Novel Molecular Imprinting Metal-complex Catalysts at Oxide Surfaces

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Introduction
Design of artificial enzymatic catalysts with a molecular recognition capability has been a long-term challenge in catalytic chemistry. Design of both active metal site and selective reaction space near the metal center is a key issue to exploit such selective catalytic systems. Molecular imprinting which aims to create solid materials possessing a cavity with memory of a template molecule (reaction intermediate/transition state analogue) is a promising way to design shape-selective reaction spaces and molecular recognition sites like enzymes. It has been applied to many processes that require simple regulation of adsorption of target molecules. However, the effective regulation of dynamic processes of catalysis beyond simple adsorption is the most difficult attempt, where it is necessary to regulate dynamic processes involving access of reactant molecules to the active site and their structural change on the site, which has been unaddressed yet. Very recently, we have succeeded in design of new catalysts by combining two ways of metal-complex attaching and molecular imprinting on oxide surfaces. A ligand of the attached metal complexes was used as a template to give a template-shape cavity for selective reaction space in a matrix. The imprinted metal complexes with the cavity of the template in matrix exhibited high activities and remarkable selectivities for desired reactants. Molecular imprinting of attached metal complexes provides a way to produce artificial enzymatic systems for various catalyses including asymmetric syntheses [1-3].

Results and Discussion
Attached metal complexes often exhibit unique catalytic properties derived from their structures formed on oxide surfaces and their ligands coordinated to the metal centers. Design of the ligands of metal complexes is a key issue for excellent catalysis. The attached metal complexes were covered by SiO$_2$ thin-overlayer matrix, and then a template ligand was removed to create a template-shape cavity in the matrix at the surface. The imprinting procedure produced not only an active unsaturated metal species but also imprinted selective reaction space. We have designed several imprinted metal monomer and dimer complexes on SiO$_2$ surfaces by use of suitable metal-complex precursors.

Fig.1 shows a preparation procedure for an imprinted Rh-dimer catalyst on a SiO$_2$ surface. A Rh dimer precursor, Rh$_2$Cl$_2$(CO)$_4$ was attached on Ox.50 by two bondings with surface oxygens maintaining the original bridged dimer structure (1). Subsequent coordination with P(OCH$_3$)$_3$ ligands converted the Rh structure from (1) to monomer pair (2). The P(OCH$_3$)$_3$ ligand is regarded as a template of a half-hydrogenated alkyl species for 3-ethyl-2-pentene. Imprinting process was conducted by CVD of Si(OCH$_3$)$_4$ and subsequent hydrolysis-polymerization to stack SiO$_2$
network matrix. Removal of a template ligand in the SiO₂ matrix was associated with dimerization of the two adjacent Rh atoms to a Rh dimer with a Rh-Rh bonding at 0.268 nm (3), while a template cavity was created near the Rh dimer in the matrix. The molecular imprinting catalyst (3) was characterized by FT-IR, XPS, solid-state NMR, elemental analysis, ICP, H₂ adsorption, BET, EXAFS, and DFT calculation.

Homogeneous complexes Rh₂Cl₂(CO)₄ and RhCl(P(OCH₃)₃)₃ were inactive for alkene hydrogenation. On the other hand, the supported Rh monomer pair (2) was active for the reaction. Further, the molecular imprinting tremendously promoted the catalytic activity, and a remarkable selectivity for alkenes with different sizes and shapes appeared. The catalytic hydrogenation of smaller alkenes than the template like 2-pentene and 3-methyl-2-pentene were promoted 51 times by the imprinting, while the hydrogenation of larger alkenes with different shapes from the template was restricted after the imprinting. The discrimination of reactants occurred at 3-ethyl-2-pentene that is a model of the template. The imprinted catalyst exhibited a remarkable shape selectivity discriminating methyl or ethyl groups of alkene reactants. Accompanied with the molecular discrimination, kinetic parameters (Eₐ, Δ‡S) for the larger alkenes remarkably decreased, as compared to those for the small alkenes, indicating a change of the rate-determining step of the reaction.

The molecular imprinting technique has also been applied to design of chiral Rh complexes on SiO₂, using chiral P and N ligands. In the chiral molecular imprinting catalysts a five-dimensional regulation of catalytic reactions can be achieved. Typical data in the chiral imprinted systems are also presented at the Meeting.

Fig. 1 Preparation steps for the imprinted Rh-dimer catalyst.

References