



Propene oxidation over palladium catalysts supported on zirconium rich ceria–zirconia



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ABSTRACT

Ceria–zirconia solid solution with the Ce/Zr ratio of 1/3 was prepared and used as support material for palladium catalysts. The palladium catalysts supported on the zirconium rich ceria–zirconia (Pd/CZ) were studied for propene oxidation reaction. In the activity tests, the influences of palladium loadings, pretreatment conditions, and reaction conditions were investigated. The catalytic activities of Pd/CZ with small amount of palladium component were strongly affected by the pretreatment conditions such as oxidative or reductive atmosphere. From IR measurements, it was suggested that the palladium species with high reducibility should be active for the complete oxidation of propene. The initial activities of Pd/CZ catalysts under the insufficient oxygen condition were equivalent to the activities under the stoichiometric condition due to the property of high oxygen storage capacity (OSC). It was revealed that CZ support helped the high dispersion of palladium oxide particles and its OSC property assisted the propene oxidation reaction.

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1. Introduction

Automobile has been an indispensable means of transportation for human life over the decades. Recently, some electric vehicles are available in several countries, whereas the automobile that runs on gasoline still remains the majority. In the case of the gasoline-fueled automobile, the treatment of exhaust gases as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxide (NO_x), and sulfur oxide (SO_x) is a significant technology, because the gases have a large impact on human body and the global environment. For example, it is believed that the photochemical oxidants are produced by the photochemical reaction of hydrocarbons and NO_x, and the oxidants induce the air pollution such as photochemical smog. The gases of NO_x and SO_x would be the main reason of acid rain and air pollution. Therefore, various types of automotive catalysts have been developed to remove their harmful gases. One of the most famous catalysts is three-way catalyst (TWC), which is composed of precious metal, ceria–zirconia, and alumina. Especially, the ceria–zirconia (CZ) solid solution has the superior characters

of high thermal stability and high oxygen storage capacity (OSC) [1–3], and it has already been put into practical use as the promoter of automotive catalysts. Furthermore, it was reported that the growth of platinum particles was inhibited by the strong interaction with ceria–zirconia system under oxidative condition. The unique effect of CZ solid solution was named as “anchor effect” [4,5]. The catalysts with CZ mixed oxide were investigated for not only the purification of exhaust gases [6,7] but also some kinds of oxidation reaction. For instance, CeO₂–ZrO₂ doped with transition metals and rare earth elements [8] was studied for soot combustion, and Co₃O₄/CeO₂–ZrO₂ composite oxide catalyst [9,10] and CeO₂–ZrO₂ [11] were investigated on total methane oxidation at low temperature. Methane combustion [12,13], toluene combustion [14], and methanol decomposition to synthesis gases [15] over palladium catalysts supported on ceria–zirconia have also been reported by several researchers. Almost all researches, however, were conducted on catalysts with cerium rich ceria–zirconia. There are only a few researches about Zr rich ceria–zirconia supported palladium catalysts for total oxidation of hydrocarbon such as methane [16,17]. Ce element is classified with the rare earth element, and the price of precious metals is extremely expensive. Therefore, the decreases of precious metals and cerium usage are desired in addition to the achievement of high catalytic performance for the strict regulation of exhaust gases such as EURO6.

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In this study, ceria–zirconia solid solution with 25% of cerium and 75% of zirconium were used for the support material, and the influence of palladium amount was carefully investigated for propene (C₃H₆) oxidation as the fundamental reaction of exhaust gas treatment. In addition, the effects of reaction conditions and pretreatment to catalysts were researched by using the different atmosphere, because the automotive catalysts were exposed to both lean and rich conditions.

2. Experimental

2.1. Preparation of CZ support and Pd/CZ catalysts

Palladium catalysts supported on ceria–zirconia were prepared according to the following procedure. First, ceria–zirconia powder was synthesized by the coprecipitation method. Cerium ammonium nitrate (Wako Pure Chemical) and zirconyl nitrate (Wako Pure Chemical) were sufficiently mixed with pure water, and excess ammonium hydroxide was added to the mixed solution. The precipitated powder was washed in pure water and dried at 110 °C for 1 day. The resultant powder was preheated at 600 °C for 3 h in air to remove the residual nitrate compounds, and calcined at 800 °C for 3 h in air for thermal stability improvement. By this process, the CZ(1/3) support with the chemical formula of Ce_{0.25}Zr_{0.75}O_x was obtained.

