Advanced Design and In-Situ Characterization of Heterogeneous Catalyst Surfaces

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1. Surface Structure and Catalytic Oxidation Mechanism of SiO_2-Supported Ru Complex Catalyst

Chemical construction of heterogeneous catalyst surfaces on a molecular level toward selective catalysis has been still developing, and the attachment of metal complexes to oxide surfaces is one of the promising ways to create regulated metal structures grafted on oxide surfaces with unique catalytic properties. Stepwise structural transformations of supported metal complexes at surfaces, for instances, chemical grafting, selective ligand elimination, site isolation, surface functionalization, often produce molecularly regulated metal structures efficient for various catalytic reactions. In particular, chemical bonding between metal complexes and support surfaces is one of key issues to create novel metal structures, which are hard to obtain in homogeneous solutions, and anchoring metal complexes to support surfaces also prevents from catalyst deactivation through unfavorable aggregation of metal species under catalytic reaction conditions.

We have prepared a SiO_2-supported Ru-monomer complex coordinating with a *p*-cymene ligand and found that the coordinating *p*-cymene ligand selectively released by an exothermic reaction using a reactant for oxidation reaction (isobutyraldehyde).[1–3] The selective elimination of the *p*-cymene ligand produced a coordinatively unsaturated Ru center, whose structure is presented in Figure 1. The coordinatively unsaturated Ru complex supported on SiO_2 exhibited high activity for aldehyde oxidation and alkene epoxidation.[2]

The SiO_2-supported Ru-monomer complex achieved tremendous TONs (turnover numbers) for the selective oxidation of various aldehydes to corresponding carboxylic acids and alkenes to corresponding epoxides with good conversion and selectivity at ambient temperature, while the homogeneous Ru-precursor complex did not show good catalytic activity for both oxidation reactions. For examples, the TON of 38,800,000 for selective isobutyraldehyde (IBA) oxidation was achieved with the selectivity of 94% and the TON of 2,100,000 for *trans*-stilbene epoxidation using IBA/O_2 was achieved with the selectivity of 90%. Furthermore, the SiO_2-supported Ru catalyst could be recycled by simple filtration and both conversion and selectivity were still constant for several runs. Ru K-edge EXAFS analysis after the selective oxidation reactions indicated the high stability of the SiO_2-supported Ru complex catalyst under the catalytic oxidation conditions.

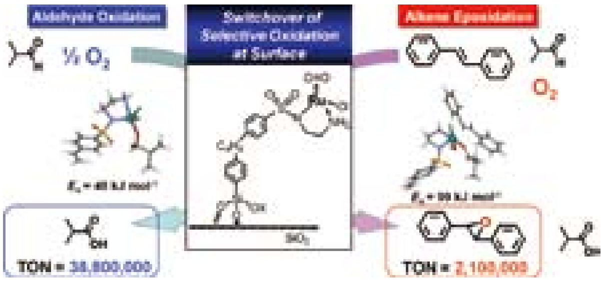

Figure 1. Switchover of selective catalytic oxidation reactions on the SiO_2-supported Ru complex catalyst.

We also found that the IBA sole oxidation with O_2, whose activation energy was 48 kJ mol^{-1} and was much smaller than that of the *trans*-stilbene epoxidation using IBA and O_2 (99 kJ mol^{-1}), was suppressed by the coexistence of *trans*-stilbene. During the catalytic epoxidation of *trans*-stilbene, co-existing IBA was stoichiometrically consumed for the epoxidation, and the facile IBA sole oxidation was found to be negligible. The switchover of the selective oxidation pathways from the IBA sole oxidation to the *trans*-stilbene epoxidation using IBA was explained in terms of energy profiles for the alternative selective oxidation pathways calculated by DFT, suggesting the preferential coordination of *trans*-stilbene to the active Ru complex at the surface.

2. Preparation, Characterization, and Shape-Selective Catalytic Performances of Molecularly Imprinted Ru-Complex Catalysts

Molecular imprinting of a supported metal complex whose ligand serves as a prescribed template is devoted to the design of shape-selective reaction space with a similar shape to the template. A molecularly imprinted cavity memorized the shape and coordination environment of the template ligand can be prepared on an unsaturated active metal center behind the template from the supported metal complex. We have designed and prepared a molecularly imprinted Ru-complex catalyst on SiO_2 and succeeded in regulating the regio- and shape-selective epoxidation of limonene.

