Polymeric foils as key element of the falling film microreactor: A concept study for enabling scalable heterogeneous catalysis in flow

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Relevance of research

In recent years, cascade reactions have become a highly interesting topic of academic research. Such multi-step chemical transformations have the potential of high synergy by combining different catalysis methods within one reaction sequence. A particular interesting synergy results from the combination of photocatalysis and biocatalysis as both methods perform under mild process conditions and can provide reactive intermediates via photocatalysis with subsequent usage in the enzymatic step. In the ILLUMINATE project, a consortium of four Fraunhofer institutes investigates the transfer of photo- and biocatalyzed cascade reactions from batch to flow by developing novel multi-step catalyst materials and continuous flow reactors (Figure 1).[1]

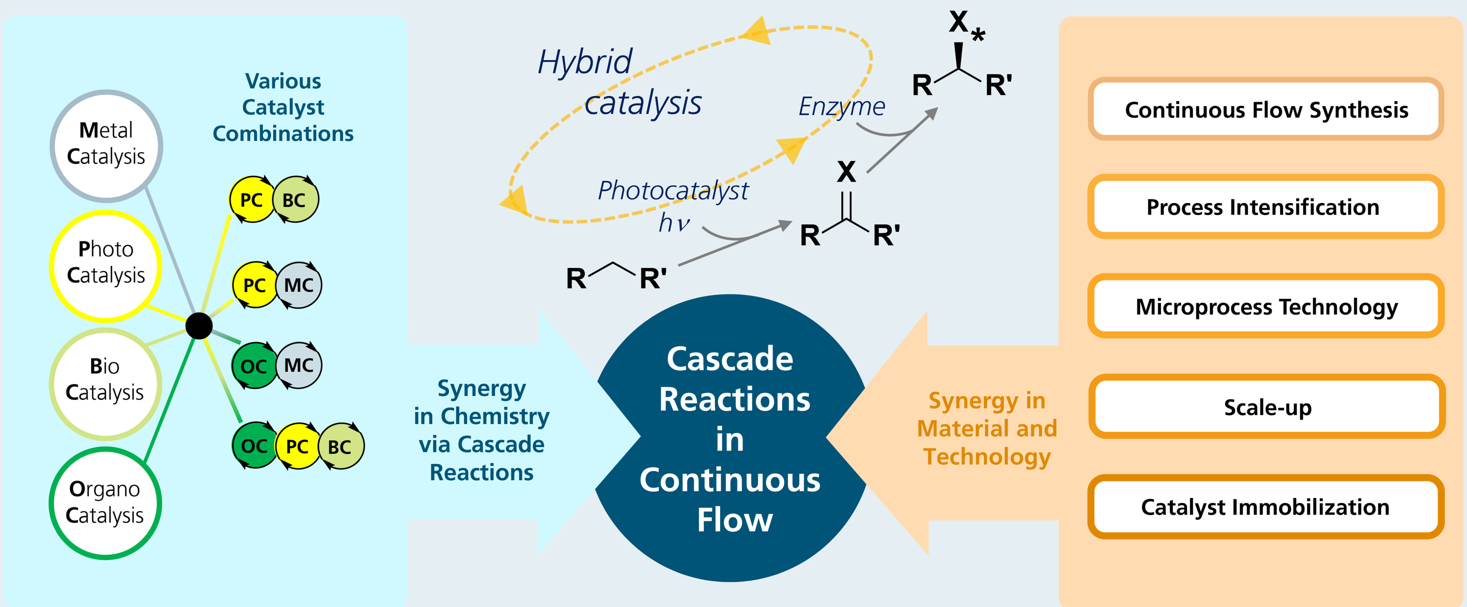

Figure 1: Cascade reactions in continuous flow – Synergy between chemistry, technology and tailor-made catalyst materials.

Technological vision

The falling film microreactor (FFMR) was conceptualized in early 2000 and resulted in a robust continuous flow reactor for gas-liquid contacting inside a thermally stabilized environment.[2] Typical applications are reactions like hydrogenations or photochemical reactions with various heterogeneous catalyst materials immobilized on the stainless-steel reaction plate.[3, 4] One drawback of the original FFMR was the expensive preparation of the stainless steel reaction plate and the tedious immobilization of catalyst material, limited to inorganic catalysts. With the rise of purely (bio)organic catalysts for the synthesis of complex fine chemicals under mild conditions, a novel concept for an advanced falling film microreactor with a transparent reaction plate was needed, which can be easily structured and functionalized for the selective immobilization of a (photo)catalyst.[1]

Hot embossing of polymeric foils

Wet-chemical inert polypropylene (PP) was selected as base material for the foil-derived reaction plate. This cheap and commercially available polymer foil was hot embossed with a microstructured embossing tool resulting in defined parallel channels (Figure 2).

