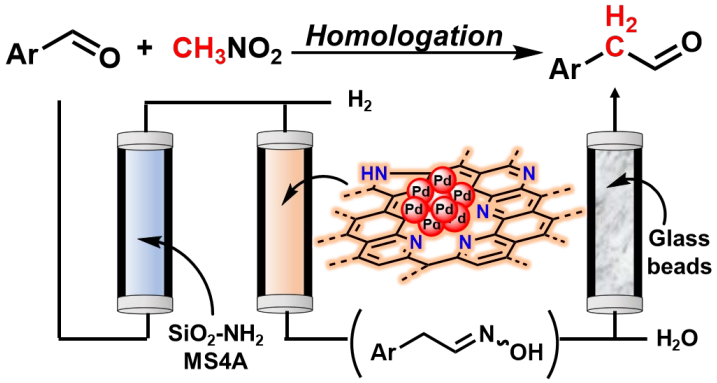
Homologation of Aryl aldehydes Using Nitromethane as a C1 Source with Nitrogen-doped Carbon Supported Palladium Catalysts

(GSC Social Cooperation Lab., The Univ. of Tokyo; School of Science, The Univ. of Tokyo) ○Tomohiro YASUKAWA, Yasuhiro YAMASHITA, Shū KOBAYASHI
Keywords: Heterogeneous Catalyst; Hydrogenation; Homologation Reaction; Flow Reaction; Nitrogen-doped Carbon

Homologation of aryl aldehydes provides useful synthetic intermediates. However, such a process requires multistep reactions with reactive reagents, which generates a significant amount of wastes and limits the scope. We designed such reactions using nitromethane as a C1 source via nitroolefin formation, partial hydrogenation to oximes, and hydration of oximes. To achieve this process, chemoselective hydrogenation reactions are needed. However, examples of selective hydrogenation of nitroolefins to oximes are very limited as it can produce several possible products. Reported systems required harsh conditions such as high pressure (10-20 bar) and substrate scope was limited.[1), 2)]

We recently developed nitrogen-doped carbon incarcerated palladium nanoparticle catalysts for selective hydrogenation of nitroolefins to oximes.[3)] The catalyst showed almost perfect selectivity, high activity, and reusability under ambient pressure. The nitrogen-dopants were essential to control the selectivity while dopant-free carbon-supported palladium catalysts gave a complex mixture.

Using the above-mentioned catalysts, three-step homologation reactions in both batch and flow systems were performed with only one purification step. Amino silica was used for the first nitroolefin formation step and the columns packed with heterogeneous catalysts were used for the flow reaction. A sequential contentious-flow system particularly worked efficiently to afford the product in high yield for more than two days.



1) A. Corma, *et al. JACS*, **2007**, *129*, 6358; 2) A. Wang, T. Zhang, *et al. Chem. Commun.* **2017**, *53*, 1969; 3) T. Yasukawa, S. Kobayashi, The 100th CSJ Annual Meeting, 4B8-37, 2020.