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Rare earth metals for automotive exhaust catalysts

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Abstract

The usage of rare earth metals for automotive exhaust catalysts is demonstrated in this paper. Rare earth metals have been widely used in automotive catalysts. In particular, three-way catalysts require the use of ceria compounds as oxygen storage materials, and lanthana as both a stabilizer of alumina and a promoter. The application for diesel catalysts is also illustrated. Effects of inclusion of rare earth metals in automotive catalysts are discussed.

Keywords: Rare earth metals; Catalyst; Exhaust gas; Environmental protection; Oxygen storage capacity

1. Introduction

Today, automobile prevails across the globe as the most popular and necessary mode of transportation in our daily lives. About 50 million cars are produced every year, and over 700 million cars are used worldwide. Thus, the use of catalysts for purifying exhaust gases, which contains pollutants such as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxides (NO_x) and particulate matter (PM), is absolutely necessary and indispensable in every vehicle. Catalysts are composed of several components, including noble metals as active site, alumina-based supports with a high surface area, and metal oxides as promoter material. Certain kinds of rare earth metals are practical to use and necessary for catalysts. The beneficial effects of rare earth metals in exhaust catalysts have been recognized [1–3]: they promote noble metal dispersion, increase thermal stability of the alumina support, promote the water gas shift and the steam reforming reactions, store and release oxygen under conditions fluctuating between oxidizing and reducing. In this paper, the usage and effects of rare earth metals in automotive catalyst are discussed. Attention is mainly focussed on ceria compounds as oxygen storage material, and lanthana as both a stabilizer of alumina and a promoter in the three-way catalyst. The use of ceria compounds in diesel catalysts is also discussed.

2. Oxygen storage capacity (OSC)

Ceria compounds can regulate oxygen storage and release properties, which is the most important and remarkable feature of the three-way catalyst. It is well known that, for the control of CO, HC and NO_x emissions, a three-way catalyst works under atmospheres with fluctuating air to fuel ratios (A/F) because the average A/F is maintained close to the stoichiometric value. An oxygen storage material is necessary to store excess of oxygen in an oxidative atmosphere and release oxygen in a reductive atmosphere. Through oxygen storage and release, a buffer is achieved between the lean-rich swings in exhaust gas composition during vehicle operation in order to maintain a stoichiometric atmosphere, in which NO_x, CO and HC are efficiently converted.

Earlier, CeO_2 was recognized as a promising material, because it keeps a cubic crystal structure even during the alternate storage and release of oxygen and its volume change is small. However, OSC and thermal durability of CeO_2 were both insufficient for automotive use. Addition of lanthanum or zirconium ions into CeO_2 improves OSC by increasing the number of oxygen defects under reductive conditions [4]. Par-

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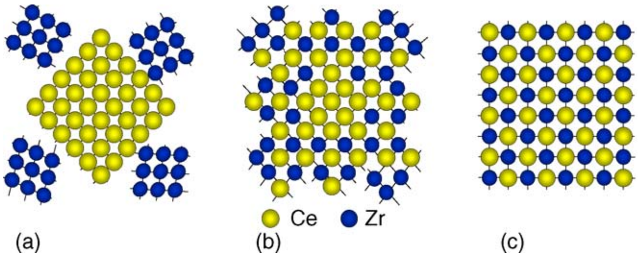

Fig. 1. Schematic illustration of the cation–cation network in the CeO_2–ZrO_2 (Ce/Zr = 1). (a) Mixture CeO_2 and ZrO_2{OSC = 160 μmol-O/g}. (b) Ce-rich and Zr-rich domains{OSC = 880 μmol-O/g}. (c) Homogeneous at atomic level{OSC = 1500 μmol-O/g} [5].

ticularly, in the case of zirconium ions, which have a smaller diameter than cerium ions, the space around the oxygen are increased, thereby facilitating reversible storage and release of oxygen in the matrix. XRD and XAFS analyses have also revealed that enhancing the homogeneity of the Ce and Zr atoms in CeO_2–ZrO_2 solid solutions increases OSC (Fig. 1) [5].

