

Electrochemical Allylation Reactions Catalyzed by Nitrogen-Doped Carbon Supported Zinc Electrodes

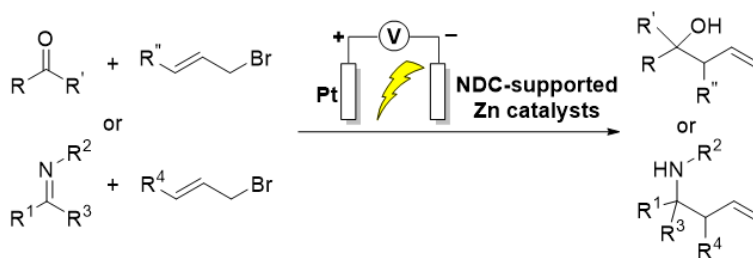
(School of Science, The Univ. of Tokyo) ○ Ryusuke MASUDA, Tomohiro YASUKAWA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Single-Atom Catalyst; Nitrogen-Doped Carbon; Electrochemical Reaction; Allylation Reaction

Heterogeneous catalysts have great advantages over homogeneous catalysts due to their reusability, applicability to continuous-flow reactions, and reducing wastes significantly. Nitrogen-doped carbon (NDC) is an attractive support for metal nanoparticles or single-atom catalysts to stabilize metal species by strong metal-nitrogen interactions.¹⁾ We have recently developed nitrogen-doped carbon incarcerated metal nanoparticle catalysts (NCI-M) prepared from poly(4-vinylpyridine) through a polymer-incarceration method for not only redox reactions but also carbon-carbon bond-forming reactions including asymmetric reactions.²⁾

Organometallic reagents hold a special place in organic synthesis because they have widespread synthetic applications based on carbon-carbon bond formation. However, in conventional methods, stoichiometric amounts of metal reagents are required in such transformations and large amounts of metallic wastes are generated, which have hindered applications to continuous-flow systems. Therefore, catalytic carbon-carbon bond-forming reactions without metallic wastes are required significantly.

We envisioned an electrochemical approach in which catalytic amounts of metals supported on nitrogen-doped carbon-based cathode form organometallic reagents and subsequent electroreduction after the reaction regenerates metal(0) on the cathode. We developed nitrogen-doped carbon-supported zinc catalysts and used them as an electrode to achieve electrochemical allylation reactions of carbonyl compounds and imines. In contrast to conventional allylation reactions using organometallic reagents, the system not only minimized metal-derived waste but also proceeded with a catalytic amount of zinc. It was also successfully applied to electrochemical continuous-flow reactions. The detail results will be reported in this lecture.



- ✓ catalytic amounts of Zn ✓ minimum amount of waste
- ✓ broad substrate scope ✓ application to flow reactions

1) He, Y.; Weniger, F.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 12582.

2) Yasukawa, T.; Yang, X.; Kobayashi, S. *Org. Lett.* **2018**, *20*, 5172.; Masuda, R.; Yasukawa, T.; Yamashita, Y.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2021**, *60*, 12786.