Multispectral diagnostics of catalytic reactions in microfluidic systems

Guda A.A.[1], Tereshchenko A. A.[1], Arzumanyan A.V.[2], Gorbunov D.N.[3], Egil N.V.[1], Zagrebaev A.D.[1], B. Protsenko, Mahmoud E. A. Eid[1], Soldatov A.V.[1]

[1] *The Smart Materials Research Institute, Southern Federal University, Russia*

[2] *A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia*

[3] *M.V. Lomonosov Moscow State University, Moscow, Russia*

guda@sfedu.ru

Optimization of the reaction conditions is an important step for improving efficiency of the catalyst utilization and meeting strict environmental aspects. The catalytical reactions benefit from reducing noble metal concentrations, improving their TONs, using nontoxic solvents and milder conditions. Microfluidic systems offer unique capabilities for high-throughput screening. Reduced reagent consumption and the ability to quickly change the composition of incoming streams and the operating mode make microreactor systems convenient for screening the influence of many parameters on product yield and process selectivity. The general workflow for autonomous microfluidic system is shown in Fig. 1. It is based on initial guess of the reaction parameters (0) and the loop (1–4) with the feedback from online spectral diagnostics of the catalyst and products (3). A rational search for optimal experimental conditions should be based on the analysis of a large amount of available literature data and preliminary numerical experiments

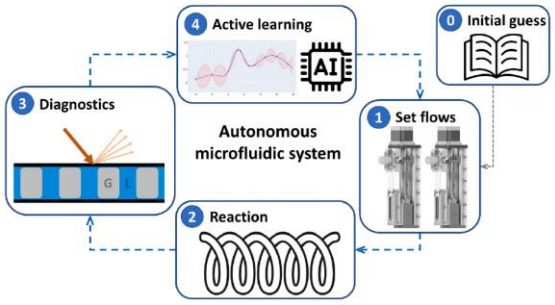

Figure 1. The scheme for autonomous microfluidic system, combining recommendation system, syringes for variation of reagent concentrations, delay line enabling needed reaction time, spectral feedback analyzed by machine learning methods.

Feedback in the autonomous system is provided by spectral data measured from the capillary in situ. The development of new spectral monitoring cells and their integration with microfluidic systems allows online monitoring of both the composition of the reaction mixture via IR-Fourier and Raman spectroscopy methods and the state of metal centres by using X-ray absorption spectroscopy. The knowledge about current and target descriptors of the catalytic system (reagent concentrations or metal local environment) is supplied to the optimisation that balance via exploration and exploitation in the space of reaction parameters and find their optimal combination. In this work we discuss in details integration of spectral monitoring to two industrially important homogeneous catalytical reactions.

Homogeneous hydroformylation is applied for aldehyde and alcohols production. Rh metal complexes allow tandem one pot reactions for converting olefins directly into alcohols and more often such reactions are performed in microfluidic flow regime both relevant from academic research and industrial automatization. The reaction yield depends on the coordination of Rh atoms or formation of Rh clusters, therefore knowledge about local atomic and electronic structure of active sites under industrial conditions is important. Rh K-edge X-ray absorption spectroscopy (XAS) is unique tool to probe coordination of Rh, however up to date there were no reports of application of this methodology to hydroformylation in microfluidic biphasic flow. Our work demonstrates the experimental setup and transmission cell developed for segmented flow operando measurements. The quantitative analysis of XAS data was performed with the library of theoretical spectra computed for relevant monomeric, dimeric and small clusters species. We demonstrate that under segmented flow presence of amine species in the reaction prevents formation of Rh clusters in favor of Rh dimers.

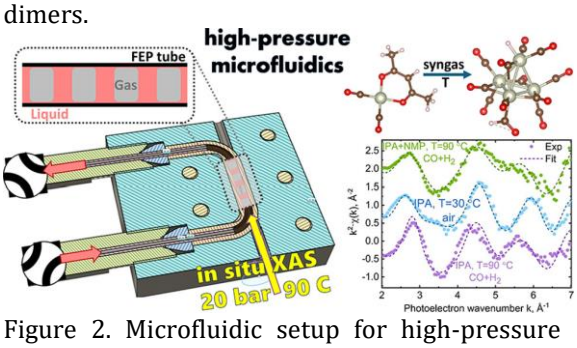

Figure 2. Microfluidic setup for high-pressure XAS diagnostics of homogeneous Rh catalytic system

Hydrosilylation of alkenes is another industrially important catalytic reaction for producing organosilanes. This process is often based on the homogeneous Pt-catalysts. Given

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the high cost of platinum and its irretrievable "scattering", the new approaches that can reduce its consumption is an important goal in the modern chemistry. Heterophase (biphase) catalytic systems for hydrosilylation offer additional advantages in terms of high activity, product separation and recycling. However, large-scale synthesis in heterophase conditions is complicated by constrained mass and heat transfer. The droplet microfluidic regime is of particular interest due to improved mass and heat transfer while being compatible with many diagnostic devices. The reaction rates were higher in capillaries due to increased specific area between catalyst and reactants, and easy separation of catalyst and product phases was achieved. We found Raman spectroscopy to be an convenient tool for online monitoring of the conversion from each droplet. Finally, we demonstrated the application of 3D-printed microfluidic reactors that provide compact design of reaction units with complex topology. These results open new perspectives for process automation and industrial applications of biphasic hydrosilylation reactions in droplet flow mode.

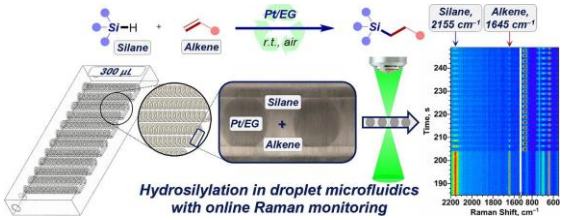

Figure 3. Microfluidic system for in situ Raman diagnostics of hydrosilylation reaction and time evolution of the spectral signal from droplet flow.

Finally we demonstrate a 3D printed microreactor and UV-VIS spectral diagnostic system were adapted for an automatic protocol for screening parameters of citrate-based droplet synthesis of gold nanoparticles. Using this system, 27 combinations of synthesis parameters were screened within an hour and data were collected from more than 1000 individual droplets with nanoparticles. The developed system allows both filtering the spectra of target droplets and conducting a comprehensive multivariate analysis of all key descriptors.

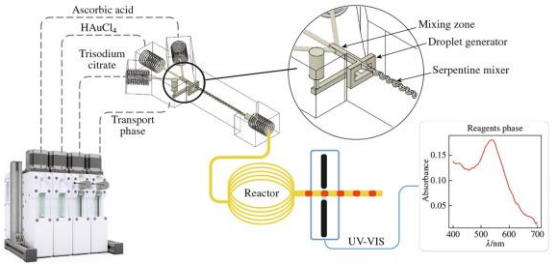

Figure 4. Microfluidic system for screening of Au NPs synthesis conditions under UV-vis spectral control.

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