In terms of the reaction rate, oxygen storage and release reaction is divided into several reaction steps, namely, reaction on precious metal, surface oxygen diffusion and bulk oxygen diffusion (Fig. 2). Oxygen surface and bulk diffusivities were found to correlate with the homogeneity of Zr and Ce atom distributions in the oxide framework among the samples in Fig. 1 by $^{18}O/^{16}O$ isotopic exchange reaction method [6].

CeO_2–ZrO_2 has higher thermal stability compared to CeO_2. The heat resistance of CeO_2–ZrO_2 can be further improved by mixing it with alumina nanoparticles (ACZ) [7]. This concept is illustrated in Fig. 3. In general, the same kind of particles coagulates easily, forming large agglomerates at relatively low temperature in air. However, if the same type of particles is isolated by another type of particles that does not react with neighboring particles at high temperature, their particles do not coagulate each other. Thus, alumina particle inhibits the coagulation of CeO_2–ZrO_2 particle by forming a diffusion barrier at high temperature. Catalysts containing oxygen storage materials could reduce pollutants, particularly NO_x, emissions during A/F fluctuation. The catalyst with ACZ decreased NO_x emission by 20% as compared to that containing CeO_2–ZrO_2 in the car running mode test after a thermally severe aging [8].

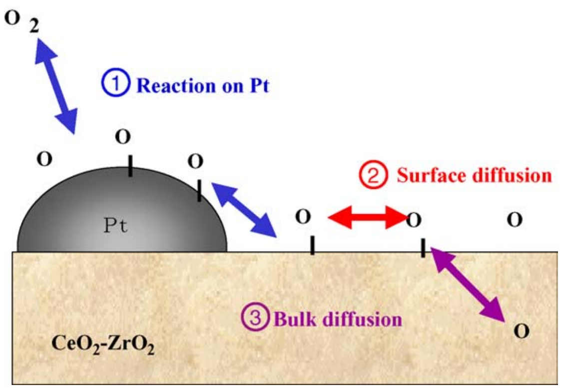

Fig. 2. Steps in oxygen storage/release reaction on Pt/CeO_2-ZrO_2 catalyst.

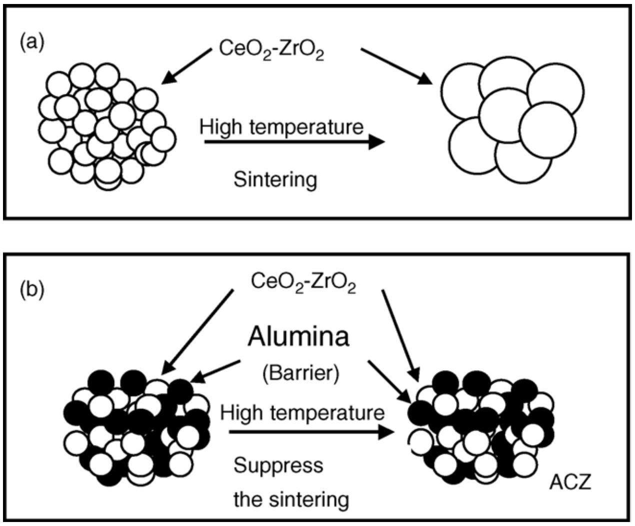

Fig. 3. Schematic diffusion barrier concept using ACZ: (a) CeO_2–ZrO_2 solid solution, (b) nanoscale mixing of alumina and CeO_2–ZrO_2 solid solution (ACZ) [7].

