On the Scale-Up of Metal-Organic Frameworks using Microreaction Technology

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The research in the field of Metal Organic Frameworks (MOFs) - porous hybrid organic-inorganic materials - has gained significantly growing interest over the past two decades. Many research groups from all over the world got actively involved researching this area and exploring the potential of these materials. Despite all this effort, these materials are mostly used in academic environment.

One of the current issues, which are limiting the implementation of MOFs in industrial applications is the inability to manufacture a significant quantity of, both chemically and thermally, stable MOFs. This inability derives from three reasons:

- The fact that most part of the research is conducted for academic purposes and is therefore confined with the synthesis of small quantities
- Technical problems concerning reproducibility and upscaling issues of the material and
- Economic reasons regarding the synthetic routes developed in lab scale.

In this work ZIF-8 (Zeolitic Imidazolate Framework - 8, Zn-2-Methylimidazolate) and UiO-66 (University of Oslo - 66, Zr-Terephthalate) were synthesized continuously by employing microreactors and the concept of flow chemistry. The microreaction technology (MRT) process turned out to be a viable alternative to the time and energy consuming conventional synthesis processes, as significantly faster reaction rates could be achieved compared to the conventional batch processes.

The two cases differed significantly concerning the results. In particular, for ZIF-8 it has been demonstrated that the implementation of microreaction technology is a powerful technique to significantly enhance productivity and repeatability. ZIF-8 was obtained at production rates of >1 kg/day and a theoretical space-time yield of 400,000 Kg/m^3*day while the production costs have been reduced to <1 €/g and the modular process setup allows easy further scale-up. Finally, by performing *in-situ* experiments during the continuous synthesis it became possible to monitor a continuous MOF synthesis using high resolution, high energy synchrotron X-ray powder diffraction. The precise adjustment of the flow and the measuring points allowed the observation of the progress of the reaction from the first seconds with high accuracy giving insight on the formation and growth of the MOF.

Conversely, the results of the process intensification in the case of UiO-66 revealed a different behavior. A correlation between intensified conditions and high product quality has been established. Escalation of the reaction conditions above a certain threshold leads to poor formation of the material and inferior product properties. Additionally, the productivity of the process is not as high as in the previous case and cannot surpass the state of the art results concerning batch reactions from the literature. Nevertheless, the material can be produced in a faster, safer and fully continuous fashion and the coordination of the Zr node can be influenced through the reaction conditions.