別紙様式８

研 究 主 論 文 抄 録

論文題目　貴金属ナノ粒子と強相互作用する担体物質および担持触媒調製法に関する研究
（Development of support material stabilizing precious metal nanoparticles and their preparation method）

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主論文要旨

A recent serious problem with precious metals including Pt, Pd and Rh is concerned with their rapidly increasing use as catalysts. Upon exposure to a high-temperature atmosphere, nanoparticles of precious metals in the catalytic converter are agglomerated into large grains with low specific surface areas and hence low catalytic activities. To counter this effect, catalysts are loaded with an excess amount of precious metals. In this regard, material chemistry to design support materials that can stabilize precious metal nanoparticles is strongly requested in response to such a serious situation. In this present work, development of support material stabilizing precious metal nanoparticles and their preparation method have been studied. Moreover, the reason for the strong metal-support interaction is discussed on the basis of local structural analysis by the use of transmission electron microscopy (TEM), X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS) with intention of expanding the knowledge of applying this phenomenon broadly to precious metal catalysts.

In Chapter 1, the background of this study is discussed.

In Chapter 2, Pd/CeO_2 activated for CO oxidation after thermal ageing prepared by impregnation method is described. The thermal aging at 900 °C in air could activate the Pd/CeO_2 catalyst for low-temperature CO oxidation, in complete contrast to other supported catalysts, which were deactivated by sintering. The strong metal-support interaction via Pd-O-Ce bonding prevented the sintering of Pd oxide species at ≤800 °C and deposited metallic Pd particles with a size of 1 to 2 nm, when the aging temperature reached to the equilibrium of PdO/Pd phase transformation. The metallic Pd nanoparticles in intimate contact with CeO_2 were responsible for CO adsorption and following reactions with oxygen near room temperature.

In Chapter 3, high-temperature thermal stability $Rh/AlPO_4$ prepared by impregnation method is described. $AlPO_4$ became an efficient and robust support material to produce optimum

metal-support interactions that could reduce significantly Rh loading, owing to thermally stable and highly dispersed Rh nanoparticles anchored strongly onto the phosphate surface (Rh-O-P). Unlike the Al_2O_3 case as a reference, moreover, Rh oxide did not cause solid-state reactions with $AlPO_4$. Nonreactive but strong anchoring effect could be considered to be a reason for the thermal stability of highly dispersed Rh nanoparticles on $AlPO_4$.

In Chapter 4, a novel dry process using arc-plasma for the supported precious metal catalysts has been demonstrated as an alternative catalyst preparation method. Arc-plasma method was able to prepare highly dispersed uniform metallic Pt, Pd and Rh nanoparticles onto Al_2O_3. As-deposited Pt catalyst exhibited a higher catalytic activity for CO oxidation, compared to the conventional Pt/Al_2O_3 prepared by impregnation.

In Chapter 5, Pd/CeO_2 prepared by arc-plasma has been studied, which is described in Chapter 2. As-prepared by arc-plasma Pd/CeO_2 showed much higher activity than as-prepared impregnation catalyst. The reason for the higher activity was probably due to higher metal dispersion and metallic state of Pd, which was effective for chemisorption of CO. Further ageing at 900 °C enhanced the catalytic activity to be more than as-deposited by arc-plasma catalyst. As in the case of the impregnated catalyst, metallic Pd nanoparticles would be regenerated as the result of decomposition of the Pd-O-Ce surface moiety. The active metallic Pd phase once formed by thermal aging at 900 °C was so stable that the low-temperature activity could be preserved after further repetition of air-aging at 600 °C.

In Chapter 6, $Rh/AlPO_4$ prepared by arc-plasma has been studied, which is described in Chapter 3. Highly dispersed crystallized metallic Rh particles with the size of 2.4±1.1 nm were deposited on the surface of $AlPO_4$, but metal-support interaction via a Rh-O-P bond was weak. As-prepared catalyst exhibited the higher CO oxidation activity than the impregnated catalyst as a consequence of high dispersion and metallic state of Rh species.

In Chapter 7, bimetal nanoparticles of Pd-M (M=Fe, Co, Ni, Cu) deposited onto CeO_2 by using dual arc-plasma have been investigated. Highly dispersed uniform nanoparticles with the average size of about 2 nm were successfully obtained. By synchronizing two pulsed arc-plasmas, single bimetal nanoparticles containing both Pd and Fe could be formed, but asynchronous pulsing yielded mixtures of each metal nanoparticle. In accordance with the structural difference, the Pd-Fe bimetal nanoparticle on CeO_2 was found to stabilize metallic states of Pd and Fe and therefore exhibited higher catalytic activities for CO oxidation.

In Chapter 8, the results concluded in the previous chapters are summarized briefly.