3. Improvements in NO_x reduction activity of the Pd catalyst

Platinum (Pt) and rhodium (Rh) are typically used for active metals in three-way catalysts. However, these metals, especially Rh, are precious, and due to the increasing

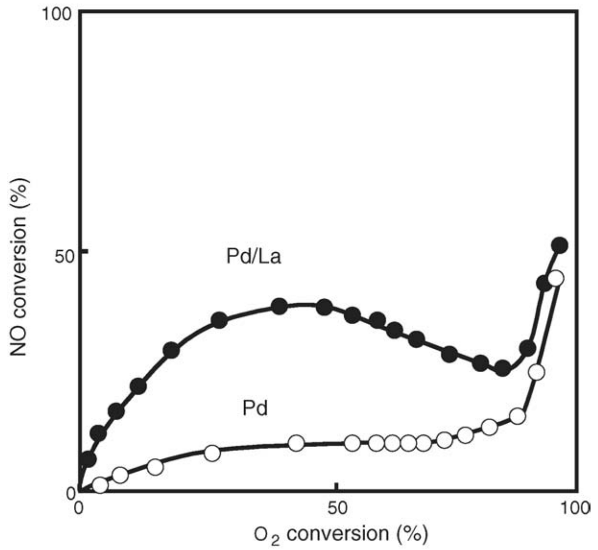

Fig. 4. Selectivity for converting NO and O_2 in simulated exhaust gas of the Pd and Pd/La catalysts. Reactant feed: 0.61% CO, 0.20% H_2, 0.15% C_3H_6, 0.1% NO, 0.54% O_2, 3% H_2O, 12.7% CO_2, N_2 balance, SV = 30,000 h^{-1}, temperature: RT ∼600 °C. Loading amount (mol/1 mol-alumina): Pd: 6.1×10^{-5}, La: 1.3×10^{-2}.

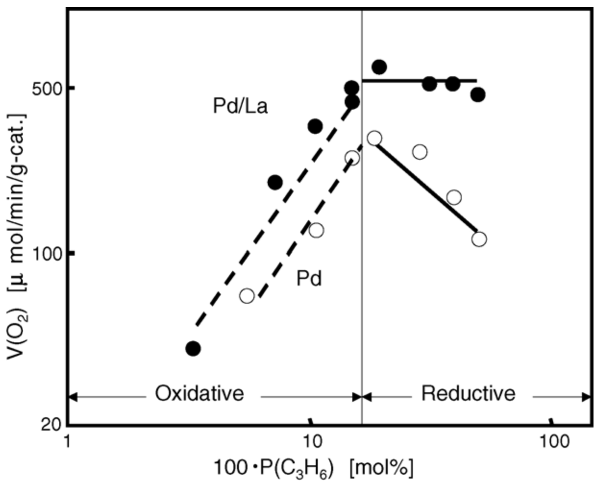

Fig. 5. Effect of C_3H_6 concentrations for C_3H_6 oxidation rate on the Pd and Pd/La catalysts. Reactant feed: 0.03–0.6% C_3H_6, 0.23% O_2, N_2 balance, SV = 30,000 h^{-1}, temperature: 500 °C, loading amount (mol/1 mol-alumina), Pd: 6.1×10^{-5}; La: 1.3×10^{-2}.

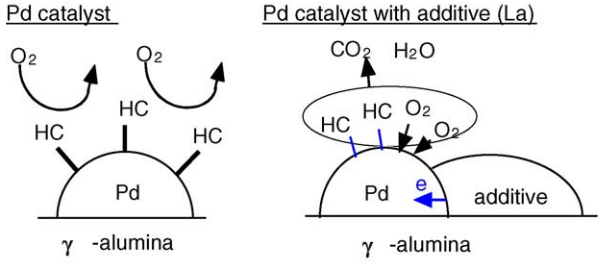

Fig. 6. Conceptional scheme showing the effect of La addition to Pd catalyst. La addition weakens the adsorption strength of Pd with HC by a moderate electron supply, and allows a smooth reaction.

