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|  | Ken Sakai |
| | Professor, Department of Chemistry, Faculty of Science, Kyushu University; Principal Investigator, International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University; Professor, Center for Molecular Systems (CMS), Kyushu University |
| | ksakai@chem.kyushu-univ.jp |
| | http://www.scc.kyushu-u.ac.jp/Sakutai/sakai_group_top.html |

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|  | Kosei Yamauchi |
| | Assistant Professor, Department of Chemistry, Faculty of Science, Kyushu University, International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University |
| | kyamauchi@chem.kyushu-univ.jp |
| | http://www.scc.kyushu-u.ac.jp/Sakutai/sakai_group_top.html |

Research keywords: Artificial Photosynthesis, Molecular Catalysis, Water Oxidation, Hydrogen Evolution, CO₂ reduction, Photocatalysis, Homogeneous Electrocatalysis, Kinetics, DFT calculations

Over the past decade, our group has focused on the molecular systems relevant to photosynthetic molecular devices.¹⁻¹¹ Our targets involve the studies on (i) water oxidation catalysis in order to uptake protons and electrons required for fuels generation, (ii) catalytic water or CO₂ reduction into sustainable fuels (*i.e.*, H₂, CO, etc.), (iii) artificial light-harvesting systems towards the effective charge separation and/or migration, and so on. In order to develop the more desirable/efficient systems in promoting all relevant processes, substantial efforts have been devoted to more carefully study the reaction kinetics and equilibria in solution that are relevant to each topic. Various techniques have been adopted to better understand the mechanistic aspects relevant to all of our systems. Some of the reaction steps of interest are not observable by any experimental techniques, and must be discussed on the basis of our DFT results, which also greatly helped us understand the mechanism of reactions. Importantly, one of our findings is that, in any catalysis, the reactivity of metal(s) can be rationally tuned by use of redox active ligands that are more or less hybridized with metal(s) in their orbitals. Such issues are often involved in our discussion. Our studies have provided new aspects on photo-induced multi-charge separation,⁵ near-infrared-driven water reduction,⁴ water oxidation catalysis using various transition metal complexes,^{1,9,11} non-precious metal based water reduction,^{2,6,10} photoelectrochemical cells for the overall water splitting,^{3,7} and cobalt porphyrin CO₂

reduction catalysis in fully aqueous media.⁸

As part of these studies, our group reported that a monocobalt polyoxometalate (Co-POM-Mo) and dicobalt (Co₂-POM-Mo) polyoxometalates (Figure 1) serves as an efficient homogeneous water oxidation catalyst (WOC) in the well-known [Ru(bpy)₃]²⁺/S₂O₈²⁻ photochemical system.¹ Under our experimental conditions, we found that both Co-POM-Mo and Co₂-POM-Mo are capable of catalyzing water oxidation, and exhibit greater turnover frequencies and turnover numbers relative to the previously reported tetracobalt polytungstate Co₄-POM-W ([Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻).

Our very recent studies involve attempts to clarify the mechanism of water oxidation by the simplest Co POM catalyst, i.e., Co-POM-Mo.¹¹ Using [Ru^{III}(bpy)₃](ClO₄)₃ as a sacrificial oxidant, a reaction of Co-POM-Mo and [Ru^{III}(bpy)₃]³⁺ has been observed using the stopped-flow technique at various catalyst concentrations and different

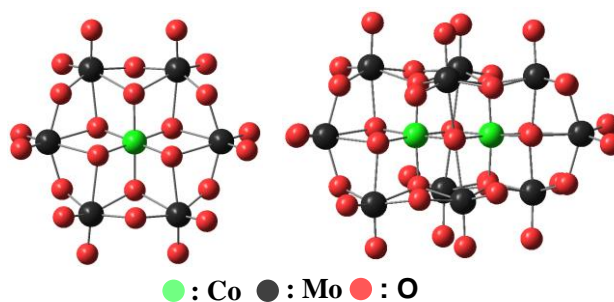


Figure 1. Co-POM-Mo and Co₂-POM-Mo.

temperatures to estimate the activation parameters for this reaction. Importantly, our DFT results are in favor of the development of a peroxo-bridged fragment via the O-O bond formation between the Co- and Mo-bound oxygen atoms upon two-electron oxidation.¹¹

Possible collaboration: Automatic H₂/O₂ gas measurement, Low temperature stopped-flow, Nanosecond Transient absorption spectroscopy, Picosecond luminescence lifetime measurement, DLS, Homogeneous electrocatalysis (TOF and overpotential estimation), Mechanistic investigation based on DFT calculations, and so on.

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Sakai,

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