Design and In-Situ Characterization of Catalyst Surfaces

Department of Materials Molecular Science
Division of Electronic Structure

TADA, Mizuki	Associate Professor
MURATSUGU, Satoshi	Assistant Professor
WENG, Zhihuan	Post-Doctoral Fellow
MAITY, Niladri	Post-Doctoral Fellow
ZHANG, Shenghong	Post-Doctoral Fellow
WATTANAKIT, Chularat	Visiting Scientist
TABTHONG, Sittichoke	Visiting Scientist
THUMRONGPATANARAKS, Wipavee	Visiting Scientist
GAN, Raymond	Visiting Scientist
JIANG, Lu	Visiting Scientist
WANG, Fei	Graduate Student
SAIDA, Takahiro	Graduate Student*
ISHIGURO, Nozomu	Graduate Student†
KUSHIDA, Yuko	Graduate Student†
VU, Thang	Graduate Student‡
FUNAKI, Yukino	Technical Fellow
USUI, Chika	Technical Fellow
GONDO, Makiko	Technical Fellow
FUKUTOMI, Yukiyo	Secretary

1. Preparation of Molecularly Imprinted Ru-Complex Catalysts for Asymmetric Transfer Hydrogenation in Water

We have prepared molecularly imprinted metal-complex catalysts on oxide surfaces, whose ligand is utilized as a template. A molecularly imprinted cavity memorized the shape and coordination environment of a template ligand can be prepared on a catalytically active metal complex behind the template from the supported metal complex. We have prepared molecularly imprinted Ru-complex catalysts on a SiO_2 surface for asymmetric transfer hydrogenation in water by stacking of organic polymer-matrix overlayers on the SiO_2 surface for the molecular imprinting of the supported Ru complex.

Molecularly imprinted Ru-complex catalysts were prepared by step-by-step procedures illustrated in Figure 1: (1) the attachment of a Ru complex on SiO_2, (2) the coordination of a template ligand ((*R*)-1-(*o*-fluorophenyl)ethanol), which is the product of *o*-fluoroacetophenone hydrogenation, (3) stacking of surface matrix overlayers using organic or inorganic polymer matrices, and (4) the removal of the template ligand from the Ru complex. We utilized hydrophobic organic polymer matrices for the transfer hydrogenation in water media and conducted several methods to prepare surface matrix overlayers on SiO_2: (a) photopolymerization of ThreeBond 3026E containing acrylate oligomer and 2-hydroxyethyl methacrylate, (b) vapor deposition polymerization of styrene and divinylbenzene, (c) precipitation polymerization of methylmethacrylate and ethyleneglycol dimethacrylate, and (d) hydrolysis-polymerization of tetramethoxysilane. The structures of the supported and molecularly imprinted Ru catalysts were characterized by XPS, solid-state NMR, XRF, TGA, UV/vis, and Ru K-edge XAFS.

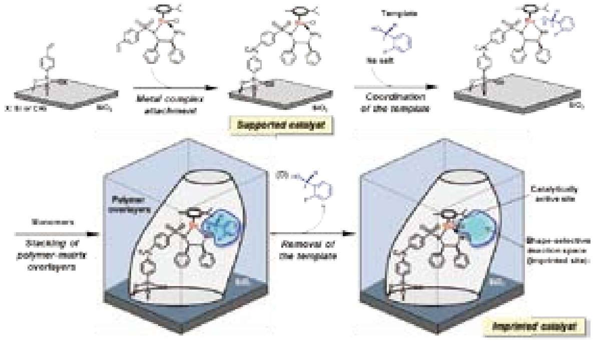

Figure 1. Preparation scheme of a molecularly imprinted Ru-complex catalyst on SiO_2 for the transfer hydrogenation of *o*-fluoroacetophenone in water.

XPS peak intensity analysis of Si 2p to C 1s of the polymer-stacked Ru catalysts showed that the stacking manner of these polymer matrices on the SiO_2 surface were significantly different. In the case of the photopolymerization of ThreeBond 3026E, we found large decrease in the peak intensity ratio, indicating that space around the supported Ru complex was covered by the polymer matrices. The stacking of the matrix overlayers changed catalytic behaviors for the *o*-fluoroacetophenone transfer hydrogenation in water and the improvement of enantioselectivity was observed.

2. Space-Resolved XAFS Analysis of A Single Catalyst Particle of A Supported Ni Catalyst Using X-Ray µ-Beam

Catalytic performances of solid catalysts depend on the structural and electronic aspects (oxidation state, coordination symmetry, local coordination structure, *etc.*) of catalysts, which are generally inhomogeneous powder assembly of solid particles with nm–µm sizes. X-ray beam for conventional XAFS (X-ray Absorption Fine Structure) is typically in mm size, which obtains macroscopically averaged structural information on the assembly of heterogeneous catalyst particles with various sizes, composition, and structures within mm-sized X-ray beam-spot. Structural bond information around a particular catalytic element in an individual catalyst particle has not been reported well because of the lack of characterization techniques with fine space resolution to directly observe such structural parameters of a single catalyst particle.

