. Introduction

Microreactors as a novel concept in chemical technology enable the introduction of new reaction procedures in chemistry, molecular biology and pharmaceutical chemistry. 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 [1]. Potential advantages of microstructured reactors (MSR) allow successfully use them to complex processes for optimization and scale-up from the laboratory scope to production. These arguments give the background to discuss the realization of the functionalization process using the microreactor.

The process of silica surface functionalization is the effective approach to receive the silica-based adsorbents that are able to extract heavy metals such as mercury from water and, as a result, have the potential for reducing water pollution and protecting ecosystems [2, 3]. 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. That is why, it is reasonable to perform computational studies of the microreactor system as well as the structural parameters of functionalized materials. 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. Thus, modeling of the functionalization process in the microreactor is an actual trend of chemical technology that provides opportunities for the synthesis of innovative materials with prescribed properties.

II. Purpose and objectives of the study

The key purpose of this paper is to explore new sorption materials as well as identifying new techniques for their preparation.

In accordance with the set goal the following research objectives are identified:

- to study the adsorptive properties of functionalized silica materials with different groups by means of quantum-chemical calculations. In this paper is presented an example of modeling the silica surface functionalized with thiourea-containing fragments;

- to investigate the approaches to the modeling of different reactions and processes in microreactors with the help of special software tools. The finite purpose of this task is to develop the mathematical model of the microreactor which could be effectively used for the synthesis of functionalized materials.

III. A general characteristic of functionalized silica-based materials

Back in the early 90s of last century, hybrid organic-inorganic materials which include functionalized organosilicon materials have received serious attention from many scientists due to the potential of properties combination for creating the novel structures [2]. In general, the class of hybrid organic-inorganic materials contains compounds that are composed of inorganic (according to our investigation, it is silicon dioxide) and organic (various radicals) components. This result can be achieved by: 1) impregnation of the inorganic part or introduction of the organic part into inorganic one in the absence of covalent bond between them; 2) formation of covalent bond between the components [3]. It should be noted that the latter type of materials is the most progressive in research and in the production scale as well.

IV. Methods of functionalized silica-based materials synthesis

A sol-gel method and a template method are the most promising approaches for obtaining functionalized silica materials. Materials received by means of the sol-gel technique are usually amorphous or have randomly arranged domains. The template synthesis method permits to obtain an ordered structure, but there are some difficulties regarding the intrinsic properties. Firstly, basic products and by-products of the reaction cannot be divided because of their covalent bonding with the silica surface. Secondly, the number of functional groups reduces significantly when the number of synthesis steps increases [3]. However, these (and other) shortcomings can be avoided by using the "direct" method of functionalization.

The core of the sol-gel method is the alkoxy-(or chlorine) silanes hydrolytic polycondensation reaction. In describing the process of transformation competing ways include: hydrolysis of bonds at the silicon atom with the formation of silanol, and polycondensation with the siloxane formation [2, 3]. But the key feature of the sol-gel synthesis is the ability to introduce different functional groups that are capable to interact selectively with the substances of various nature.

Therefore, the main goal of the functionalized silica materials synthesis is the combination of organic and inorganic components. For example, the inorganic

component can improve mechanical, thermal, structural stability of new compounds, while the organic component provides the specificity of the actions in these substances. In addition, the sol-gel process allows regulating the degree of interpenetration of organic and inorganic fragments at the molecular level to create the organic-inorganic hybrid materials with prescribed properties [3]. Further the influence on structural and adsorptive abilities as well as physical and chemical properties of the product can be carried out at all stages of the synthesis.

To provide the necessary physical, chemical, structural and adsorptive properties of the sample, it is possible to vary the nature and the value of output ingredients, catalyst, solvent, aging conditions and hydrogels washing and drying. A serious task is to regulate the concentration of ligand groups and their distribution on the silica surface. Furthermore, the essential aspect for the majority of applied problems is the opportunity to form both of the monolayer of molecules on the surface and polymolecular coverage. By virtue of requirements described above, it is reasonable to conduct computer calculations of the materials molecular structure by means of the quantum-chemical modeling. On the basis of the theoretical experiment result the process of silica functionalization can be simulated for determining the technological characteristics of the process in terms of sustainable development. The modeling provides clear guidance for sustainable chemical synthesis and production of new materials with useful properties.