global demand and consumption of automotive catalysts, a substitute for Rh in the three-way catalyst has been highly desired. Initially, Pd was not used as a main active metal for the three-way catalyst because of its poor NO_x reduction activity. However, it was found that addition of rare earth metals, in particular La, to Pd catalysts improved their NO_x reduction activity [9,10], particularly under a reducing atmosphere of exhaust gases. The addition of La is believed to (1) enhance NO_x chemisorption, which in turn leads to the selective reduction of NO_x, rather than oxygen (Fig. 4) and (2) suppress the strong adsorption of HC on Pd (Fig. 5), thus allowing NO_x reduction to proceed smoothly. Similar effects were observed in the case of addition of alkaline earth metals to the Pd catalyst [11,12]. Rare earth and alkaline earth additives increase the electron density of Pd on the catalyst and weaken the adsorption strength of Pd with HC (Fig. 6).

4. Thermal stability for alumina support

Since catalysts can be exposed to high temperatures, occasionally above 1000 °C, during high-speed cruising, thermal degradation constitutes an important cause of catalyst deactivation. Transitional alumina as catalyst support is transformed into α-alumina, which decreases its high surface area significantly under high temperature operation. This leads to agglomeration of noble metal on the catalyst support, and thus a decrease of catalytic activity [13,14].

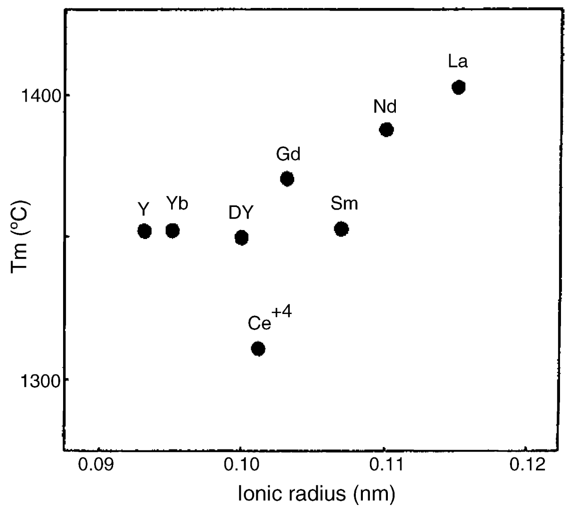

Fig. 7. α-Transformation temperature Tm of alumina modified with various rare earth metals (3 mol%), measured at a heating rate of 10 K min^{-1}.

It has been reported that addition of rare earth and alkaline earth compounds are effective for suppressing α-transformation in alumina [13–16]. This is exemplified in Fig. 7 for rare earths modified aluminas. La^{3+} with large ionic radii is most effective in improving thermal stability. It was concluded that La can easily insert into cation defects in transition alumina with the spinel structure and La^{3+} will inhibit the diffusion of Al^{3+} and O^{2-} ions and prevent transition aluminas from sintering and transforming into α-alunina. Fig. 8 shows that modification of alumina with only a small amount of La dramatically improved thermal stability. Excess

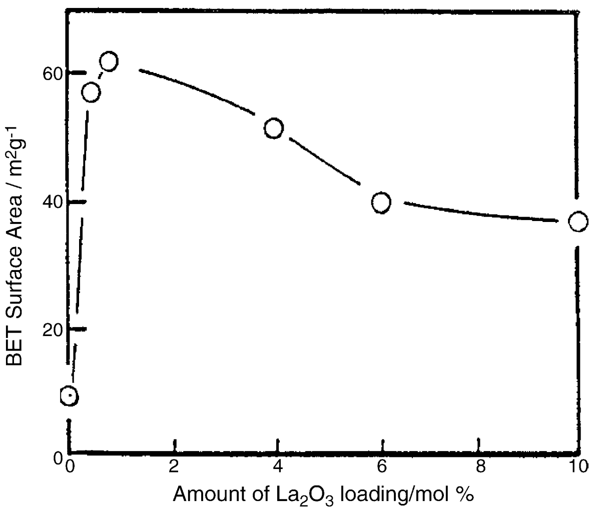

Fig. 8. Influence of amount of La loading on the stability of γ-alumina calcined at 1200 °C for 5 h.

