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...
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


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