

Local Coordination Structures of SiO₂-Supported Coordinatively Unsaturated Ru Complex for Alkene Epoxidation

We have prepared a Ru-monomer complex on an SiO₂ surface, which was found to be active for the selective oxidation of aldehydes and the epoxidation of alkenes. The local coordination structures of the SiO₂-supported Ru-complex catalysts were characterized by means of Ru K-edge EXAFS combining FT-IR, SS-NMR, DR-UV/vis, XPS, etc. The Ru K-edge EXAFS suggested the formation of isolatedly located, unsaturated Ru-monomer complex on SiO₂. The attachment of the Ru complex onto the SiO₂ surface inhibited the unfavorable aggregation of the catalytically active Ru complex under reaction conditions and we found that the reaction mechanism switched over from the sole oxidation of aldehyde to alkene epoxidation with co-oxidation of aldehyde on the catalyst.

Many useful chemicals are produced by heterogeneous catalysts, which offer not only easy separation of catalysts and products from reaction media but also high durability and unique catalytic activity derived from unique structures of active metal species on supported surfaces. We prepared an SiO₂-supported Ru complex by selective ligand elimination on the SiO₂ surface and found the formation of an isolatedly located, unsaturated Ru-monomer complex, which was active for alkene epoxidation reaction using aldehyde/O₂.

The SiO₂-supported unsaturated Ru complex was prepared via step-by-step reactions in three steps using (*p*-cymene)Ru{[H₂NCH₂CH₂NHSO₄C₉H₇]Cl} as a precursor. The precursor complex was grafted to the *p*-styryl moiety functionalized on an SiO₂ surface. Further treatment by isobutyraldehyde (IBA) and O₂ promoted the selective elimination of the *p*-cymene ligand from the supported Ru complex, forming an unsaturated

Ru-monomer complex on SiO₂. The Ru complexes synthesized/transformed on the SiO₂ surface were characterized by ¹³C and ²⁹Si solid-state NMR, FT-IR, diffuse-reflectance UV/Vis, XPS, Ru K-edge EXAFS (Extended X-ray Absorption Fine Structure), and hybrid DFT calculations [1]. Ru K-edge EXAFS measured at AR-NW10A showed the local coordination structures of the SiO₂-supported Ru complexes, whose coordination numbers and bond distances are presented in Fig. 1. After the release of the coordinating *p*-cymene ligand, there were two chemical bonds: two Ru-N bonds (coordination number (CN) = 2.2 ± 1.5) at 0.207 ± 0.003 nm and a Ru-Cl bond (CN = 1.3 ± 1.5) at 0.234 ± 0.004 nm. No Ru-Ru bonding was observed in agreement with a Ru-monomer complex structure immobilized at the SiO₂ surface. All peaks of ¹³C NMR attributed to the *p*-cymene ligand disappeared, agreeing with the curve-fitting results of Ru K-edge EXAFS.

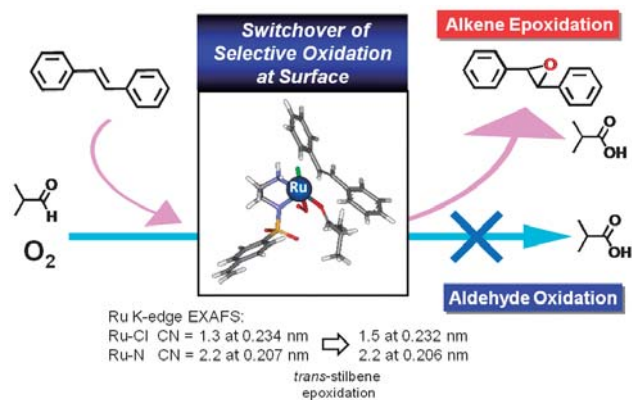


Figure 1
Scheme of switchover of selective oxidation reaction on SiO₂-supported Ru complex and curve-fitting results of Ru K-edge EXAFS of the supported Ru complex.

The site-isolated Ru-monomer complex on SiO₂ achieved selective *trans*-stilbene epoxidation with turnover number (TON) of 2,100,000. We also found that the IBA sole oxidation with the activation energy of 48 kJ/mol, which is much easier than the *trans*-stilbene epoxidation with the activation energy of 99 kJ/mol, was significantly suppressed by the coexistence of *trans*-stilbene. The switchover of the oxidation pathways from the IBA sole oxidation to the *trans*-stilbene epoxidation with co-oxidation of IBA can be explained in terms of energy profiles for the alternative selective oxidation pathways, resulting in the preferential coordination of *trans*-stilbene to the Ru-complex at the surface.

After the catalytic epoxidation of *trans*-stilbene, the structure of the unsaturated Ru complex remained unchanged. Ru K-edge EXAFS showed two kinds of chemical bonds of Ru-Cl (CN = 1.5 ± 2.3, bond distance = 0.232 ± 0.006 nm) and Ru-N (CN = 2.2 ± 1.8, d = 0.206 ± 0.003 nm), and these structural parameters were almost the same as those for the 3-coordinated unsaturated Ru-monomer structure before the epoxida-

tion reaction. This kind of unsaturated species easily aggregates in solutions and indeed the elimination of *p*-cymene caused the aggregation of the formed unsaturated Ru species in the case of the homogeneous Ru-precursor complex. The low stability of unsaturated metal complexes leading to aggregation or decomposition in solutions prevents the exploitation of metal-complex catalysis. The attachment of metal-complex on support surfaces for the isolation of unsaturated metal centers is a promising, powerful platform not only for improving catalytic activity but also for clarifying the key issues for selective catalysis by metal-complex structures.

REFERENCE

- [1] M. Tada, S. Muratsugu, M. Kinoshita, T. Sasaki and Y. Iwasawa, *J. Am. Chem. Soc.* **132** (2010) 713.

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