



Three way catalytic activity of thermally degenerated Pt/Al₂O₃ and Pt/CeO₂–ZrO₂ modified Al₂O₃ model catalysts



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ABSTRACT

The effect of ceria and ceria–zirconia modification to alumina on the three-way catalytic (TWC) performance of alumina supported Pt catalyst was investigated. Sintering of Pt was induced by thermal treatment at 1000 °C and suggested the inhibition effect of sintering by doping Ce on Al₂O₃ support. TWC activity for three catalysts follows the sequence of Pt/Ce_{0.8}Zr_{0.2}O₂/Al₂O₃ > Pt/CeO₂/Al₂O₃ >> Pt/Al₂O₃. Low temperature CO conversion increased clearly upon the addition of CeO₂ and CeO₂–ZrO₂ into Pt/alumina, indicating that the OSC promotes CO oxidation activity and NO is reduced by C₃H₆ in light-off process. TWC performance with 0.5 Hz dynamic condition at 620 °C indicated better conversions with the same sequence corresponding to OSC of each catalyst. In model transient experiment, CO conversion in rich phase with the sequence of Pt/Ce_{0.8}Zr_{0.2}O₂/Al₂O₃ > Pt/CeO₂/Al₂O₃ >> Pt/Al₂O₃ indicated that the OSC of CeO₂ and Ce_{0.8}Zr_{0.2}O₂ solid solution on alumina was a major cause for improvement of CO conversion in total dynamic operation even after thermally aged Pt catalysts. Regarding NO_x conversion in model transient experiment, the NO_x (NO + NO₂) low concentration versus time is delayed (with more NO_x removal activity) in the cyclic rich to stoichiometric condition for catalysts with OSC component of CeO₂ and Ce_{0.8}Zr_{0.2}O₂. The oxidized and recovered state of Pt on ceria zirconia should be related to NO removal reaction. Under rich-lean cycle condition, total oxidation and reduction of catalyst affect both transient CO and NO conversions over Pt, so that oxygen storage/release functions of OSC catalyst are effective to total buffering to A/F fluctuation.

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1. Introduction

Three-way catalyst (TWC) has satisfied several factors of catalysis and materials aspect in use of engine exhaust treatment system. A lot of research has been performed in order to elucidate and improve automotive catalyst operation [1,2]. The modern commercial TWC formulation typically consists of the combination of the catalyst such as cerium, zirconium and aluminum oxides and precious metals. The incorporation of ceria and ceria zirconia into automotive catalysts was a major advance in the ability of TWCs to perform at high efficiency. Furthermore, the advanced ceria zirconia materials enable TWC to storage/release oxygen through redox processes involving the Ce⁴⁺/Ce³⁺ couple to possess high oxygen storage capacity (OSC). Many studies have been carried out about OSC of ceria zirconia catalyst, since OSC to buffer A/F fluctuation

is the most important factor besides catalytic metal itself [2–13]. Improvement of CO oxidation in rich phase was confirmed due to OSC [14–19]; however, NO_x reduction must be also achieved with complexity under dynamic condition at the same time. One of the characteristic studies to design and optimize TWC is the understanding of various operating parameters especially for dynamic or transient performance [20–30]. The design of transient reactions becomes more important recently, depending on driving cycles and modes in new type engine such as hybrid system. Recent work has achieved to observe the reversible behavior of well dispersed Pt under model rich lean transient by using the excellent physical techniques such as high intense X-ray absorption spectra and high resolution electron microscopy. The ideal interaction appears generally with high dispersed state of Pt on support materials leading to higher performance [31–36]. Thus, the most important factor, besides OSC, is reversible dispersion of metal such as Pt under rich-lean fluctuating condition.

On the other hand, although it is not so frequently focused as target samples, the deactivation and its improvement is one of the most important works for advancing depollution by TWC [37–52].

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It is usually a complex phenomenon due to the presence of many components and species, and among them thermal effect is always caused during exhaust catalyst usage. The precious metal particles are preferable to be a few nm in diameter, but its sintering during operation is a major factor to decrease in the catalytic activity. It is reported that the sintering of a catalyst depends on temperature and in addition is more severe in oxidizing than in reducing atmospheres [39–41]. Studies for improvement provide the improving method such as the addition of the third elements, replacing support materials and the application of recent advanced materials and processing in practice. In this context, it is interesting to study how the degenerated catalyst behaves in three way catalysis reactions especially under dynamic condition, in which metals and OSC components have already sintered. Even about well-known elemental combination, such catalysts should have no more ideal interaction of metal-supports or advanced OSC components. We think that a study on the deeply sintered catalyst may become a reference toward future development with low precious metal loading catalyst with effective OSC components. In addition to materials characterization, the light-off TWC performance and transient A/F catalytic behavior should be evaluated using model mixed gas flow over sintered catalysts. In this work, Pt/alumina catalysts modified with and without OSC components are compared during a periodic feed of H₂ (rich condition) and O₂ (lean condition) regarding with both OSC and transient activity of Pt catalyst by using H₂ as a reducing probe. Catalytic materials stabilization and reaction performance after high temperature heat treatment are examined, and Pt loaded Ce and Ce–Zr impregnated alumina have shown improved CO, C₃H₆ activities by direct OSC and high NO reductive efficiency during stoichiometric phase transient from rich condition in O₂–H₂ cyclic operation.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by the combination of two step impregnation process of alumina powder, Ce and Zr precursors and Pt solution. In the preparation of modified supports, ceria or ceria and zirconia were added by impregnation of the gamma (γ)-Al₂O₃ powder (Nikki Universal, Japan) with an aqueous solution of Ce(NO₃)₃ (Wako Chemicals, Japan) or the mixed solution of Ce(NO₃)₃ and ZrO(NO₃)₂ (Wako Chemicals, Japan). The composition of (CeO₂)_x(ZrO₂)_y(Al₂O₃)_z supports were as x/y/z = 0/0/1.0, 0.3/0/1.0, and 0.24/0.06/1.0 as molar ratio to Al₂O₃. The slurry of aqueous metal nitrates with alumina powders was agitated for 1 h in air, and was heated at 110 °C for 12 h in air. The dried samples were heated at 500 °C, followed by high temperature heat treatment at 1000 °C for 3 h in air, and then ground. 0.5 wt% Pt catalysts to each supports were prepared by the impregnation method using aqueous 4.5 wt% Pt(NO₂)₂(NH₃)₂ (Tanaka Noble Metals, Japan). They were dried at 110 °C for 12 h in air and heated at 500 °C, and then the Pt catalysts were heated at 1000 °C for 3 h in air. In the present work, we compare three catalysts of 0.5 wt% Pt/Al₂O₃, 0.5 wt% Pt/CeO₂/Al₂O₃ and 0.5 wt% Pt/Ce_{0.8}Zr_{0.2}O₂/Al₂O₃. The heat treatment at 1000 °C was applied twice (support) in order to give thermal degradation state.

