Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformation processes. In one active area of investigation, we are developing the heterogeneous aquacatalytic systems. Various types of catalytic organic molecular transformations, e.g., carbon–carbon bond forming cross-coupling, carbon–heteroatom bond forming reaction, aerobic alcohol oxidation, etc., were achieved in water under heterogeneous conditions by using amphiphilic polymer-supported transition metal complexes and nanoparticles (Figure 1), where self-concentrating behavior of hydrophobic organic substrates inside the amphiphilic polymer matrix played a key role to realize high reaction performance in water.

Selected Publications
1. A Vesicular Self-Assembled Amphiphilic Palladium NNC-Pincer Complex-Catalyzed Allylic A arylation of Allyl Acetates with Sodium Tetraarylborates in Water \(^1\)

The allylic arylation of various allyl acetates with sodium tetraarylborates proceeded in water in the presence of a vesicular self-assembled amphiphilic palladium NNC-pincer complex to give the corresponding arylated products in high yield, whereas the same complex as an amorphous powder did not promote the reaction efficiently. The formation of a vesicular structure was therefore shown to be essential for efficient promotion of the reaction.

Figure 2. Allylic arylation reaction in water in the presence of a self-assembled vesicular amphiphilic palladium NNC-pincer complex.

2. Organoborane-Catalyzed Hydrogenation of Unactivated Aldehydes with a Hantzsch Ester as a Synthetic NAD(P)H Analogue \(^2\)

We have developed a method for the hydrogenation of unactivated aldehydes, using a Hantzsch ester as a NAD(P)H analogue in the presence of an electron-deficient triarylborane as a Lewis acid catalyst. Thus, tris[3,5-bis(trifluoromethyl)phenyl]borane efficiently catalyzes the hydrogenation of aliphatic aldehydes with a Hantzsch ester in 1,4-dioxane at 100 °C to give the corresponding aliphatic primary alcohols in up to 97% yield. Aromatic aldehydes also undergo the hydrogenation, even at 25 °C, to furnish the corresponding aromatic primary alcohols in up to 100% yield.

Figure 3. Organoborane-catalyzed hydrogenation of aldehydes with a Hantzsch ester.

3. Recyclable Polystyrene-Supported Copper Catalysts for the Aerobic Oxidative Homocoupling of Terminal Alkynes \(^3\)

Polystyrene-supported copper(II) \(N,N',N''\)-tetraethyldi-ethylenetriamine \([\text{Cu}(II)–\text{TEDETA}]\) complexes were prepared by immobilization of TEDETA onto crosslinked polystyrene resin, followed by complexation with copper salts. The polystyrene-immobilized \(\text{CuSO}_4–\text{TEDETA}\) complex efficiently catalyzed the oxidative homocoupling of terminal alkynes under air to give the corresponding 1,3-diynes in up to 99% yield. The catalyst was easily recovered by simple filtration and reused eight times without significant loss of catalytic activity.

Figure 4. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

4. Instantaneous Click Chemistry by a Copper-Containing Polymeric-Membrane-Installed Microflow Catalytic Reactor \(^4\)

Instantaneous Huisgen cycloaddition has been achieved by developing a novel catalytic dinuclear-copper-complex-containing polymeric-membrane-installed microflow device. The microflow device instantaneously promotes the click reaction with a variety of alkynes and organic azides to afford the corresponding triazoles in quantitative yield.

Figure 5. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

References