

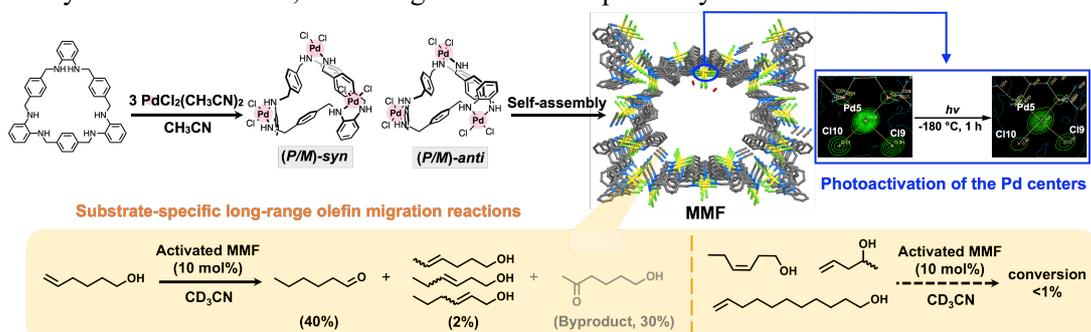
Development of substrate-specific long-range olefin migration reactions catalyzed by active palladium sites in a porous metal-macrocycle framework

(¹Graduate School of Science, the University of Tokyo, ²Institute for Catalysis, Hokkaido University, ³Institute for Molecular Science) ○Mengying Han,¹ Shohei Tashiro,¹ Takafumi Shiraogawa,² Masahiro Ehara,³ Mitsuhiro Shionoya¹

Keywords: Self-assembly; Porous crystal; Pd complex; Olefin migration; Heterogeneous catalyst

Encapsulation of substrates into the confined space of porous crystals with well-defined active sites on the pore surfaces improves reaction efficiency and selectivity, making them promising heterogeneous catalysts. Our group has previously reported the synthesis of metal-macrocycle frameworks (MMFs), novel porous crystals formed by the self-assembly of four stereoisomers of the trinuclear Pd^{II} complexes of macrocyclic hexamines. MMF has one-dimensional channels with a pore size of $1.4 \times 1.9 \text{ nm}^2$ and five enantiomerically-paired binding sites. Furthermore, the Pd-Cl bonds at the ceiling of the MMF channels were partially dissociated by photo-irradiation, and the activated Pd centers were found to function as the reaction sites for the olefin migration reaction of many aromatic substrates.^[1] In this study, we developed a method to use photo-activated MMF as a heterogeneous catalyst for olefin migration reactions^[2] and further extended the substrate range to several alkenyl alcohols. In particular, substrate-specific long-range olefin migration reactions were examined using MMF catalyst.

When 10 mol% photo-activated MMF was used as a catalyst, 5-hexen-1-ol underwent a long-range olefin migration reaction to give hexanal (40% conversion) as the main product. The total conversion of the internal olefin species was less than 2% throughout the reaction, indicating that the reaction proceeds by a chain-walking mechanism. On the other hand, the olefin migration using a homogeneous PdCl₂(MeCN)₂ catalyst proceeded in a stepwise manner, giving internal olefins as the main products. Theoretical calculations were applied to simulate the reaction pathway of the long-range migration reaction to further support the proposed reaction mechanism. Furthermore, due to the spatial effect of the MMF channels, alcohol substrates with long or branched chains and internal olefin structures hardly reacted under the catalytic action of MMF, indicating the substrate-specificity of the reactions.



[1] M. Shionoya, *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 16610. [2] M. Shionoya, *et al.*, *Chem. Asian J.* **2021**, *16*, 202.