A molecularly imprinted Ru-complex catalyst was prepared by step-by-step procedures: (1) the attachment of a Ru complex on SiO_2, (2) the coordination of limonen-10-ol (template), which possesses a similar shape to an intermediate of terminal C=C bond epoxidation of limonene, (3) stacking of surface SiO_2-matrix overlayers, and (4) the removal of the template ligand from the Ru site. The structures of the supported and molecularly imprinted Ru catalysts were characterized by solid-state NMR, FT-IR, XRD, XRF, UV/vis, BET, and Ru K-edge XAFS.

We found that the molecularly imprinted Ru 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 limonene epoxidation. Internal epoxide (62% selectivity) was preferably obtained on the supported Ru catalyst, while the molecularly imprinted Ru catalyst produced terminal epoxide of limonene with 63% selectivity. We found that the selectivity for the terminal epoxide increased to 90% and that for the internal epoxide decreased to 9% when SiO_2-matrix overlayers were prepared by the addition of 1.0 wt% 3-(2-imidazolin-1-yl)-propyltriethoxysilane to $Si(OCH_3)_4$ (TMOS). The basic compound was suggested to promote the hydrolysis-polymerization of TMOS, as a result, fine imprinted cavity for the limonene epoxidation was suggested to be prepared.

We have also designed novel molecularly imprinted Ru catalysts for the asymmetric transfer hydrogenation of ketones. An NH_2 binding site was spatially arranged on the wall of molecularly imprinted matrix overlayers as shown in Figure 2. A template ligand (**B**) with a carbamate moiety was coordinated to a SiO_2-supported Ru complex (**A**). (**B**) is composed of three parts: (**a**) *o*-hydroxybenzhydrol moiety, which is a molecularly imprinted structure and has a similar shape to the product of *o*-fluorobenzophenone (*o*-F-BP), (**b**) a carbamate moiety (–NHCOO–), and (**c**) a 3-triethoxysilylpropyl ($–Si(OC_2H_5)_3$) branch. Then, SiO_2-matrix overlayers were stacked by the chemical vapour deposition and during the subsequent hydrolysis- polymerization of TMOS, the branch ((**B**)-(**c**)) was taken in the wall of the SiO_2-matrix overlayers. Finally, the carbamate moiety ((**B**)-(**b**)) was broken to $–NH_2$, CO_2, and –OH, and then the coordination of (**B**)-(**a**) was removed to prepare the molecularly-imprinted Ru catalyst (**C**). The NH_2 binding site originally coordinated to the imprinted template (**B**)-(**a**) was fixed on the wall of the SiO_2-matrix overlayers and is regarded to be coordinated to the F-substituent of *o*-F-BP by hydrogen bonding. The molecularly imprinted cavity acted as an efficient reaction space for the shape-selective transfer hydrogenation of *o*-F-BP.

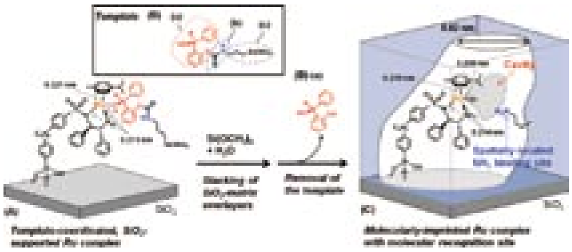

Figure 2. Design of a molecularly imprinted Ru-complex catalyst with a molecular binding site for asymmetric transfer hydrogenation of *o*-F-BP.

References

1) M. Tada, Y. Akatsuka, Y. Yang, T. Sasaki, M. Kinoshita, K. Motokura and Y. Iwasawa, *Angew. Chem., Int. Ed.* **47**, 9252–9255 (2008).
2) M. Tada, S. Muratsugu, M. Kinoshita, T. Sasaki and Y. Iwasawa, *J. Am. Chem. Soc.* **132**, 713–724 (2010).
3) M. Tada, *Bull. Chem. Soc. Jpn.* **83**, 855–876 (2010) (Award Accounts).

Awards

TADA, Mizuki; Presentation Award for Young Researcher (Catalysis Society of Japan).
TADA, Mizuki; 2010 The Young Scientist's Prize of The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan.
MURATSUGU, Satoshi; The 26th Inoue Research Award for Young Scientists (Inoue Foundation for Science).
MURATSUGU, Satoshi; CSJ Presentation Award 2010 (The Chemical Society of Japan).
MURATSUGU, Satoshi; The Royal Society of Chemistry Poster Prize (Japan-UK Symposium: Catalysis for a Sustainable World).

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