論文 / 著書情報
Article / Book Information

題目(和文)	Ruコア／Ptシェル系ナノ粒子の不均一表面における電子構造及び化学反応性に関する研究
Title(English)	Study on the Electronic Structure and Chemical Reactivity of the Heterogeneous Surface of Ru-Core/Pt-Shell Nanoparticles
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質科学創造	専攻	
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要旨（英文 800 語程度）

Thesis Summary (approx.800 English Words)

Pt-shelled nanoparticles, in which an ultrathin Pt shell completely covers a nanoscale core composed of another metal, are known to exhibit unique chemical and electrochemical properties as catalysts. The electronic-structure-reactivity relationship present on their nanoscale surface is commonly modeled on the atomically flat surface of ultrathin Pt film/bulk substrate systems, although even ideal cuboctahedral nanoparticles have a more heterogeneous surface consisting of high-coordinated sites on flat facets and low-coordinated sites between intersecting facets. Coordination-number-dependent electronic effects, as well as core-induced electronic effects (i.e., heterometallic bonding effects (ligand effects) and lattice-mismatch-induced shell strain effects (strain effects)), on the individual surface Pt atoms must be elucidated to understand the origin of the surface reactivity of Pt-shelled nanoparticles.

A series of samples of carbon-supported, Pt-shelled Ru nanoparticles with a Ru core size of approximately 1.9 nm and varying shell thickness were prepared using a wet-chemical method. Based on the size distribution histograms, the average Pt shell thicknesses of the prepared samples were estimated to be approximately 1.3, 1.8, 2.7, 3.6, and 4.9 monoatomic layers, respectively. Atomic-resolution transmission electron microscopy images indicated that the Ru cores and Pt shells had a hexagonal close-packed-like structure and a face-centered cubic-like structure, respectively. The Pt shell surface was found to consist of not only flat Pt{111} facets, but also atomically corrugated Pt{110} and Pt{311} facets. The flat Pt{111} facets are most likely to deposit epitaxially on flat Ru{0001} facets, whereas the formation of the corrugated Pt facets may be affected by similarly corrugated Ru{10-10} and Ru{10-11} facets. Typically, to minimize the surface energy, atomically flat {111} and {100} facets are formed on nanoscale Pt surfaces, where low-coordinated step sites are formed as occasional defects. On the Pt-shelled Ru nanoparticles, however, low-coordinated step sites, with a coordination number of 7, and their adjacent high-coordinated trough sites, with a coordination number of 10 or 11 are crystallographically defined abundant sites and were thus expected to have a major impact on the nanoscale surface reactivity.

Electrochemical water dissociation ($H_2O \rightarrow OH_{ad} + H^+ + e^-$) on the Pt-shelled Ru nanoparticles were evaluated based on the anodic oxidation of the surface Pt atoms in Ar-saturated 0.1 M $HClO_4$ at 298 K. For a 3.1 nm pure Pt nanoparticle reference, the onset potential for OH chemisorption was approximately 0.5 V vs. the reversible hydrogen electrode. For the Pt-shelled Ru nanoparticle samples, however, the onset potential was approximately 0.4 V, at which OH is known to chemisorb exclusively on low-coordinated Pt sites because of their higher affinity for OH. Interestingly, the onset potential remained essentially constant irrespective of shell thickness.

Electrochemical CO oxidation ($CO_{ad} + OH_{ad} \rightarrow CO_2 + H^+ + e^-$) on the Pt-shelled Ru nanoparticles was also evaluated based on the anodic oxidation of a saturated CO adlayer on the surface Pt atoms in Ar-saturated 0.1 M $HClO_4$ at 298 K. The Pt-shelled Ru nanoparticle samples exhibited more negative onset potentials and thus weaker CO chemisorption than the pure Pt nanoparticle reference. Furthermore, with decreasing shell thickness, the onset potential shifted in the negative direction.

Valence-band region spectra of the surface of the Pt-shelled Ru nanoparticle samples were obtained at beamline 12 of the SAGA Light Source (Saga, Japan). The Pt-shelled Ru nanoparticle samples exhibited band-tail broadening compared to the pure Pt nanoparticle reference. High-coordinated Pt atoms can experience a greater number of interactions from neighboring atoms and can be greatly influenced by the ligand and strain effects, which are most likely to shift their local d states to lower energies and broaden the valence band. As a result, the interaction weakens between the CO $2\pi*$ orbital and the low-lying d states of highly coordinated surface atoms. CO chemisorption on high-coordinated Pt trough sites can weaken with decreasing shell thickness and thus with the intensifying ligand and strain effects. This is consistent with the electrochemical CO oxidation results.

Meanwhile, the Fermi edges of the Pt-shelled Ru nanoparticle samples were quite sharp compared to the pure Pt nanoparticle reference. Low-coordinated Pt atoms have fewer neighboring atoms and experience fewer interactions with the surroundings, and therefore, may be less influenced by the ligand and strain effects. Instead, the effect of low coordination can have a major impact, shifting the local d states of low-coordinated surface Pt atoms upward in energy and increasing the density of states around the Fermi level. When the O 2p orbital of OH interacts with such high-lying Pt d states, a large proportion of the resultant Pt-OH antibonding states are shifted above the Fermi level and are unoccupied, causing strong Pt-OH bonding. This is also in good agreement with the electrochemical results, which suggested strong OH chemisorption on low-coordinated sits.

In summary, an atomic-scale change in shell thickness can modify the local electronic structure and corresponding chemical properties of the high-coordinated surface sites on Pt-shelled nanoparticles, while the low-coordinated surface sites maintain high-lying d states and high chemical reactivity irrespective of shell thickness. This finding may offer a strategy for the rational design of the catalytic properties of nanoscale surfaces.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).