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Promotional Effect of Support Materials in the Three-Way Catalysis of Supported Metal Catalysts
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Three-way catalysts provide an efficient means of reducing the pollutant emission from gasoline-powdered vehicles by simultaneously removing compounds such as NO_x , CO, and hydrocarbons. As the regulatory requirements to reduce automotive emissions become increasingly strict, the development of effective support materials to enhance the catalytic efficiency of platinum group metals, which are widely used in three-way catalysts as active components, is of great importance. For this purpose, the role played by basic metal additives and oxygen storage materials (OSMs) in platinum group metals (PGM) based three-way catalysts were investigated systematically. Basic metal additives, such as La, Ba, and Sr, which are used widely in three-way catalysts to enhance the thermal stability of support materials, were found to enhance the catalytic performance efficiently of PGM-based three-way catalysts. Pt/OSM catalysts with high content of CeO_2 exhibit higher three-way catalytic efficiency.

Chapter 2 demonstrates the promotional effect of La in $\text{Pd/La}(x)/\text{Al}_2\text{O}_3$ ($\text{La} = 0, 5, 15$, and $30 \text{ wt}\%$) catalysts for three-way catalytic (TWC) reactions using a combination of kinetic and spectroscopic measurements as well as theoretical calculations. The obtained results show that the supported metallic Pd particles on La-containing Al_2O_3 supports are more electron deficient than those on pristine Al_2O_3 which results in a higher reactivity toward NO and a suppression of the poisoning effect of CO. A higher NO conversion efficiency is attained over these $\text{Pd/La}/\text{Al}_2\text{O}_3$ catalysts. In addition to investigations using powdered catalyst samples, we prepared and examined monolithic honeycomb catalyst samples in TWC reactions, which revealed $\text{Pd/La}/\text{Al}_2\text{O}_3$ exhibited superior performance for NO_x reduction compared to $\text{Pd}/\text{Al}_2\text{O}_3$. Moreover, we investigated the optimal La loading for TWC reactions and found that a loading of $15 \text{ wt}\%$, which was higher than that for the conventionally used industrial catalysts $\text{Pd/La}(5)/\text{Al}_2\text{O}_3$ ($\text{La} = 5 \text{ wt}\%$) optimized to keep the high specific surface area, is more effective for the TWC process. We have also performed a practical test using a commercial vehicle. The results showed that the catalytic system containing $\text{Pd/La}(15)/\text{Al}_2\text{O}_3$ exhibits improved conversions for the exhaust gasses including NO_x , CO, and hydrocarbons compared with the one containing $\text{Pd/La}(5)/\text{Al}_2\text{O}_3$.

Chapter 3 further shows the promotional effect of La in $\text{Pd/La}(x)/\text{Al}_2\text{O}_3$ ($x = 5, 15$, and $30 \text{ wt}\%$) in three-way catalytic process. La was found to enhance the NO conversion effectively via disproportionation reaction to yield surface nitrite species and gas-phase N_2O . A higher loading amount of La ($15 \text{ wt}\%$) favored the stable dispersion of Pd nanoparticles against sintering and in turn, retained a higher catalytic activity in $\text{Pd/La}(15)/\text{Al}_2\text{O}_3$ during the NO_x reduction process after the aging treatment.

Chapter 4 extended the metal additives to La, Ba, and Sr and shows their role in Pd-based

three-way catalytic system using various spectroscopic and kinetic methods. Metallic Pd⁰ species on Sr/Al₂O₃ and Ba/Al₂O₃ supports were found to be more electron-rich compared with those on pristine Al₂O₃, whereas those on La/Al₂O₃ were more electron-deficient. Consequently, Pd/La/Al₂O₃ showed a lessened CO poisoning effect during NO reduction reactions. Evaluations were performed using powdered catalysts as well as monolithic honeycomb catalysts under conditions simulating actual use. Pd/La/Al₂O₃ was observed to promote the catalytic reduction of NO most efficiently, while Pd/Ba/Al₂O₃ exhibited the highest activity for the oxidations of CO and C₃H₆. The present data suggest that the optimal metal additive for a Pd-based TWC will be determined by the specific application. The selection of such metals should take into account not only the stability but also the promotional effect during the exhaust purification process.

Chapter 5 demonstrates the role of Ba in an Al₂O₃-supported Pd-based catalyst under practical three-way catalysis conditions. The addition of Ba was found to reduce all of the emissions monitored (NO_x, CO, and non-methane hydrocarbons) in the vehicle exhaust gas; it also suppressed supported-metal aggregation, which is a requirement of a high-performance catalyst. In addition, infrared spectroscopic studies using model powder catalysts revealed that the efficient formation of intermediate surface nitrate species and their subsequent reactions with reductant gases, such as CO, H₂, and C₃H₆ (as a hydrocarbon), play key roles in reducing emissions. This process is akin to the NO_x storage and reduction (NSR) mechanism, which is commonly used to control diesel emissions.

Chapter 6 shows the promoting effect of basic metal additives on NO reduction over Pt-based three-way catalysts. The catalytic activities of the Pt/M/Al₂O₃ (M = Ba, La, or Sr) catalysts for NO, CO, and total hydrocarbons were superior to those of Pt/Al₂O₃; moreover, Ba enhanced the catalytic activity of Pt-based catalysts more efficiently than La and Sr. The Pt⁰ species loaded on Ba/Al₂O₃ were more electron-rich than those loaded on Al₂O₃, thereby promoting NO dissociation into N and O atoms, as revealed by the AP-XPS results. Moreover, the efficient formation of intermediate surface NO_x species, including nitrites and nitrates, and their reactivities toward reductant gases, such as H₂ or CO, were critical for promoting the effect of Ba on the NO reduction reaction.

Chapter 7 demonstrates the effect of oxygen storage materials, including CeO₂ and CeO₂-ZrO₂ solid-solutions having different ceria contents, on the performance of Pt-based three-way catalysts. Pt⁰ species loaded on OSMs having a higher ceria content were found to be more electron deficient. The increasing ceria content in fresh OSM-supported Pt catalysts (Pt/OSMs) enhanced not only the formation of nitrite species and their reactivity toward CO but also the resistance to CO poisoning during NO-CO reactions.

Chapter 8 is the general summary. Support materials play an important role in enhancing the catalytic efficiency of PGM-based catalysts in three-way catalysts. Basic metal additives, such as La, Ba, and Sr, which are used widely in three-way catalysts to enhance the thermal stability of support materials, were found to enhance the catalytic performance efficiently via modifying the electronic state of metallic Pt/Pd species and enhancing the formation of reactive intermediate.