

In the environment and also in cell, Inorganic small molecules, such as O₂, H₂O₂, and NO, are ubiquitous, therefore their selective conversion is essential to maintain biological functions. Conversion of inorganic small molecules are difficult to control due to the large variety of intermediate species in their reactions. Biological systems control small molecule redox processes by employing finely-designed transition-metal complexes embedded in protein scaffolds. This fact encourages us to understand reaction of inorganic small molecules at the molecular level. In this view point, I investigated reaction intermediate generated in reactions of late-transition-metal complex and inorganic small molecules.

(1) Activation of H₂O₂

Hydrogen peroxide (H₂O₂) is cheap and environmentally benign oxidant producing water as a sole bi-product. Reaction of H₂O₂ was examined with di-(μ-oxido)di-nickel(II) complex supported by a pyridyl-alkylamine ligand at -30°C. The generated species showed high reactivities toward various organic substrates at the temperature. The reactive species was fully characterized as di-(μ-oxido)dinickel(III) complex with UV-vis, EPR, resonance Raman, and CSI-MS spectroscopy. The X-ray crystal structure of the complex was successfully obtained by careful handling of its unstable crystal. Its electronic structure was further discussed based on its SQUID and EPR data, and DFT calculations based on X-ray structure. As a result, this complex was found to be the first example of di-(μ-oxide)di-nuclear-metal complex with ferromagnetically coupled metal centers [*Angew. Chem., Int. Ed.* **2018**, *57*, 7640–7643 (DOI: 10.1002/anie.201802779)].

Catalytic activity of nickel complexes with similar ligand systems were examined toward benzene hydroxylation with hydrogen peroxide. One of the nickel complexes exhibited highly reactivity and selectivity for formation of phenol product. This system was also applicable to toluene hydroxylation. Remarkably, *p*- and *o*-cresol were generated in the catalytic system rather than benzyl alcohol [*J. Am. Chem. Soc.* **2015**, *137*, 10870-10873 (DOI: 10.1021/jacs.5b04104)].

Alkyl hydroperoxides can be generated from H₂O₂, and they show similar tendencies in with H₂O₂, therefore their reactivity with transition-metal complex were also investigated to gain insight into O-O bond activation reaction [*J. Am. Chem. Soc.* **2015**, *137*, 10870-10873 (DOI: 10.1021/jacs.5b04104); *J. Inorg. Biochem.* **2017**, *177*, 375-383 (DOI: 10.1016/j.jinorgbio.2017.08.016); *Chem.–Eur. J.* **2019**, *25*, 11157–11165 (DOI: 10.1002/chem.201902669)].

(2) Activation of NO

Nitric oxide (NO) is found in our body as a neurotransmitter and a messenger molecule. Current our society utilizes catalysts to purify huge volume of NO gas

emitted from turbine in power plants, vehicle engines, etc. Therefore, the fundamental reaction mechanism of NO with transition-metal ions merits considerable attentions. I investigated reactions of NO with copper complexes supported by pyridyl-alkylamine ligand systems. Copper(I) complexes were oxidized to the corresponding copper(II) complexes generating N_2O and NO_2^- . Notably, the copper(II) complexes with the same series of ligand system reacted with NO. Reaction rates for those two types of reaction can be explained by redox potentials of those copper(I/II) complex; copper(I) complexes with more negative oxidation potential show higher reactivity, and copper(II) complexes with more positive reduction potentials show higher reactivity, respectively. One of the copper(II) complex reacted with NO to produce Cu-NO adduct with a characteristic N=O stretching IR peak around 1640 cm^{-1} . This adduct decayed in the presence of alcohol and amine to generate corresponding nitroso alcohol and nitroso amine, respectively. The reaction was kinetically analyzed by UV-vis and NMR spectroscopies [This will be presented in the 100th CSJ annual meeting].

(3) Activation of O_2

Molecular oxygen (O_2) is abundant oxidant, however its reaction is hard to control. I studied the effect of coordination structure of copper complex on its reactivity toward O_2 [*Inorg. Chem.* **2014**, *53*, 8786-8794 (DOI: 10.1021/ic501461n); *Inorg. Chim. Acta* **2018**, *471*, 91-98 (DOI: 10.1016/j.ica.2017.10.031); *Z. Anorg. Allg. Chem.* **2018**, *644*, 780-789 (DOI: 10.1002/zaac.201800083); *Eur. J. Inorg. Chem.* **2018**, 1976-1983 (DOI: 10.1002/ejic.201800029); *Commun. Chem.* **2019**, *2*, Article number: 12 (DOI: 10.1038/s42004-019-0115-6)]. Also examined was application of copper-oxidase to organic synthesis [*Eur. J. Org. Chem.* **2018**, 1789-1796 (DOI: 10.1002/ejoc.201800188)].