V. Quantum-chemical modeling of the functionalized silica surface

Construction and previous optimization of structures was performed with a help of the molecular mechanics approximation methods using MM+ force field. The main task of this stage was to find the initial geometrical parameters of the molecules. Theoretical investigations of clusters were carried out by the approach "ab initio" (from first principles). In search of the optimal geometry of clusters there were placed no restrictions on symmetry and the main requirement was to achieve a minimum total energy and a stability of the cluster. For the calculations we used the method of density functional theory (DFT) B3LYP approximation with a local approximation of exchange-correlation potential (basis set 6-31 G(d, p)) [4].

VI. Implementation of the microreaction systems in chemical production

A large number of applications within the last decade have clearly demonstrated fundamental advantages for microreactors compared to the lab-scale equipment. Their main feature is to provide the intensification of mass and heat transfer due to the flow regime improvement. Moreover smaller devices require less space, materials, and energy and often have shorter response times.

The key advantages of the microreactor are: Decrease of the linear dimensions, Increase of the surface-to-volume ratio, Improvement of the mass transfer, Increase of the number of units, Production flexibility, Safety and sustainability, Approaches to the modeling processes in the microreactor.

This system includes a set of equations of various types (from the linear to differential equations in partial derivatives) and requires special mathematical methods to

solve the specific problems. It should be noted that the determination of boundary conditions and assumptions is the influential stage of modeling [5]. The theoretical calculations aimed at proving of this assumption and, thereby, reliable reproduction of the actual experiment by means of simulation. At present, there are a lot of successful commercial software packages for modeling complex chemical processes. The most popular of them are Aspen HYSYS, Aspen Plus, ANSYS, CHEMCAD, Pro II, Mathcad, COMSOL Multiphysics.

VII. Case study of quantum-chemical calculations of the silica surface functionalized with thiourea-containing groups

In order to analyze the process of functionalization in the microreactor firstly we investigated the parameters of structures with different functional groups. Here we presented the molecular structure of silica surface functionalized with thiourea-containing fragment as the case study. This choice is caused by the projected useful properties of such polysiloxane xerogels that are able to sorb ions of noble metals and heavy metals including such dangerous ions for the human as Hg²⁺ (mercury) [2, 3]. In our previous work, we have also described the results of the study on the behavior of nitrogen- and phosphorus-containing groups of functionalized silica surface.

Based on the quantum-chemical modeling of silica surface functionalized with thiourea groups [$\equiv(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$], it has been shown that hydrogen bonds can be formed between donor and silanol groups both in the presence and absence of the water molecule. Geometry was optimized (Fig. 1) and geometric parameters (Table 1) and spectra frequencies (IR and NMR) were calculated for these fragments.

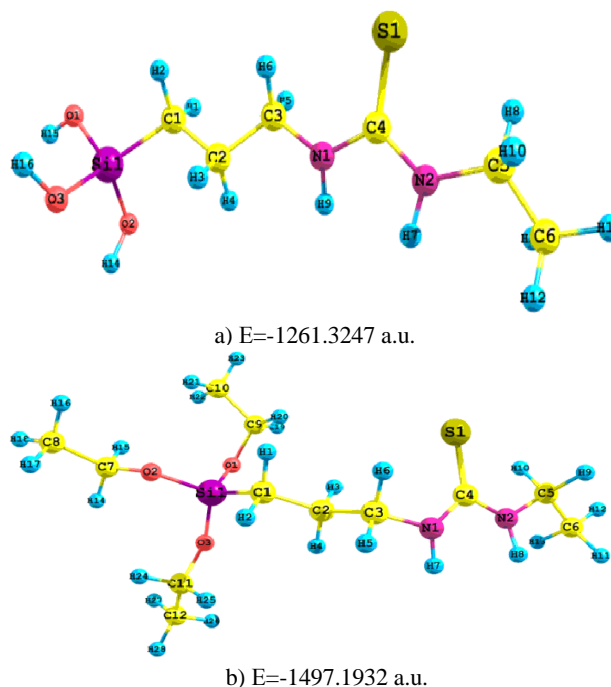


Fig. 1. Optimized geometry of fragments of silica surface functionalized with thiourea group:
 a – $(\text{HO})_2\text{Si}(\text{OH})(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$;
 b – $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$
 (where E is the total energy of the fragment)

