Development of Heterogeneous Catalysis toward Ideal Chemical Processes

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

Selected Publications

Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Complex.
1. Self-Assembled Polymeric Pyridine Copper Catalysts for the Huisgen Cycloaddition with Alkynes and Acetylene Gas: Application in Synthesis of Tazobactam

Novel convoluted polymeric pyridine copper(I) catalysts PVPy-Cu were developed for Huisgen cyclization of organic azides with alkynes and acetylene gas. They were readily prepared by our molecular convolution of CuSO₄·5H₂O and poly(4-vinylpyridine) (PVPy) in the presence of sodium ascorbate with/without various sodium salts in water. Their structural investigation was conducted with XANES and EXAFS as well as DFT calculation. The Huisgen cycloaddition of a variety of alkynes and acetylene gas was carried out with 100 to 800 mol ppm Cu of PVPy-Cu in water whose turnover numbers reached up to 10,000. This catalytic system was applied to synthesis of tazobactam, an inhibitor of bacterial β-lactamases.

![Figure 2. Synthesis of Tazobactam through the Huisgen Cyclization with Acetylene Gas Using a Polymeric Cu Catalyst.](image)

2. Iterative Preparation of Platinum Nanoparticles in an Amphiphilic Polymer Matrix: Regulation of Catalytic Activity in Hydrogenation

We have demonstrated that iteration of the seeded preparation of platinum nanoparticles dispersed in an amphiphilic polystyrene–poly(ethylene glycol) resin (ARP–Pt) regulates the activity of the catalyst in the hydrogenation of aromatic compounds in water and is accompanied by a slight modification of its structural properties. Platinum nanoparticles dispersed in the amphiphilic polymer prepared through four iterations (ARP–Pt G5) showed a much higher catalytic activity than that of the initial ARP–Pt (G1) in the hydrogenation of aromatic compounds in water. These results suggest that iteration of the seeded preparation of nanoparticles can be an effective method for the precise regulation of the catalytic activity and the structural properties of the resulting catalyst.

![Figure 3. Regulated Hydrogenation with Iteratively Generated Polymeric nanoPt Catalysts.](image)

3. Solvent-Free A³ and KA² Coupling Reactions with Mol ppm Level Loadings of a Polymer-Supported Copper(II)-Bipyridine Complex for Green Synthesis of Propargylamines

A copper(II)–bipyridine complex immobilized on amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin (PS–PEG-BPy–CuBr₂) has been developed. The immobilized copper(II)–bipyridine complex at a mol ppm level of loading efficiently catalyzed the three-component coupling of aldehydes or ketones, amines, and alkynes (A³ or KA² coupling) under solvent-free conditions to give the corresponding propargylamines in good-to-excellent yields. Moreover, a ten-gram-scale green syntheses of propargylamines proceeded with excellent atom economy (E factor ≥ 0.38) through a solvent-free A³ coupling using 5 mol ppm of PS–PEG-BPy–CuBr₂. The total turnover number and turnover frequency of the catalyst reached as high as 178 800 and 7450 h⁻¹, respectively.

![Figure 4. Preparation of Propargylamines by A³ Coupling Reaction with ppm Loading Level of a Polymeric Cu(II) Catalyst.](image)

References