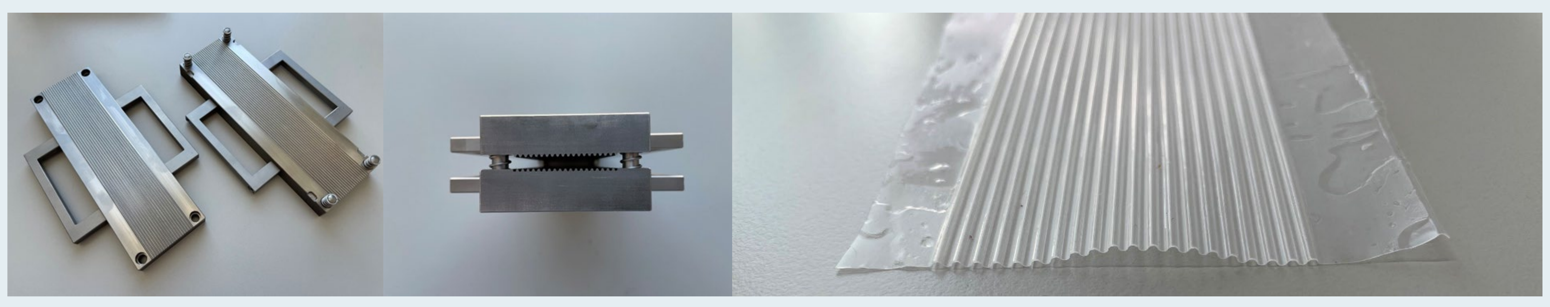

Figure 2: Custom-made embossing tool (left, middle) for the hot embossing of 50 µm thick PP foils with microchannels of 1200 µm width and 600 µm depth.

Functionalization of polymeric foils

Surface activation was done with plasma technology resulting in active functional groups like amines, aldehydes or carboxylic acids. Immobilization of various catalyst materials now can be done by standard amide coupling and condensation reactions as well as via ionic interactions, e.g, ammonium versus carboxylate ions (Table 1).

Table 1: Materials on foil surface and their applications in synthesis

TiO_2	H_2O_2 production
Decatungstate $W_4O_{10}^{4-}$	Oxidation
Anthraquinone sulfonic acid	Oxidation & H_2O_2 production
Tetracarboxyphenyl porphyrin	Oxidation
Graphitic carbonitride	Oxidation & H_2O_2 production
Enzymes (KRED, ADH, UPO, …)	Reduction & oxidation
SiO_x film	Wetting of foil surface

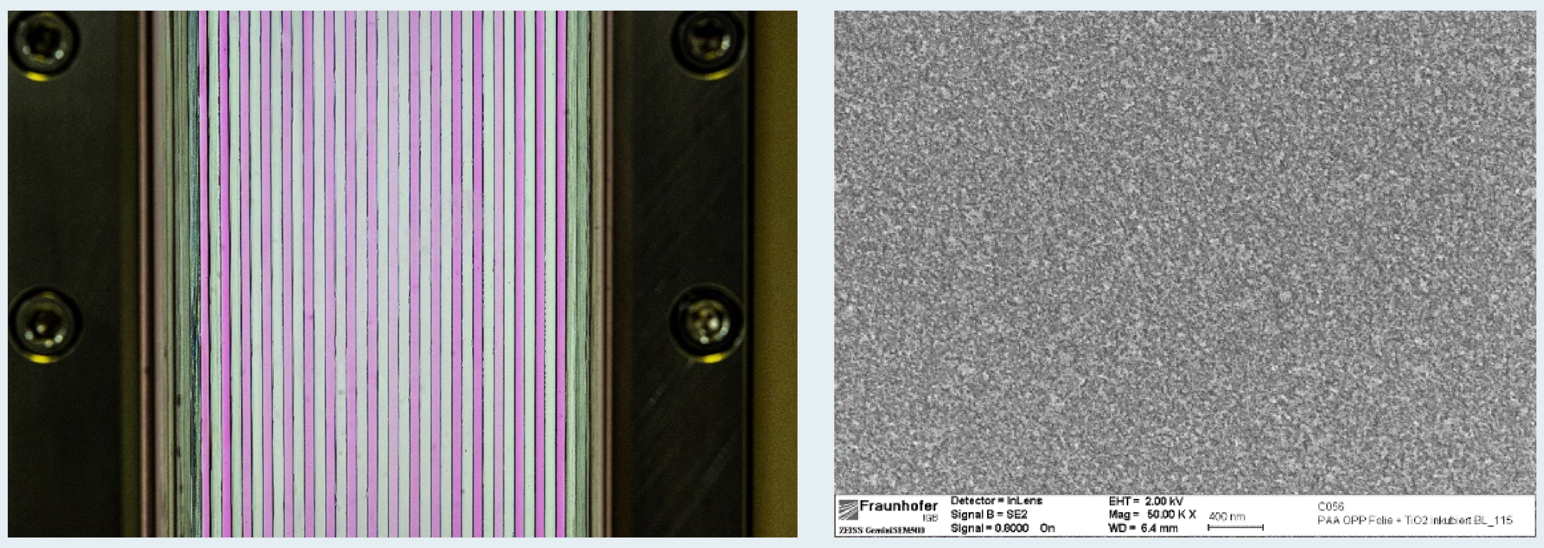

Figure 3: Rose Bengal-stained DI water flowing down in SiO_x functionalized channels of the microstructured PP foil (left); TiO_2 particles on a polyacrylic acid functionalized PP foil (right).

Reactor design and light sources

For a stable and easily exchangeable usage of the final polymeric foil, a frame was designed, which is placed inside the novel FFMR housing (Figure 4 top & middle). In the current concept study, gas-liquid-solid contacting is possible with irradiation from both sides of the foil. Two arrays with each carrying 14 high-power LED emitters can be magnetically attached to the FFMR housing (Figure 4 bottom). Selective irradiation is possible with wavelengths from 365 nm to 650 nm allowing multiple photochemical reaction classes.

Future work is dedicated to the design of a multi-foil staple photoreactor and the efficient immobilization of further catalysts materials like organocatalysts and chiral metal complexes.

Figure 4: Disassembled FFMR with central frame carrying the PP foil (top); assembled FFMR installed as single reactor module (middle); high-power LED array with magnets for easy attachment to the reactor housing.

[1] Partially funded by the Fraunhofer Society and the Federal Ministry of Education and Research BMBF (Illuminate Project, Grant # 031B1121).
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