TABLE 1
BASIC GEOMETRICAL PARAMETERS OF THE OPTIMIZED FRAGMENTS

Bridging	Length (Å)	Valence angle	Value (degree)
(HO) ₂ Si(OH)(CH ₂) ₃ NHC(S)NHC ₂ H ₅			
Si1-O3	1.666	O1-Si1-O2	111.5
Si1-C1	1.865	N2-C4-S1	123.0
S1=C4	1.684	C3-N1-C4	124.6
N1-C4	1.367	N1-C4-N2	113.5
(C ₂ H ₅ O) ₃ Si(CH ₂) ₃ NHC(S)NHC ₂ H ₅			
Si1-O1	1.649	O1-Si1-C1	113.2
Si1-C1	1.874	C3-N1-C4	124.4
S1=C4	1.686	C4-N2-C5	124.1
N2-C4	1.364	N1-C4-N2	113.6
N1-C4	1.366		

As a result of the atomic relaxation, it was determined that an adsorption band of the hydrogen bond is slightly shifted to the lower frequencies, but it significantly increases with appearance of the water molecule (Fig. 2).

The theoretical analysis of the NMR spectra of studied fragments permits to identify the causes that determine the behavior of the modified silica surface layer. The values of the chemical shifts of shielding constant at nuclei ¹³C were found when forming the hydrogen bonds between the donor and silane groups. A comparison between the resonance frequencies of the theoretical NMR spectra with the similar

experimental values revealed that computer fragments calculations of silica surface functionalized with thiourea groups are in good agreement with the data of synthesized adsorbents (Table 2) [3].

It should be noted that the lab synthesis of silica compounds with sulfur-containing functional groups has been carried out in the O. O. Chuiko Institute of Surface Chemistry. Yu. Zub reported the experimental results of the adsorption capacity of such materials in his doctoral thesis [3].

He examined the sorptive properties of mesoporous silica surface functionalized with thiourea ligand group regarding mercury ion (II). By virtue of the analysis of adsorption isotherms, it has been shown that the growth in the density of functional groups results in the increase of their inaccessibility when sorbing the metal ions. Consequently, the adsorption properties of mesoporous silica materials containing thiourea group on the surface layer depend on the content of the functional groups and the nature of the porous structure. The low density of ligand groups improves the extraction of mercury while the increase in density of functional groups leads to the impediment of the complexing process. These arguments confirm the necessity of the accurate process control to obtain materials with prescribed properties. Microreaction technology can help to carry out the synthesis under optimal conditions for producing highly selective sorbents that have the potential for water disinfection and purification.

