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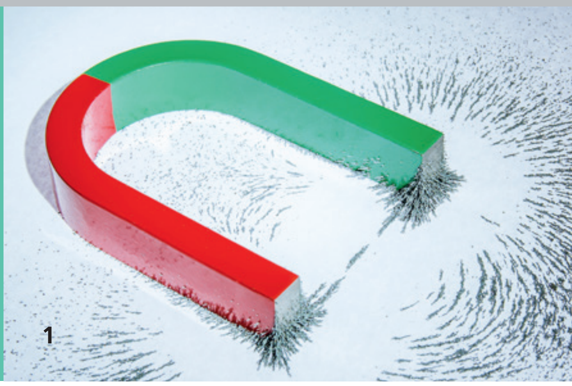

1 *Visualization of magnetic field lines with iron turnings around a horseshoe magnet*

2 *Stainless steel capillary micro-reactor with integrated heat exchanger in closed magnet array housing.*

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MAGNETIC CATALYST IMMOBILIZATION IN MICROREACTORS

Applications in catalysis

Transition metal catalyzed reactions are fundamental synthetic strategies to construct complex organic molecules. Palladium e.g. is a prominent example for a commonly used precious metal. It is often utilized to activate precursor molecules prior to a carbon-carbon coupling step. A broad variety of ligand systems thereby allows the delicate control over the activity and selectivity of the noble metal center. Beside the use of molecular catalysts heterogeneous systems have become a very important research field as well, especially since the development and utilization of nanoparticulate transition metals. These nanoparticles can be used as highly active catalysts supported onto so-called "semi-heterogeneous" materials. Common matrices are for example polymer chains with high steric hindrance, amphiphilic block copolymers, metalorganic frameworks or dendrimer systems. The stabilization of catalytically active nanoparticles inside a macroscopic matrix can allow easy separation from the reaction solution by filtration for a repetitive use of the same catalyst material. Enhancing these supports with magnetic properties allows the extraction of the catalyst material from the reaction solution with strong rare-earth magnets. Repetitive use of the catalyst material is now possible without separation of the catalyst from the reaction vessel.

Microreactors for magnetic catalyst immobilization

With the advent of continuous-flow synthesis and appropriate laboratory equipment, new approaches for catalysis have become possible. Microstructured reactors demonstrate e.g. better mixing of liquid reagents or improved gas-liquid contacting. A more efficient heat management allows the use

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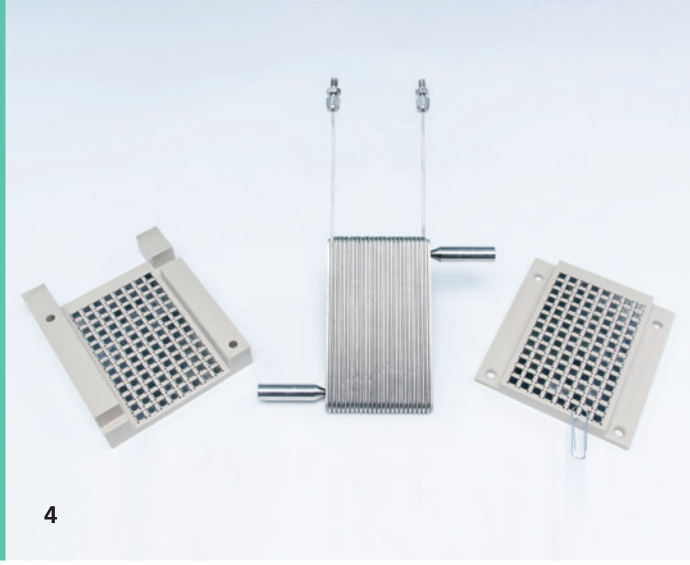

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of higher concentrated solutions of starting materials while minimizing hot-spot and byproduct formation. Increased process safety is achieved by shrinking the reaction volume from a big vessel to a small, but continuously running microreactor. With the tremendously decreased reaction volume, solution temperature and pressure regimes are feasible which would be irresponsible for classical batch vessels. But for a sufficient use of heterogeneous catalysts, some hurdles have to be overcome. Powder catalysts, for example, might clog the thin capillaries or channels of the microreactor resulting in a high pressure drop. Immobilization of powder catalysts is possible on exchangeable metal or ceramic open foam pellets but this approach requires reactor tube diameters in the centimeter scale, again with a sophisticated heat management. Direct attachment of catalyst material on the channel walls is possible for glass ware with classical silane chemistry. But stainless steel capillaries for high pressure and temperature applications are out of the scope for this approach.

To overcome these obstacles, a novel continuous-flow reactor concept was developed for the magnetic fixation of catalyst material inside stainless steel capillaries or glass microchannels. The key part of this concept is the reactor housing which carries a large number of small rare-earth magnets on both the bottom and top plate. The microreactors fit into the base plate (Fig. 2 & 4) whereas the top plate is directed by steel pins and fixed to the inserted microreactor by the mutual magnetic interactions between the magnets from both plates. This arrangement allows the reversible fixation of catalyst material on both capillary sides in closest proximity to the magnets. Necessary heat transfer to the catalyst and the reaction solution is possible via the integrated heat exchanger in the capillary carrier. For the visualization of the immobilization process a glass microreactor can be inserted as well. The latter allows also photo-chemical applications with the immobilized catalyst in the light transparent glass micro-channels.

Continuous-flow Suzuki coupling reaction with immobilized palladium catalyst

To validate the new reactor concept a Suzuki cross coupling reaction was performed. The formation of 4-methoxy biphenyl from 4-bromo anisole and phenyl boronic acid was used as benchmark. Magnetic, dendron-functionalized iron oxide particles were used as semi-heterogeneous support which agglomerated upon interaction with *in-situ* formed palladium nanoparticles. The preformed catalyst was suspended in a water-dioxane solvent composition and incorporated into the microreactor. Upon interaction with the magnets the catalyst material accumulated along the field lines of the magnets. The reactor was heated to 90 °C via the integrated heat exchanger while the reaction solution was pumped through the stainless steel capillary at 10 bar. After a residence time of 15 min (equivalent to a flow rate of 0.2 mL/min) a conversion of 17 % was achieved with 53 % selectivity to 4-methoxy biphenyl. This successful validation of the new reactor concept opens a broad field for experimental evaluation for catalyst testing and process optimization with magnetically fixable catalyst materials of different kinds. The microreactor concept itself allows thereby the application of physical parameters (high temperature and pressure, photonic contacting) which are not easily accessible for this catalyst class in batch vessel.

Literature

T. H. Rehm, A. Bogdan, C. Hofmann, P. Löb, Z. Shifrina, D. Morgan, L. Bronstein, ACS Appl. Mater. Interfaces 2015, 7, 27254-27261.

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3 *Close-up view on top magnet array housing*

4 *Disassembled microreactor for magnetic fixation of catalyst material inside stainless steel capillary*