

MERIT Internship Report

Mengying Han

Shionoya Lab. Department of chemistry, Graduate school of science

Period

10/4/2021 ~ 11/12/2021

Host Organization

Ehara Group, Institute for Molecular Science (IMS)

Research Topic

Theoretical studies on the mechanism of long-range olefin migration reactions catalyzed by porous supramolecular crystals

Research Summary

This part was abstracted for confidential reasons.

[Research Background and Purpose]

Our lab has developed a novel porous crystal, metal-macrocycle framework (MMF) which is formed by the self-assembly of four stereoisomers of macrocyclic Pd(II) complex. In previous research, we have succeeded in using pre-photoactivated MMF crystals as catalysts for the olefin migration reactions under a typical heterogeneous condition.^[1] With this method, we recently found that some substrates could undergo a long-range olefin migration reaction with good yields. During the reaction, the total conversion of the internal olefin species was very low, indicating that the long-range migration reaction proceeded by a chain walking mechanism. Furthermore, the reactions are substrate-specific, and substrates with the same functional group but longer or branched chains could not react.

To better clarify the reaction pathway of the MMF-catalyzed long-range olefin migration reaction and study the steric effects during the reactions which might lead to the substrate-specificity, I did internship at Ehara Group at IMS to study and conduct theoretical calculations about these reactions.

[Research Methods and Contents]

Gaussian 16 A.03 was used for all the calculations.

(1) Simulation of the reaction pathway of the long-range olefin migration of Substrate 1.

To simulate the reaction pathways of olefin migration in MMF nanochannels, computational model systems of Pd-H species were adopted to simulate the alkyl mechanism pathway. All calculations were performed by the density functional theory (DFT) with the B3LYP functional. The LANL2DZ basis set with relativistic effective core potential (RECP) was employed for the Pd atom. For the other atoms, 6-31G(d) or 6-311+G(d,p) basis sets was used.

Due to the functional group of Substrate 1, there were two possible reaction pathways. I calculated the energy of the selected intermediates of both pathways and made energy profiles of them. One pathway was considered as the real pathway of the long-range olefin migration reaction as the energy changes were more reasonable.

(2) Studies on the steric effects during the long-range olefin migration of Substrate 2.

Substrate 2 could not undergo the long-range olefin migration reaction. It was considered that the steric effects might result from (1) some part of Substrate 2 interacted with the inner walls of MMF nanochannels and (2) Substrate 2 couldn't rotate smoothly inside MMF channels due to its big size.

To simulate these situations, the Quantum Mechanics/Molecular Mechanics (QM:MM) calculation using the our own N-layer integrated molecular orbital molecular mechanics (ONIOM) method was applied. The QM/MM approach is a molecular simulation method that combines the strengths of the highly accurate quantum mechanics calculations and the highly efficient molecular mechanics calculations, thus allowing for the study of complicated chemical systems. Here, the inner QM cluster of the ONIOM calculation was composed of the substrate and the Pd-H and/or Pd-Cl species and was treated by the DFT with the B3LYP functional. The LANL2DZ and 6-31G(d) were adopted as the basis sets. For the outer QM region which describes the environmental effects of the single nano-channel of the MMF, the semi-empirical PM6 method was employed. The MMF structure used here was obtained from its SXRD structure.

The results were as follows. (1) Even if Substrate 2 interacts with MMF, the energy of the system would not be significantly higher than the case where no interactions existed. (2) The energies of the intermediates of Substrate 2 during the rotation didn't differ largely, therefore the rotation seemed to be able to proceed smoothly.

In this research, the reaction pathway of Substrate 1 has been successfully clarified with theoretical calculations. Although the nonreactivity of Substrate 2 hasn't been well explained by the proposed two reasons, continuous efforts will be made in the future to solve the problem through experiments and theoretical calculations.

Acknowledgement

I would like to express my sincere gratitude to Prof. Masahiro Ehara for teaching me knowledge and skills about theoretical calculations and providing guidance on my research both at IMS and remotely when I went back to UTokyo. I also want to thank Dr. Pei Zhao for teaching me the usages of different software related to calculations. I'm also grateful for my supervisors, Prof. Mitsuhiko Shionoya and Prof. Shohei Tashiro for supporting me to participate in this internship and offering guidance on my research. Finally, I would like to thank MERIT program for supporting my internship with financial aids.

References

[1] M. Shionoya, et al, *Chem. Asian J.* **2021**, *16*, 202-206.