Nitrogen-Doped Carbon-Incarcerated Zinc Catalysts as Less Sacrificial Electrodes for Electrochemical Allylation Reactions

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

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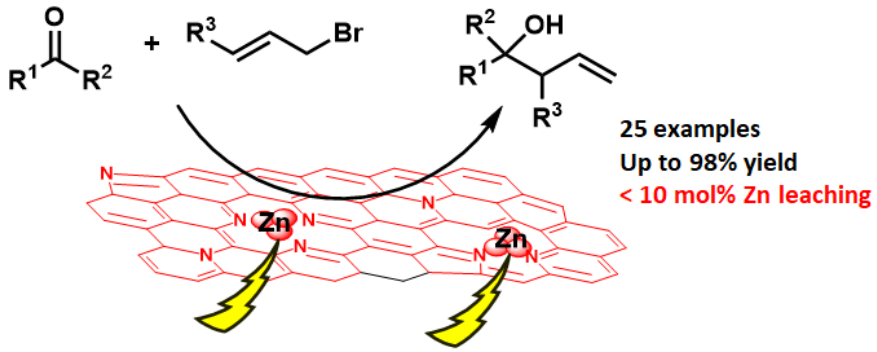
Metal nanoparticle catalysts have been of great interest because they can show unique activity and selectivity that differ from those obtained with bulk metals and metal complexes. The use of nitrogen-doped carbon (NDC) as a support would overcome many of limitations of metal nanoparticle catalysis for organic synthesis such as metal leaching because of strong interactions between nitrogen dopants and metals.[1)] However, electrochemical organic transformation, especially C−C bond-formation reactions, using electrodes prepared from NDC-supported metal catalysts remain challenging. These reactions are known to be clean and powerful redox processes that use electrons as traceless reagents. Indeed, bulk base metals such as zinc or iron are often consumed, and repeated use of such electrodes is still difficult. Recently, electrochemical allylation of carbonyl compounds in water using a zinc electrode has been developed with a catalytic amount of zinc consumed.[2)] Nevertheless, a large amount (ca. 25 mol%) of zinc still leached out and an excess amount of zinc was used in terms of substrate amount. Moreover, the system required a divided cell and substrate scope was limited.

We have developed electrochemical allylation reactions of carbonyl compounds using cathodes prepared from NDC-incarcerated zinc catalysts. A range of aldehydes and ketones afforded the desired allylic alcohols in high yields with <10 mol% zinc leaching. NDC-stabilized zinc nanoparticle species showed advantages in terms of scope for heteroaromatic substrates compared with bulk zinc electrodes and enabled to use an undivided cell. Heterogeneous nature of active species was suggested by the hot filtration test.



1) M. Beller, *et al*. *Angew. Chem. Int. Ed*. **2016**, *55*, 12582. 2) J. M. Huang, *et al*. *Chem. Commun*. **2010**, *46*, 2286.