

Preparation, In situ Characterization, and Functionalization of Catalyst Surfaces by the Immobilization and Coordination Control of Multi-Metallic Complexes

A number of useful chemical products have been produced by heterogeneous catalysts with multi-metallic sites and the development of heterogeneous catalysts with high reactivity, stability, and selectivity is one of the challenging issues in many chemical fields. Cooperative interactions on multi-metallic sites often bring about integrated catalysis on heterogeneous surfaces; however, it is still difficult to control multi-metallic species on heterogeneous surfaces toward selective catalysis. I investigated the construction of heterogeneous surfaces by the immobilization and coordination control of multi-metallic complexes and converted their coordination structures to catalytically active species supported by in situ step-by-step characterization of catalyst surfaces. I also developed methods to functionalize multi-metallic structure-supported heterogeneous surfaces for selective catalysis.

(1) Chemical grafting of multi-metallic coordination complexes on amorphous solid surfaces

I prepared several multi-metallic coordination complexes with chemical grafting moiety onto amorphous solid surfaces (oxide surfaces, carbon surfaces), and succeeded in chemical grafting of the multi-metallic complexes regulating their coordination structures (Ref 11: *PCCP* **2012**, Ref 15: *Dalton Trans.* **2013**, Ref 21: *Chem. Lett.* **2014**, Ref 23: *PCCP* **2015**). The attachment and subsequent stepwise structural transformations of the multi-metallic complexes produced unique metal coordination structures, which were different from those in solutions or single crystals, and molecularly regulated, surface-bounded multi-metallic coordination complexes were successfully obtained. Stepwise characterization of the surface-bounded multi-metallic complexes revealed the coordination structures on the heterogeneous surfaces.

(2) In situ characterization of surface-coordinated multi-metallic complexes

I performed in situ stepwise characterization of surface-coordinated multi-metallic complexes (Ref 11: *PCCP* **2012**, Ref 15: *Dalton Trans.* **2013**, Ref 21: *Chem. Lett.* **2014**, Ref 23: *PCCP* **2015**) and found a unique surface-assisted hydrogenation mechanism on supported dimeric species (Ref 11: *PCCP* **2012**). The structural transformation at the interface of a coordinating Ir dimer and Al₂O₃ surface was found to be a key to hydrogenation catalysis and the role and dynamic behaviors of the coordination interface were proposed. The formation pathways of active Ru nanoclusters from coordinated Ru trinuclear complex were also revealed by in situ characterization (Ref 23: *PCCP* **2015**).

(3) Selective catalysis on surface-functionalized multi-metallic structures

I prepared catalytically active multi-metallic structures for selective catalysis based on the surface-coordinated multi-metallic complexes. Selective alcohol oxidation and selective hydrogenation of nitriles to primary amines were achieved on Ru nanoclusters that were formed directly on surface from surface-coordinated Ru trinuclear complexes (Ref 15: *Dalton Trans.* **2013**, Ref 23: *PCCP* **2015**). Surface modification by matrix overlayers made of polymers and molecular binding sites attained new functionalities to the catalytically active metal centers. A stable catalytically active Mn center was obtained by surrounding a surface-coordinated Mn oxotetranuclear complex with a polymer matrix overlayers while maintaining high selectivity for olefin epoxidation (Ref 18: *ACS Catal.* **2013**). A shape-selective imprinted cavity whose shape was similar to a template ligand, and a molecular binding site that had a strong binding constant to a target molecule, were able to create in the close proximity to catalytically active metal centers, and enhanced reactivity, regio- and shape-selectivity on the target molecule were achieved (Ref 9: *Chem. –Eur. J.* **2012**, Ref 13: *Acc. Chem. Res.* **2013**, Ref 16: *Chem. Commun.* **2013**).