We have investigated the structural information of a single catalyst particle of a supported Ni catalyst ($NiO_x/Ce_2Zr_2O_y$ ($0 \le x \le 1$, $7 \le y \le 8$) for CH_4 steam reforming by 2-dimensional scanning µ-XRF and µ-XAFS analysis using an X-ray µ-beam (1000 nm (*h*) × 800 nm (*v*)). X-ray beam at Ni K-edge (8332 eV) was focused by Kirkpartick-Baez (KB) mirrors at the BL37XU beamline at SPring-8. The catalyst particles (average particle size = 750 ± 370 nm) were dispersed on a thin SiO_2 membrane substrate and the membrane was mounted on a piezoelectric translation stage for scanning µ-XRF and µ-XAFS. Fluorescent X-rays emitted from the sample were detected by a 19-element Ge detector.

2-Dimensional scanning µ-XRF mapping showed the position of each catalyst particle on the SiO_2 substrate (Figure 2 (A)). Significant contrast of the Ni Kα and Ce Lα + Lβ fluorescent X-rays was observed as shown in Figure 2 (A) and the size of the high X-ray intensity area was consistent to the size of the catalyst particles. Ni K-edge µ-XANES of both $Ni/Ce_2Zr_2O_7$, which was active for the CH_4 steam reforming, and $NiO/Ce_2Zr_2O_8$, which was inactive for the reaction, were measured at the positions of the catalyst particles, and the µ-XANES spectra of the both catalysts were significantly different each other as shown in Figure 2 (B) ((a) and (c)).

Figure 2 (C) shows a Ni K-edge µ-EXAFS Fourier transform of a single catalyst particle of the inactive $NiO/Ce_2Zr_2O_8$, recorded for 3 h. To our knowledge, the local coordination structure of the supported Ni species on a single catalyst particle was successfully analyzed for the first time by µ-EXAFS with the spatial resolution to the size of the catalyst particle. The Ni K-edge µ-EXAFS analysis of $NiO/Ce_2Zr_2O_8$ revealed the local coordination of the catalytically inactive Ni species (Ni–O and Ni–Ni), which was attributed to the NiO species. The µ-XAFS technique would be promising to explore new *in situ* space-resolved catalysis science, to understand catalysis of a single nanoparticle excluding noise information from the heterogeneous properties of the catalyst particle assembly.

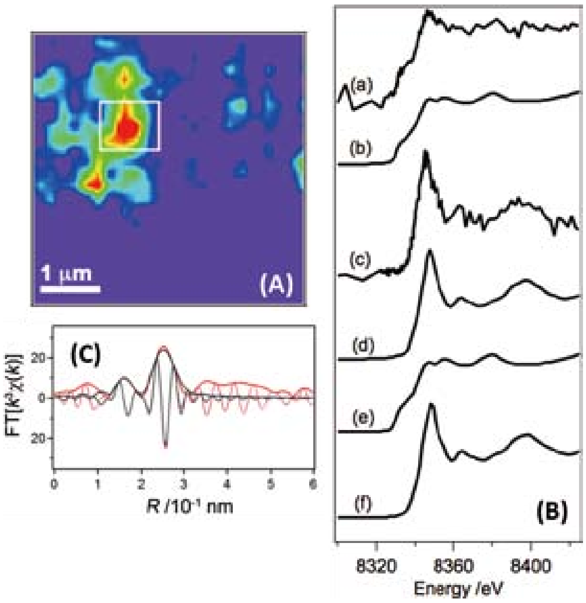

Figure 2. (A) A 2D-scanning Ni Kα XRF mapping image of $Ni/Ce_2Zr_2O_7$. 1 pixel = 200 nm. A white square in the image represents the beam area of (B)-(a). (B) Ni K-edge XANES spectra: (a) µ-XANES of a $Ni/Ce_2Zr_2O_7$ particle, (b) conventional XANES of $Ni/Ce_2Zr_2O_7$ powder assembly, (c) µ-XANES of a $NiO/Ce_2Zr_2O_8$ particle, (b) conventional XANES of $NiO/Ce_2Zr_2O_8$ powder assembly, (e) Ni foil, and (f) NiO. (C) Ni K-edge Fourier transform of a $NiO/Ce_2Zr_2O_8$ catalyst particle. Red and black lines represent on the observed and fitted spectra.

References

1) Z. Weng, S. Muratsugu, N. Ishiguro, S. Ohkoshi and M. Tada, *Dalton Trans.* **40**, 2338–2347 (2011).

2) M. Tada, N. Ishiguro, T. Uruga, H. Tanida, Y. Terada, S. Nagamatsu, Y. Iwasawa and S. Ohkoshi, *Phys. Chem. Chem. Phys.* **13**, 14910–14913 (2011).

---

* carrying out graduate research on Cooperative Education Program of IMS with Sinshu University

† carrying out graduate research on Cooperative Education Program of IMS with The University of Tokyo

‡ carrying out graduate research on Cooperative Education Program of IMS with JAIST