La loading of alumina decreases the surface area of alumina through La aluminate formation.

5. Diesel catalysts

The diesel engine is well known to be highly fuel-efficient. However, PM is the most complex of diesel emissions, and the emission problems with soot and NO_x have not been completely solved. PM is composed of soot, heavy HCs as soluble organic fraction and sulfates.

Due to the low temperature of diesel exhaust gas, temperature of a diesel catalyst may easy fall below the light-off temperature, necessitating additions of an HC adsorbent, typically a zeolite. Adsorbed HC on zeolite also serves to improve NO_x conversion effectively with increasing temperature, but excess HC adsorption induces a decrease in NO_x conversion by HC poisoning on the catalyst. The addition of ceria compounds improves NO_x conversion (Fig. 9). Ceria compounds can supply oxygen and suppress HC poisoning on the catalyst. On the other hand, sulphates in the exhaust gas can react with ceria compounds and significantly hinder the catalyst performance.

Removal of soot is most difficult, but has achieved by filtration using a diesel particulate filter with micropores. However, the filter is apt to plugged by soot accumulating. So, regeneration of the filter is very necessary, being the key point of this technology. Several methods have been proposed. One unique method uses fuel additives of CeO_2-based material [17]. Organic cerium compounds in fuel decomposes and are oxidized during combustion. In the process, these oxides come into contact with soot and become highly dispersed in it. As the contact between soot and catalyst is a big problem for oxidation catalysts, soot combustion is promoted greatly using the fuel additives. However, this method has a technical problem, causes a big concern of releasing the additives into the atmosphere.

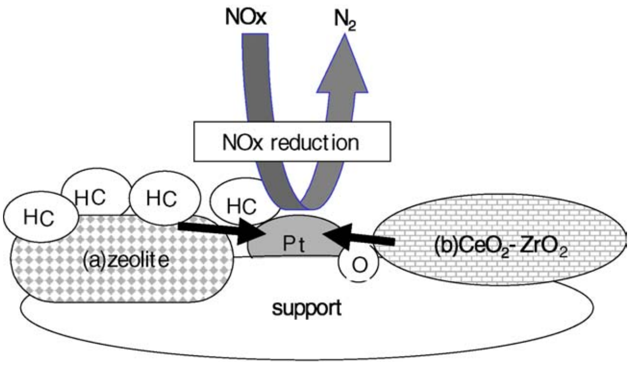

Fig. 9. Conceptual scheme of zeolite and CeO_2–ZrO_2 enhanced NO_x catalyst for diesel engine. (a) Zeolite: HC adsorb at low temperature and desorb at increasing temperature, (b) CeO_2–ZrO_2:oxygen release and suppress HC poisoning.

Ceria and lanthana compounds represent rare earth metals that are used in automotive exhaust catalysts described above. In addition, La-perovskite has been in practical use in three-way catalysts [18]. La lies at the body center of the perovskite cubic unit cell as a stabilizer for the perovskite framework. The use of rare earth metals has been and is still being researched extensively in an effort to enhance catalytic activities for automotive use. We expect these studies to yield great advances in purification of exhaust gases and fuel economy through the use of rare earth metals in near future.

6. Conclusions

Rare earth metals have been widely used in automotive exhaust catalysts, in particular, ceria compounds with their high oxygen storage capacity and lanthana with its proper basicity and large ionic size. The performance of catalysts has been dramatically improved through the use of these materials. However, the stringent emission restrictions are set up in near future, and also that will spread all over the world. Our further efforts will be aimed at fully exploiting the potential of rare earth metals in the automotive catalyst so that we can approach the eventual goal of zero emission.

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