

Advanced Design and In-Situ Time-Resolved Analysis of Catalyst Surfaces

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1. Advanced Design of Catalytically Active Structures at Surfaces

Although many useful chemicals have been produced by heterogeneous solid catalysts, the molecular-level design of heterogeneous catalyst surfaces has not been established yet. On heterogeneous catalyst surfaces with the limited accessibility of reactants, rate enhancement and new catalysis can often be obtained on novel unsaturated metal structures, which are hard to be isolated in homogeneous solutions. We have succeeded in preparing novel catalytically active structures on oxide surfaces for selective catalysis by attaching techniques of some organic acid-base catalysts or metal-complex catalysts.¹⁻⁶⁾



Figure 1. The step-by-step preparation and photo-induced structural transformations of novel unsaturated Ru complexes on a SiO₂ surface for the selective photo-oxidation of cycloalkanes.¹⁾

For examples, the photo-irradiation of a Ru complex supported on a SiO₂ surface was found to promote the selective formation of two different unsaturated Ru complexes under O₂ or N₂ atmosphere, one of whose structures with an appropriate Ru–H conformation efficiently catalyzed the selective photo-oxidation of cycloalkanes with O₂. The active Ru complex

immobilized at double sites on SiO₂ was prepared by the photo-induced selective elimination of a *p*-cymene ligand accompanied with dissociative coordination of a surface OH group to the unsaturated Ru center (Figure 1). The two supported Ru complexes were reversible for the structural transformation by photo-excitation with different wavelength and atmospheres.¹⁾

2. Design of Molecular-Imprinted Metal-Complex Catalysts for Regio- and Shape-Selective Catalysis

Molecular imprinting of supported metal complex in which a specific ligand serves as a prescribed template is devoted to tailor-made design of catalyst architecture for selective integrated catalysis. A selective reaction cavity memorized the shape and coordination environment of a ligand, which is a template for molecular imprinting, can be selectively created right beside an unsaturated active metal atom on a support surface. We have designed and prepared a novel molecular-imprinted Ru-complex catalyst on a SiO₂ surface and succeeded in regulating the regio- and shape-selective epoxidation of limonene using O₂.

A molecular-imprinted Ru-complex catalyst was prepared by following step-by-step procedures: (1) the attachment of a precursor Ru complex onto a SiO₂ surface, (2) the coordination of limonene-10-ol (template), which possesses a similar shape to an intermediate of terminal C=C bond epoxidation of limonene, (3) stacking of surface SiO₂-matrix overlayers, and (4) the removal of the template ligand to create a shape-selective reaction space (cavity) on the active Ru site (Figure 2). The structures of the supported and molecular-imprinted catalysts were characterized by means of solid-state NMR, FT-IR, XRD, XRF, UV/Vis, BET, and XAFS. We found that the molecular-imprinted catalyst designed for the terminal C=C bond epoxidation of limonene exhibited fine shape selectivity discriminating a methyl group of alkene reactants and high regioselectivity for the epoxidation of the terminal C=C bond of limonene.

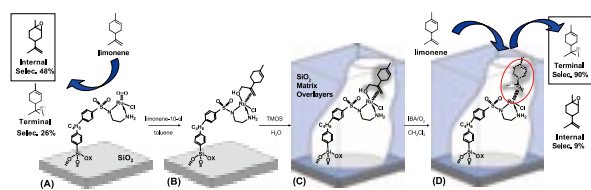


Figure 2. Design of a molecular-imprinted Ru-complex catalyst for the terminal C=C bond epoxidation of limonene.

We have also designed novel molecular-imprinted Ru catalysts for the asymmetric transfer hydrogenation of ketones. Molecular recognition sites spatially locating the imprinted matrix was designed at the molecularly imprinted catalyst surface for the first time.

3. In-Situ Time-Resolved XAFS and Raman Spectroscopy for Reaction Mechanism of Selective Alcohol Oxidation on Supported Vanadium Catalysts

Vanadium is one of the most active metals for oxidation catalysis and supported V catalysts on various oxide surfaces have been utilized for selective alcohol oxidation to aldehyde at low temperatures. Their catalytic activity and aldehyde selectivity highly depend on the structures of supported V species, however the catalytic reaction mechanism of selective alcohol oxidation has not been demonstrated yet. We have developed in-situ time-resolved energy-dispersive XAFS (DXAFS) and in-situ time-resolved Raman spectroscopy, which can monitor dynamic structural changes in active catalysts *under working conditions in real time*,⁷⁾ and the structural kinetics and reaction mechanism of selective ethanol oxidation on V/SiO₂ and V/ γ -Al₂O₃ catalysts were investigated.

Figure 3 shows a series of V K-edge DXAFS spectra recorded every 150 ms for the oxidation of ethanol on a V/ γ -Al₂O₃ catalyst. The analysis of DXANES spectra revealed rate constants and activation energies for the oxidation/reduction and symmetry changes of the active V catalyst. Ethanol smoothly reacted with V⁵⁺ species, forming the stoichiometric amount of acetaldehyde, and the V catalyst reduced with the rate constant of 0.19 s⁻¹. The further adsorption of ethanol varied the symmetry of the supported V species with the rate constant of 0.12 s⁻¹. When O₂ admitted to the reduced V catalyst, CO and CO₂ were obtained as major C products. The rate constants and activation energies for the V oxidation were estimated to be 1.59 s⁻¹ and 52 kJ mol⁻¹, respectively. These results suggest

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that low acetaldehyde selectivity on the V/ γ -Al₂O₃ catalyst is caused by the oxidation process with O₂ on the reduced V species.

On the other hand, a SiO₂-supported V catalyst exhibited high acetaldehyde selectivity and there were no significant changes in in-situ V K-edge XAFS and Raman spectroscopy. On the SiO₂ surface, it is suggested that the bond breaking of a V–O–Si bond forms a V–O–Et species, which selectively converts to acetaldehyde. The in-situ time-resolved DXAFS and Raman spectroscopy revealed the relationship between the structures of supported V species and their ethanol oxidation performances, the structural kinetics of the active V catalysts, and the reaction mechanism of the ethanol oxidation catalysis for the first time.

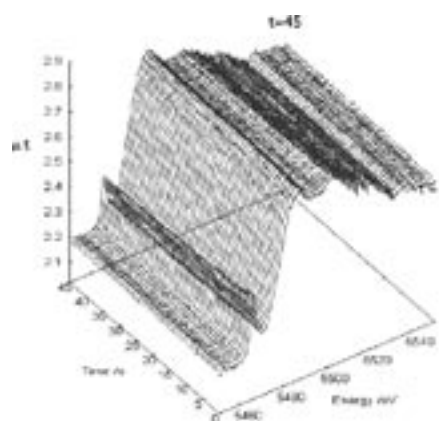


Figure 3. A series of V K-edge DXAFS spectra for the selective oxidation of ethanol on a V/ γ -Al₂O₃ catalyst at 553 K. DXAFS spectra were recorded every 150 ms and presented every 900 ms.

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