

立方体型[Mo₃S₄Pd]クラスターを触媒とするプロトン還元反応機構解析

Calculation on the mechanism of proton reduction catalyzed by cubic [Mo₃S₄Pd] clusters

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研究成果概要

Background: Transition metal complexes and clusters can be used as homogeneous catalysis to perform N₂ reduction and catalytic H₂ evolution under mild conditions. Quantitative mechanistic details are very important for experimental researchers to understand atomic scale chemical events. In this direction, quantum chemical calculations, employing Density functional theory (DFT), are essential.

Objectives: The Ohki group at the ICR developed a [Cp^{SiEt₃}₃Mo₃S₄Pd]Cl cluster that can perform hydrogen evolution in the presence of HOCH₂CF₃. A detailed computational study was performed to rationalize the mechanisms of the full catalytic cycle.

Computational methods: The possible spin states [Cp^{SiEt₃}₃Mo₃S₄Pd]Cl cluster and the mechanism of the hydrogen evolution and catalytic reduction of CO₂ to CO were calculated using DFT.

Results and discussions: The ground state of the [Cp^{SiEt₃}₃Mo₃S₄Pd]Cl is the closed-shell singlet, $S = 0$. Starting from this, the active intermediate, [Cp^{XL}Mo₃S₄Pd], can be formed through a free energy barrier of 26.4 kcal/mol. After that, subsequent protonation and one electron reduction steps occur through relatively low energy barriers to produce H₂. This study gave important electronic structural and mechanistic implications to develop novel transition metal clusters for catalytic H₂ evolution under mild conditions. The mechanism of the catalytic reduction of CO₂ to CO is under investigation.

発表論文(謝辞あり)

H. Izu, D. G. Bhave, Y. Matsuoka, W. M. C. Sameera, K. Tanifuji, Y. Ohki, “Synthesis, Characterization, and Catalytic Activity of a Cubic [Mo₃S₄Pd] Cluster Bearing Bulky Cyclopentadienyl Ligands”, *Eur. J. Inorg. Chem.* 2023, 26, e202300399.