

Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

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Various transition metal-catalyzed organic molecular transformations in water were achieved under heterogeneous conditions by use of a self-assembled polymeric imidazole-copper catalyst, a boron-iridium heterobimetallic polymeric catalyst, or resin-supported iron nanoparticles which were designed and prepared by this research group. In particular, development of a highly active reusable poly(imidazole-copper) and an iron-catalyzed hydrogenation of under flow conditions are highlights among the achievements of the 2012–2013 period to approach what may be considered ideal chemical process of next generation. Representative results are summarized here under.

1. Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry¹⁾

Self-assembly of copper sulfate and a poly(imidazole-acrylamide) amphiphile provided a highly active, reusable, globular, solid-phase catalyst for click chemistry. The self-assembled polymeric Cu catalyst was readily prepared from poly(*N*-isopropylacrylamide-co-*N*-vinylimidazole) and CuSO₄ via coordinative convolution. The surface of the catalyst was covered with globular particles tens of nanometers in diameter, and those sheetlike composites were layered to build an aggregated structure. Moreover, the imidazole units in the polymeric ligand coordinate to CuSO₄ to give a self-assembled,

layered, polymeric copper complex. The insoluble amphiphilic polymeric imidazole Cu catalyst with even 4.5–45 mol ppm drove the Huisgen 1,3-dipolar cycloaddition of a variety of alkynes and organic azides, including the three-component cyclization of a variety of alkynes, organic halides, and sodium azide. The catalytic turnover number and frequency were up to 209000 and 6740 h⁻¹, respectively. The catalyst was readily reused without loss of catalytic activity to give the corresponding triazoles quantitatively.

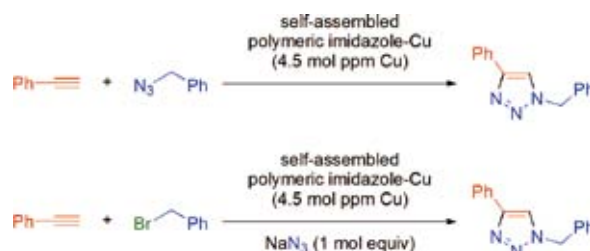


Figure 1. Click reaction catalyzed by self-assembled polymeric imidazole-Cu.

2. Polymeric Bimetallic Catalyst-Promoted In-Water Dehydrative Alkylation of Ammonia and Amines with Alcohols²⁾

A dehydrative alkylation with three kinds of Ir/B heterobimetallic polymeric catalysts in water is reported. The poly-

meric heterobimetallic catalysts were readily prepared by ionic convolution of a poly(catechol borate) and iridium complexes. The N-alkylation of ammonia and amines with alcohols, as alkylating agents, was carried out with a heterogeneous catalyst (1 mol% Ir) at 100 °C without the use of organic solvents under aerobic and aqueous conditions to afford the corresponding alkylated amines in high yield.

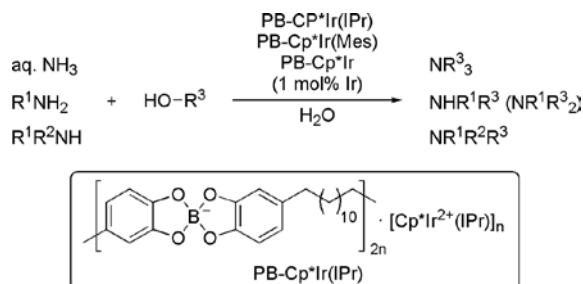


Figure 2. In-water dehydrative alkylation of ammonia and amines with alcohols using polymeric bimetallic catalysts.

3. Highly Efficient Iron(0) Nanoparticle-Catalyzed Hydrogenation in Water in Flow³⁾

Highly efficient catalytic hydrogenations are achieved by using amphiphilic polymer-stabilized Fe(0) nanoparticle (Fe NP) catalysts in ethanol or water in a flow reactor. Alkenes, alkynes, aromatic imines and aldehydes were hydrogenated nearly quantitatively in most cases. Aliphatic amines and aldehydes, ketone, ester, arene, nitro, and aryl halide functionalities are not affected, which provides an interesting chemoselectivity. The Fe NPs used in this system are stabilized and protected by an amphiphilic polymer resin, providing a

unique system that combines long-term stability and high activity. The NPs were characterized by TEM of microtomed resin, which established that iron remains in the zero-valent form despite exposure to water and oxygen. The amphiphilic resin-supported Fe(0) nanoparticles in water and in flow provide a novel, robust, cheap and environmentally benign catalyst system for chemoselective hydrogenations.

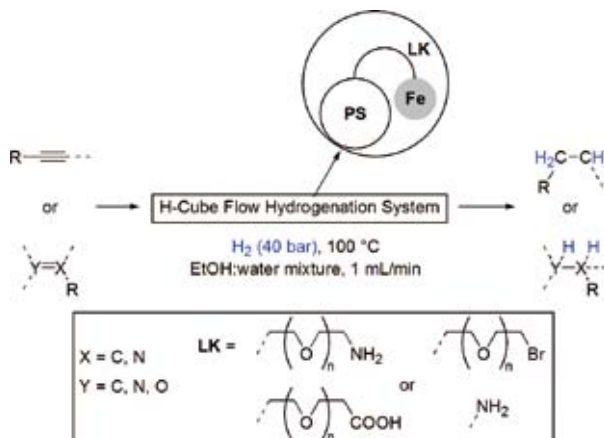


Figure 3. Schematic of hydrogenation reactions undertaken with polymer supported iron nanoparticles, under flow conditions (PS = polystyrene).

References

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- 2) Y. M. A. Yamada, H. Ohta, Y. Yuyama and Y. Uozumi, *Synthesis* **45**, 2093–2100 (2013).
- 3) R. Hudson, G. Hamasaka, T. Osako, Y. M. A. Yamada, C.-J. Li, Y. Uozumi and A. Moores, *Green Chem.* **15**, 2141–2148 (2013).

Awards

OSAKO, Takao; Shionogi & Co. Ltd., Award in Synthetic Organic Chemistry, Japan.

HAMASAKA, Go; Nagoya University Ishida Prize.