

Theoretical Study on Reaction Pathway and Ligand Design for Nitrogen Fixation Catalyzed by Molybdenum Complexes

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(モリブデン錯体を用いた触媒的窒素固定の反応経路と配位子設計に関する理論的研究)

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論 文 内 容 の 要 旨

Nitrogen fixation, which converts chemically inert dinitrogen (N_2) to reactive ammonia (NH_3), is an important catalytic process in modern industrial chemistry. In industry, the Haber-Bosch process is energy-intensive, requiring harsh reaction conditions of high temperature and high pressure with synthesis gas (H_2). On the other hand, in nature, NH_3 is catalytically produced by the enzyme nitrogenase under mild conditions of room temperature and atmospheric pressure. Achievement of artificial nitrogen fixation under mild conditions is considered one of the challenging topics. One of the promising ways for it is to develop molecular catalysts with Mo centers, which are contained in the active site FeMo-cofactor of nitrogenase. The author performed density functional theory (DFT) calculations for reaction analyses and ligand designs for molecular catalysts containing molybdenum atoms in this thesis. General Introduction of this thesis is given in Chapter 1.

In Chapter 2, the author analyzed a reaction mechanism for nitrogen fixation catalyzed dinitrogen-bridged dimolybdenum-dinitrogen complexes bearing PNP and PCP-type pincer ligands $[MoL(N_2)_2]_2(\mu-N_2)$ ($L = PNP$ or PCP) using DFT calculations. The author proposed a catalytic cycle that maintains an $Mo-N\equiv N-Mo$ moiety for converting a terminal N_2 ligand to NH_3 . The DFT calculations revealed that a formal charge imbalance between metal centers, such as $Mo^I-N\equiv N-Mo^0$ rather than $Mo^0-N\equiv N-Mo^0$, is important for protonation of the terminal N_2 ligand, which is considered the most difficult reaction step in the catalytic cycle.

The dinitrogen-bridged dimolybdenum-dinitrogen complexes with $Mo^I-N\equiv N-Mo^0$ or

$\text{Mo}^0\text{-N}\equiv\text{N-Mo}^0$ moieties in Chapter 2 reductively activate a terminal N_2 ligand and undergo the catalytic cycle following the classical Yandulov-Schrock cycle. On the other hand, a dinitrogen-bridged dimolybdenum-dinitrogen complex with a more oxidative $\text{Mo}^I\text{-N}\equiv\text{N-Mo}^I$ moiety, which should be yielded by two-electron reduction of an Mo-trihalide complex $[\text{MoI}_3(\text{PNP})]$ or $[\text{MoCl}_3(\text{PCP})]$, promotes an N–N bond cleavage of the bridging N_2 ligand, resulting in a shortcut of the Yandulov-Schrock cycle. In Chapter 3, this difference in the catalytic cycle was explained in terms of the electronic structure of the $\text{Mo-N}\equiv\text{N-Mo}$ moiety of the dinitrogen-bridged dimolybdenum complex. The more oxidative $\text{Mo}^I\text{-N}\equiv\text{N-Mo}^I$ moiety produces two equivalents of stable Mo^{IV} -nitride complexes via the N–N bond cleavage. On the other hand, the extra electrons in the $\text{Mo}^0\text{-N}\equiv\text{N-Mo}^0$ moiety occupy the p-antibonding $\text{Mo}\equiv\text{N}$ bond of the Mo^{III} -nitride complex after the cleavage, thus prohibiting the cleavage reaction.

In Chapter 4, the author designed PCP ligands based on DFT calculations. The excellent catalytic activity of the nitrogen fixation has been exhibited using an Mo-trihalide complex bearing the PCP ligand $[\text{MoCl}_3(\text{PCP})]$ as a molecular catalyst in the presence of water as a proton source and SmI_2 as an electron source. Focusing on the PCET process to the Mo-nitride complex $[\text{MoIN}(\text{PCP})]$ in the catalytic cycle, the author designed PCP ligands to control the electronic state of Mo-PCP complexes by introducing substituents and fused benzene rings into the PCP ligand. The author estimated the catalytic activity from the strength of the formed N–H bond of the corresponding Mo-imide $[\text{MoI}(\text{NH})(\text{PCP})]$. As a result, introducing electron-withdrawing substituents and fused benzene rings into the PCP ligand leads to the enhance in the strength of the N–H bond, because of the enhancement of the p-accepting ability of the PCP ligand. Thus, the author succeeded in proposing a direction for ligand design for nitrogen fixation catalyzed by the molybdenum complex.

General conclusion has been shown in Chapter 5. In this thesis, the author performed DFT calculations to develop molecular catalysts containing molybdenum atoms for nitrogen fixation through understanding and ligand design of the molecular catalysts. The molecular catalysts are unique because their catalytic cycle includes dimolybdenum intermediates with an $\text{Mo-N}\equiv\text{N-Mo}$ moiety. In reaction analyses, the role of the $\text{Mo-N}\equiv\text{N-Mo}$ moiety in the catalytic reaction is theoretically explained. In ligand designs, focusing on the most important reaction step in the catalytic cycle, the author proposed strategies and useful indicators for the ligand design obtained by DFT calculations.

〔作成要領〕

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