THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VII International scientific school-conference for young scientists

October 11-15, 2022

Tomsk 2022

Ag/SiO_2 monoliths in the continuous-flow liquid-phase hydrogenation of p-nitrophenol

O.Yu. Miskevich, M.A. Baryshnikov, T.I. Izaak

Tomsk State University, Tomsk, Russia

olga.vodorezova@yandex.ru

Hierarchical porous monoliths have a high porosity and a large surface to volume ratio. This makes it attractive for use as a catalyst support in flow reactors. The flow reactor has advantages that allow reactions to be carried out more selectively and safely due to efficient mixing, improved heat and mass transfer [1]. Silica monolith consists of a porous skeleton with mesopores and interskeletal macropores. Due to the widely studied silica surface chemistry, the structure and composition of the catalyst can be controlled during the synthesis. The size and shape of the catalyst depends on the container in which it is prepared [2]. Recent studies [3] showed the successful implementation of monolithic catalysts in various chemical and biochemical flow processes. However, in order to use the full potential of the porous silica monoliths as flow reactors, several problems still need to be solved. For example, the effect of structure on the properties and catalytic activity of monolithic catalysts, as well as their role in diffusion limitations, has been little studied. The aqueous-phase hydrogenation of p-nitrophenol to p-aminophenol with excess NaBH4 as a reducing agent was used as a test reaction to study the influence of structure of the silica monolith on catalytic activity in continuous flow. In addition, nitrophenol is a wastewater pollutant and can adversely affect humans and the environment. The 4-aminophenol formed during the reduction process is used in the pharmaceutical industry, the production of paints, etc.

Here, we report the study of catalytic activity of cylindrically shaped Ag-loaded silica monoliths. For the preparation of catalysts, silica monoliths with two mean macropore width of 7 or 21 μm and mesopore width of 5–50 nm or 5–38 nm were obtained, which were designated A65 and A60, respectively. The monolithic catalysts were prepared by reducing silver nanoparticles in the pores of the support.

It was found that silver particles are distributed on the surface of the skeleton and in mesopores. Moreover, the catalyst Ag/A65 with a smaller macropore size is characterized by a narrower distribution of the silver particles over the surface of the skeleton. Catalysts were placed in heat shrink tube for use as a flow reactor. No influence of flow rate on conversion at a fixed contact time was observed. This indicates the absence of external mass-transfer limitations or stagnant layer formation in the macropores of the monolithic catalysts. The effective rate constants of the hydrogenation of 4-nitrophenol were determined. For the Ag/A60 catalyst, the effective reaction rate constant was lower than for Ag/A65. This is probably due to the effect of internal diffusion on the rate of the catalytic flow reaction in the Ag/A60 catalyst with the narrower mesopore size distribution.

Thus, for the synthesis and successful application of catalysts based on monolithic porous silica in a flow reactor, it is necessary to find a balance between its structure (high permeability, low pressure drops, strength, mesoporous structure) and the distribution of the active component in the catalyst.

References

1. Galarneau, A.; Sachse, A.; Said, B.; Pelisson, C. H.; Boscaro, P.; Brun, N.; Fajula, F. *Comptes Rendus Chimie* **2016**, *19*(1–2), 231–247.
2. Galarneau, A.; Abid, Z.; Said, B.; Didi, Y.; Szymanska, K.; Jarzębski, A.; Fajula, F. *Inorganics* **2016**, *4*(2), 9.
3. Szymanska, K.; Ciemięga, A.; Maresz, K.; Pudło, W.; Malinowski, J.; Mrowiec-Białoń, J.; Jarzębski, A. B. *Front. Chem. Eng.* **2021**, *3*, 789102.