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# 学位論文審査の要旨

博士の専攻分野の名称 博士（工学） 氏名 全 載完

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## 学位論文題名

Development of Pd-Based Alloy Catalysts Highly Selective for deNO<sub>x</sub> reactions

(deNO<sub>x</sub>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<sub>x</sub>, 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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>) 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<sub>2</sub> remains a significant challenge because a significant amount of undesired by-products, such as N<sub>2</sub>O, 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<sub>2</sub> under lean conditions. This thesis efforts on purification of NO<sub>x</sub> 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<sub>x</sub>.

Chapter 2 presents the development of Pd-based pseudo-binary alloy catalyst for selective reduction of NO without emission of N<sub>2</sub>O 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<sub>2</sub>O<sub>3</sub>, gave high NO conversion at low temperature region and Pd-In intermetallic catalysts, PdIn/Al<sub>2</sub>O<sub>3</sub>, gave high N<sub>2</sub> selectivity below 250°C. PdIn/Al<sub>2</sub>O<sub>3</sub> catalyst displayed excellent N<sub>2</sub> selectivity even at low temperatures (100% at 200°C). The catalytic activity of PdIn was further improved by substituting a part of In with Cu, where a Pd(In<sub>1-x</sub>Cu<sub>x</sub>) pseudo-binary alloy structure was formed. The optimized catalyst, Pd(In<sub>0.33</sub>Cu<sub>0.67</sub>)/Al<sub>2</sub>O<sub>3</sub>, facilitated the complete conversion of NO to N<sub>2</sub> (100% yield) even at 200°C 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 the use of precious metal. A series of Cu-Pd alloy nanoparticles supported on Al<sub>2</sub>O<sub>3</sub> were prepared by a deposition-precipitation method using urea and tested as catalysts for deNO<sub>x</sub> 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<sub>2</sub>O<sub>3</sub>, Cu<sub>5</sub>Pd/Al<sub>2</sub>O<sub>3</sub> exhibited outstanding catalytic activity and N<sub>2</sub> selectivity in NO reduction by CO: the complete conversion of NO to N<sub>2</sub> was achieved even at 175°C for the first time, with long-term stability for at least 30 h. High catalytic performance was also obtained in the presence of O<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> (model exhaust gas), where a 90% decrease in Pd use was achieved with minimum evolution of N<sub>2</sub>O. Kinetic and DFT studies demonstrated that N-O bond breaking of the (NO)<sub>2</sub> 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<sub>x</sub> reaction under excess O<sub>2</sub> 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<sub>x</sub>Pt<sub>1-x</sub>)In pseudo-binary alloy structure was formed. The optimized catalyst, namely, (Pd<sub>0.5</sub>Pt<sub>0.5</sub>)In/CeO<sub>2</sub>, improved the N<sub>2</sub> yield (>80%) even in the presence of excess oxygen ( $\lambda \sim 1.50$ ), where the operating  $\lambda$  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<sub>1-x</sub>Cu<sub>x</sub>)/Al<sub>2</sub>O<sub>3</sub>, three improved point of redox properties: (1) N<sub>2</sub>O adsorption and decomposition (N<sub>2</sub>O → N<sub>2</sub> + O) were drastically enhanced by In, thus resulting in high N<sub>2</sub> 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 → N + O). Chapter 3 conclude that N-O bond breaking of the (NO)<sub>2</sub> dimer was the rate-determining step and was kinetically promoted by the isolated Pd. Chapter 4 conclude that a PdPt based alloy, (Pd<sub>0.5</sub>Pt<sub>0.5</sub>)In, effectively react the NO reduction by CO in excess O<sub>2</sub> 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<sub>2</sub> concentration and temperatures.

Considering these research achievements, we conclude that the author is eligible to have a Doctor degree of engineering.