学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　全 載完

学 位 論 文 題 名

Development of Pd-Based Alloy Catalysts Highly Selective for deNO_x reactions

（deNO_x反応に高い選択性を示すPd系合金触媒の開発）

Three-way catalysts simultaneously purify HC, CO and NO_x, and are essential for gasoline vehicles. Three-way catalyst applied to the gasoline engine is composed of platinum group metals (Pt, Rh, and Pd) as the main active site, and is supported on a support (SiO_2, Al_2O_3, CeO_2) having excellent thermal and mechanical stability. In the case of Pd catalyst, its prominent oxidation activity for hydrocarbons and CO. However, the controlling the selectivity of NO reduction to N_2 remains a significant challenge because a significant amount of undesired by-products, such as N_2O, which is a powerful greenhouse effect gas, are particularly generated when CO is used as a reductant under low temperature. I propose catalyst design based on Pd-based alloy that is effective for catalyst preparation to solve the problems (low activity and selectivity in low temperature region) in three-way catalysts. Furthermore, this catalyst design was employed to improve NO conversion to N_2 under lean conditions. This thesis efforts on purification of NO_x gas by using three Pd-based alloy catalysts. 1) Pd-based pseudo-binary alloy catalyst, 2) Cu-Pd single atom alloy, and 3) Pd-Pt based pseudo-binary alloy catalyst. Three different types of alloy systems are developed for efficient reduction of NO_x.

Chapter 2 presents the development of Pd-based pseudo-binary alloy catalyst for selective reduction of NO without emission of N_2O at low temperatures, which has been unprecedented previously by conventional Pd based catalysts. First, I screened various Pd based bi-metallic catalysts for NO–CO reaction. The results showed that a Pd-Cu alloy catalyst, $PdCu/Al_2O_3$, gave high NO conversion at low temperature region and Pd-In intermetallic catalysts, $PdIn/Al_2O_3$, gave high N_2 selectivity below 250℃. $PdIn/Al_2O_3$ catalyst displayed excellent N_2 selectivity even at low temperatures (100% at 200℃). The catalytic activity of PdIn was further improved by substituting a part of In with Cu, where a $Pd(In_{1-x}Cu_x)$ pseudo-binary alloy structure was formed. The optimized catalyst, $Pd(In_{0.33}Cu_{0.67})/Al_2O_3$, facilitated the complete conversion of NO to N_2 (100% yield) even at 200℃ and higher, which has never been achieved using metallic catalysts. The formation of the pseudo-binary alloy structure was confirmed by the combination of HAADF-STEM-EDS, EXAFS, and CO-FT-IR analyses. A detailed mechanistic study based on kinetic analysis, operando XAFS, and DFT calculations revealed the roles of In and Cu in the significant enhancement of catalytic performance.

Chapter 3 presents the Cu-Pd single atom alloy catalyst for reduction of NO, which minimizes th e use of precious metal. A series of Cu–Pd alloy nanoparticles supported on Al_2O_3 were prepared by a deposition-precipitation method using urea and tested as catalysts for deNO_x reactions. XRD, HAADF-STEM, XAFS, and FT-IR analyses revealed that single-atom alloy structure was formed when the Cu/Pd

ratio was 5, where Pd atoms were well isolated by Cu atoms. Compared with Pd/Al_2O_3,Cu_5Pd/Al_2O_3 exhibited outstanding catalytic activity and N_2 selectivity in NO reduction by CO: the complete conversion of NO to N_2 was achieved even at 175℃ for the first time, with long-term stability for at least 30 h. High catalytic performance was also obtained in the presence of O_2 and C_3H_6 (model exhaust gas), where a 90% decrease in Pd use was achieved with minimum evolution of N_2O. Kinetic and DFT studies demonstrated that N–O bond breaking of the $(NO)_2$ dimer was the rate-determining step and was kinetically promoted by the isolated Pd.

Chapter 4 shows Pd-Pt based pseudo-binary alloy catalyst efficient for deNO_x reaction under excess O_2 lean conditions, which has never been achieved by three-way catalysts. The catalytic performance of PdIn catalyst was further improved by substituting a part of Pd with Pt, where a $(Pd_xPt_{1-x})In$ pseudo-binary alloy structure was formed. The optimized catalyst, namely, $(Pd_{0.5}Pt_{0.5})In/CeO_2$, improved the N_2 yield (>80%) even in the presence of excess oxygen (λ~1.50), where the operating λ window was significantly expanded toward the lean side. The long-term stability and lean-rich cycle tests were performed to evaluate the catalytic performance. The formation of the pseudo-binary alloy structure was confirmed by the combination of HAADF-STEM-EDS, and CO-FT-IR analyses.

Chapter 5 shows the general conclusion of the thesis. Chapter 2 conclude that a Pd based pseudo binary alloy catalysts, $Pd(In_{1-x}Cu_x)/Al_2O_3$, three improved point of redox properties: (1) N_2O adsorption and decomposition ($N_2O \rightarrow N_2 + O$) were drastically enhanced by In, thus resulting in high N_2 selectivity; (2) CO oxidation was promoted by In, thus leading to enhanced low-temperature activity; and (3) Cu substitution improved NO adsorption and dissociation ($NO \rightarrow N + O$). Chapter 3 conclude that N–O bond breaking of the $(NO)_2$ dimer was the rate-determining step and was kinetically promoted by the isolated Pd. Chapter 4 conclude that a PdPt based alloy, $(Pd_{0.5}Pt_{0.5})In$, effectively react the NO reduction by CO in excess O_2 lean condition. Substituted Pt of this alloy structure provided an expanded operating window of three-way catalytic system. And, the combination of the positive effect of Pt and PdIn enabled the development of a highly active and selective NO reduction by CO at various O_2 concentration and temperatures.