2.2. Physical characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Miniflex II apparatus (Rigaku, Japan) using Cu–K α radiation operating at 30 kV and 15 mA with 0.02° step size scanning from 20° to 80° (2 θ). Raman spectra were measured with a NRS-3100 Raman Spectrometer (JASCO, Japan) equipped with a TE-cooled charge

coupled device (CCD) detector and a green laser ($\lambda = 532$ nm) under the ambient atmosphere. The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were determined by nitrogen physisorption at 77 K using a Tristar II apparatus (Micrometrics, USA) after degassing the samples in flowing nitrogen at 200 °C for 1 h. A field emission scanning electron microscope (FESEM, JSM7000F, JEOL Japan) was used for analysis of the morphology of samples at 30 keV.

2.3. Chemical characterization

The H₂ temperature programmed reduction (H₂–TPR) experiments were performed with a BP-1S TPD/TPR instrument (Henmi sliderule Co., Japan). In the reduction step, 100 mg of the sample was progressively heated from 30 to 1000 °C with a heating rate of 10 °C min^{−1} by flowing mixture of 5 vol% H₂ in Ar as a reducing gas. The hydrogen consumption as a function of the reduction temperature was continuously monitored by a cell of thermal conductivity detector (TCD). After the measurement of H₂–TPR, the amount of absorbed oxygen (OSC) was measured by the pulse injection of oxygen gas in flowing Ar at 600 °C by detecting TCD in the same apparatus. The second run of TPR–OSC measurement was used as data in present experiment. The dispersion of Pt (adsorbed CO/Pt molar ratio) was obtained from CO chemisorption measured by the pulse method of CO at room temperature in BP-1. The sample was reduced with H₂ at 400 °C for 1 h and then cooled to room temperature in flowing He. The data was used in this work after the reducing procedure was continuously repeated two times for the same samples in the apparatus.

2.4. Activity measurements

TWC activity tests were carried out in a continuous flow reactor using 100 mg powder in a quartz tube under a gas mixture with a flow rate of 500 ml min^{−1}. The gas composition was the stoichiometric condition as steady state base gas: 400 ppm C₃H₆, 1000 ppm NO, 0.30% CO, 0.33% O₂, 0.10% H₂, 2.0% H₂O and N₂ to balance with space velocity of 300,000 ml g^{−1} h^{−1}. In light-off measurement, the static activities were evaluated during heat-up procedure at 4 °C min^{−1}. Before the light-off activity measurements, the catalysts were pre-heated for 1 h at 800 °C, then cooled down to room temperature in the same mixed flowing gas mixture. The temperature was increased from 50 °C to 650 °C at a rate of 4 °C min^{−1} by programmed infrared heater system. The effluent gas was continuously analyzed with the use of PG-240G (Horiba, Japan) gas analyzer attached with non-dispersive infrared (CO, CO₂) and chemiluminescence (NO_x: NO and NO₂) detector, and VMS-1000F (Shimadzu, Japan) flame ionization detector (FID) apparatus. Conversion efficiencies were calculated with different of CO, VOC and NO_x concentration at reactor outlet between initial mixed gas concentrations.

In comparative static and dynamic measurement at around 620 °C were performed after pre-heat treatment under dynamic condition for 1 h at 800 °C. N₂ or alternating gas of H₂/N₂ (1 s) and O₂/N₂ (1 s) was input to steady state 500 ml base gas mentioned above in order to make static and dynamic condition of alternative reducing (H₂/N₂) and oxidizing (O₂/N₂) condition at 0.5 Hz; where $\Delta\lambda = 0$ and ± 0.0015 . The effluent gas was continuously analyzed by the same apparatus during dynamic operation. Also, stoichiometric window experiments (rich-lean transient) at 600 °C were carried out. Once the temperature was stabilized at 600 °C, the stoichiometric flow was kept, and then switched to the reducing condition (60 s) and back to a stoichiometric gas (60 s) and then changed to the oxidizing condition (60 s), repeatedly. The mixed gas cycled by alternating the following reducing (+0.10% H₂), stoichiometric and oxidizing (+0.05% O₂) condition by adding 15 ml of

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