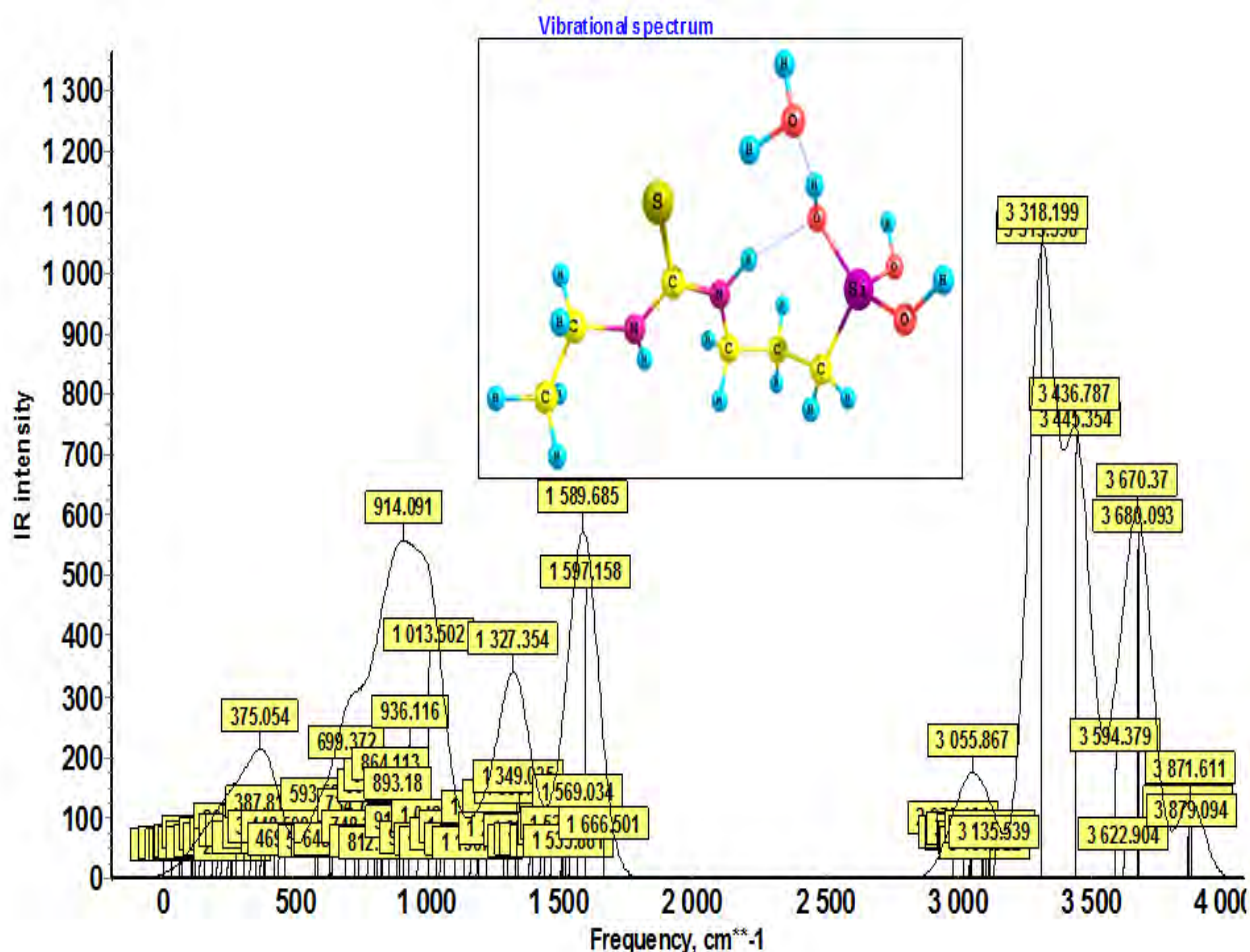


Fig. 2. IR vibration spectrum of the fragment functionalized with thiourea group in the presence of the water molecule

TABLE 2
EXPERIMENTAL AND CALCULATED VALUES
OF THE CHEMICAL SHIFTS IN THE ^{13}C NMR SPECTRA
OF THIOUREA-CONTAINING FRAGMENTS

Type of the nucleus	$[\equiv\text{Si}(\text{H}_2\text{C}_2\text{H}_5)_3\text{NHC}(\text{S})\text{NHC}(\text{S})\text{NH}_2]$, ppm	$[\equiv\text{Si}(\text{H}_2\text{C}_2\text{H}_5)_3\text{NHC}(\text{S})\text{NH}(\text{C}_5\text{H}_2\text{C}_6\text{H}_3)]$ (with intramolecular bond), ppm	$[\equiv\text{Si}(\text{H}_2\text{C}_2\text{H}_5)_3\text{NHC}(\text{S})\text{NH}(\text{C}_5\text{H}_2\text{C}_6\text{H}_3)]$ (experimental values for mesoporous silica), ppm
$^{13}\text{C}_1$	11.9 (7.40) ¹	12.0 (13.7) ²	9.0
$^{13}\text{C}_2$	26.8 (22.36) ¹	25.0 (24.1) ²	23.1
$^{13}\text{C}_3$	51.0 (46.15) ¹	50.0 (48.1) ²	46.8
$^{13}\text{C}_4$	192.5 (181.27) ¹	194.4 (189.5) ²	181.4
$^{13}\text{C}_5$	42.4 (39.20) ¹	42.5 (42.6) ²	39.6
$^{13}\text{C}_6$	14.6 (14.19) ¹	14.1 (13.7) ²	12.8

¹ $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$

² $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5 + \text{H}_2\text{O}$

Conclusion

The adsorption properties of functionalized silica materials were approved in the context of water purification and the implementation of microreactors for the process of silica surface functionalization was discussed.

Quantum-chemical modeling of innovative silica-based materials that can be used for water treatment was performed. Thiourea-containing fragments were considered as the case study for identification of the

theoretical experiment technique. The adequacy of the results of quantum-chemical modeling was confirmed by comparing the calculated values of IR and NMR spectra against the similar data of practical experience.

The analysis of approaches to modeling the process of functionalization in the flow microreactor was conducted. The simulation results of various technological operations were studied and the potential benefits of microdevices were confirmed in the context of sustainable manufacturing. The next step of this investigation will be the development of a mathematical model of the functionalized silica materials synthesis in the flow microreactor and its realization in the appropriate software environment. Ultimately, a clear guidance for sustainable chemical synthesis and large-scale production of functionalized sorbents will be provided and used for water treatment.

References

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