



Title	Synthesis and Structure-dependent Properties of Novel Binary Nanoparticles [an abstract of dissertation and a summary of dissertation review]
Author(s)	Md. Jafar, Sharif
Citation	北海道大学. 博士(理学) 甲第11147号
Issue Date	2013-09-25
Doc URL	http://hdl.handle.net/2115/53924
Rights(URL)	http://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	Md._Jafar_Sharif_abstract.pdf (論文内容の要旨)



[Instructions for use](#)

学位論文内容の要旨

博士の専攻分野の名称 博士（理学） 氏名 Md. Jafar Sharif

学位論文題名

Synthesis and Structure-dependent Properties of Novel Binary Nanoparticles

(新規2元系ナノ粒子の合成と構造に依存した物性の評価)

Metal nanoparticles (NPs) have gained much attention as building units of functional materials because they exhibit novel properties arising from unique electronic and geometric structures. Properties of NPs composed of a single component are controlled by the structural parameters such as size and shape. In contrast, properties of NPs can be regulated more extensively by introducing a secondary component because they are dependent also on composition and mixing mode of the two components. In my doctoral work, I developed synthetic methods of novel binary NPs with controlled compositions and mixing modes and studied their magnetic and catalytic properties.

In chapter 2, I studied magnetic properties of homogeneously mixed FeCo nanoalloys (NAs), prepared by hydrogen reduction method. In general, the magnetic properties of FeCo NPs are deteriorated as compared to the corresponding bulk because of inhomogeneous mixing, poor crystallinity and surface oxidation. I demonstrated that these problems were overcome by preparing FeCo NAs by heating polyethylene glycol (PEG)-stabilized FeCo oxide nano-composites (Fe_2O_3 , CoO) at 450 °C under hydrogen (0.1 MPa) for 0.5 h. Detailed structural analysis using high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning TEM EDS and powder X-ray diffraction (XRD) revealed that FeCo NAs form a highly crystalline structure in which the two elements are mixed homogeneously. This result indicated that hydrogen not only reduced the oxide phase to metallic phase, but also promoted the diffusion of atoms during the heat treatment of the FeCo oxide composites. In addition, a carbon layer was formed on the surface of NAs by the calcination of PEG and, as a result, the FeCo NAs were protected against the oxidation. $\text{Fe}_x\text{Co}_{100-x}$ NAs with the composition range of $20 \leq x \leq 80$ (diameter 30–55 nm) were successfully prepared in a similar way and their magnetic properties were studied as a function of the composition. The saturation magnetizations showed the highest value (250 emu/g) for the $\text{Fe}_{70}\text{Co}_{30}$ NA, which is comparable to that of the $\text{Fe}_{70}\text{Co}_{30}$ bulk alloy (245 emu/g). The high magnetization is attributable to highly crystalline and homogeneously mixed structure of the FeCo NAs.

In chapter 3, I obtained RhCu NAs with a solid solution structure for the first time and studied their catalytic properties. I found that Rh-Cu NPs with a solid solution structure were formed by the co-reduction of the Rh and Cu ions in the presence of PVP whereas these metals do not form a solid solution structure in the bulk according to the phase diagram. XRD measurement of the $\text{Rh}_x\text{Cu}_{100-x}$ ($40 \leq x \leq 75$) NAs revealed a formation of a single-phase face centered cubic structure in which the two metals are randomly mixed except $\text{Rh}_{40}\text{Cu}_{60}$. The enhancement of miscibility between Rh and Cu in NPs was ascribed to the high surface energy of NPs. I demonstrated that the RhCu NAs hydrogenated 4-nitrobenzaldehyde efficiently and selectively to 4-aminobenzaldehyde with a maximum selectivity for $\text{Rh}_{50}\text{Cu}_{50}$ under mild conditions (0.1 MPa of H_2 at 298 K). I proposed that the high selectivity is associated with selective adsorption of the NO_2 group onto a strongly polarized surface of the RhCu NA

formed by the charge transfer from Cu to Rh.

In chapter 4, I compared the catalysis of PVP-stabilized metal (Ir, Pd, Pt, Rh, Au) NPs with the size of ~2 nm using hydrogenation of 4-nitrobenzaldehyde as a test reaction. It was found that all the NPs except Au:PVP reduced 4-nitrobenzaldehyde efficiently under mild conditions (0.1 MPa of H₂ at 298 K). However, the selectivity to 4-aminobenzaldehyde was strongly dependent on the metal: Ir NPs yielded 4-aminobenzaldehyde almost selectively (99%), whereas Pd, Pt, and Rh NPs additionally produced sizable amount (30–90 %) of 4-aminobenzyl alcohol. Ir:PVP reduced various nitroaromatics containing >C=O, –CN and –Cl functional groups selectively to the corresponding aniline compounds, while the other functional groups remained intact. Ir NPs showed a similar activity and selectivity to that of the original one upto third run, retaining the similar size and distribution. Detailed structural analysis by XPS and XAFS revealed that small IrO₂ domains are distributed on the surface of Ir NPs. The highly selective catalysis was ascribed to a cooperative effect between selective adsorption of nitroaromatics on the IrO₂ phase and activation of H₂ on the Ir (0) phase. The partially oxidized Ir NPs prepared in this study can be viewed as a new type of catalyst, which corresponds to an inverse system to the conventional metal catalyst supported on metal oxides. The benefit of this novel structure is that the interfacial area between oxide phase and metallic phase is greatly enhanced.

In Chapter 5, I discussed the summary and the future prospect of these works.