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令和4年度　　京都大学化学研究所　スーパーコンピュータシステム　利用報告書

CO が配位した生体模倣型[Mo_3S_4M] (M = Fe, Co, Ni)クラスター錯体の理論計算
CO-Bound Biomimetic [Mo_3S_4M] (M = Fe, Co, Ni) Clusters: A Computational Study

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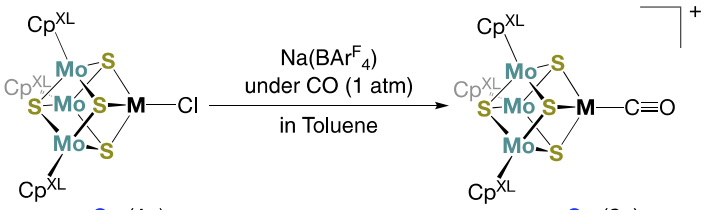
研究成果概要

Transition metal clusters can be used as catalysts to perform chemically or biologically relevant reactions.[1,2] Relationships between the electronic structure and reactivity can be established by employing density functional theory (DFT). We have developed [Mo_3S_4M]-type clusters (M = Fe, Co, Ni), consisting bulky cyclopentadienyl ligands (Cp^{XL}, $C_5Me_4SiEt_3$). CO can be coordinated to [Mo_3S_4M] cubes. According to experimental data, $[Cp^{XL}{}_3Mo_3S_4M(CO)]^+$ (M = Co, Ni) is stable, while $[Cp^{XL}{}_3Mo_3S_4Fe(CO)]^+$ complex revealed unexpected instability. Their M-CO interactions were analyzed by DFT calculations.

An energy decomposition analysis (EDA) together with the natural orbitals for chemical valence (NOCV) was performed to rationalize the M-CO interactions. The interaction energy between M and CO follows the order of Fe-CO (-101.1 kcal/mol) > Co-CO (-81.5 kcal/mol) > Ni-CO (-77.3 kcal/mol). In all three cases, orbital interactions become dominant compared to electrostatic, dispersion, and solvent interactions. According to EDA-NOCV, π back-donation from Co to π*(CO) is stronger than σ CO to M(d) σ donation for all three systems. These findings give quantitative insights to develop bio-mimetic catalysts for the direct conversion of CO into hydrocarbons.



発表論文（謝辞あり）

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(2) W. M. C. Sameera, Y. Takeda, Y. Ohki, "Transition Metal Catalyzed Cross-coupling and Nitrogen Reduction Reactions: Lessons from Computational Studies", *Adv. Organomet. Chem.*, **78**, 35-78 (2022).

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