Secondly, Pd component was loaded on the CZ(1/3) support by the conventional impregnation method. The powder of CZ support was impregnated with a nitrate solution of Pd(NO₂)₂(NH₃)₂ (Tanaka Kikinzoku Kogyo), and it was dried at 110 °C for 1 day. After the heat-treatment at 600 °C for 3 h, the catalyst was also calcined at 800 °C for 3 h in air as well as CZ support. The loadings of palladium in the samples were set at 0.04, 0.2, 1.0 and 5.0 wt.%. The y wt.% Pd/CZ(1/3) catalysts were hereinafter called “yPd/CZ”.

2.2. Propene oxidation tests

The activities of Pd/CZ catalysts for propene oxidation were measured with a typical fixed-bed flow reactor. The as-calcined catalysts with the amount of 100 mg were pretreated at 600 °C in a flow of 10% O₂/N₂ (50 ml min⁻¹) in the reactor, and then the catalytic reaction tests were carried out by passing gaseous mixtures composed of propene (3345 ppmC), O₂ (0.5% or 0.4%), and N₂ gas as diluted gas with a total flow rate of 500 ml min⁻¹ (space velocity: 300,000 ml g⁻¹ h⁻¹). The oxygen concentration of 0.5% and 0.4% corresponds to the stoichiometric condition and the oxygen deficient condition of 20%, respectively, when the catalytic reaction proceeds as the total oxidation (C₃H₆ + 9/2O₂ → 3CO₂ + 3H₂O). The reacted gases were analyzed by a flame ionization detector (FID) (Shimadzu, VMS-1000F) and a portable gas analyzer (HORIBA, PG-230). The propene conversion to CO₂ was calculated with CO₂ concentration at reactor outlet. The temperature was increased from 50 to 600 °C at a rate of 10 °C min⁻¹. After the reaction test, the catalyst was heat-treated at 600 °C under a flow of 10% H₂/N₂ (50 ml min⁻¹), and the same reaction test was conducted for the investigation of the effect of pretreatment condition. The amount of catalyst was set at 100 mg, and the thickness of catalytic layer in the reactor was about 2 mm. Therefore, it is considered that the temperature around samples must be homogeneous.

2.3. Characterization of Pd/CZ(1/3) catalysts

Several kinds of characterization of as-calcined catalysts were carried out so as to reveal the correlation between catalytic activities and the loading of palladium, and to realize the variation of activities due to pretreatment and reaction conditions. The BET surface area of the catalysts was estimated by TriStar II

(micromeritics®), after the heat treatment at 300 °C for 3 h under vacuum. X-ray diffraction (XRD) analysis and Raman spectroscopy were conducted with MiniFlex II (Rigaku) and NRS-3100 (JASCO), respectively, in order to investigate the crystal phase and structure. The XRD patterns were recorded by using Cu K α radiation. In the Raman spectroscopy, the Nd: YVO₄ laser with a 532 nm line was used at around 10 mW power. In addition, the O₂–CO₂–H₂–CO pulse method [18] was performed to estimate the more precise dispersion of palladium particles. The microstructures of catalysts were observed by transmission electron microscopy equipped with field emission gun (FE-TEM) (JEM2100F, JEOL) at the accelerating voltage of 200 kV. TEM images were recorded by CCD camera.

Fourier transform infrared (FT-IR) spectroscopy, temperature-programmed reduction (TPR) measurement and evaluation of oxygen storage capacity (OSC) were also carried out to investigate the chemical properties of prepared catalysts. FT-IR spectra of adsorbed CO were acquired with FT/IR-4200 (JASCO) at a resolution of 4 cm⁻¹. After a sample disk was pretreated at 400 °C for 1 h in 26.7 kPa (200 Torr) of oxygen or hydrogen, it was evacuated at 400 °C for 1 h. Then, IR cell with pretreated catalyst was filled with 6.7 kPa (50 Torr) of CO gas at room temperature. After the cell was evacuated, IR spectra were carefully recorded. The reducibility of Pd/CZ catalysts, in other words, the reactivity of oxygen species in catalysts was investigated by TPR measurement. The as-calcined catalyst was heated in 5% H₂/Ar at a heating rate of 10 °C min⁻¹, and the outlet gas was recorded by TCD detector (BP-1, HEMMI Slide Rule). After H₂-TPR measurement, the amount of adsorbed oxygen was evaluated by the pulse method of oxygen gas. The as-calcined catalysts were pretreated at 300 or 400 °C before the several characterizations. The chemical state of catalysts would not change due to the pretreatments, because the catalysts were calcined at higher temperature of 800 °C.

3. Results and discussion

3.1. Catalytic activities on propene oxidation

The results of propene oxidation tests under stoichiometric condition (O₂: 0.5%) over Pd/CZ catalysts after the oxidation and reduction treatment are shown in Fig. 1. A reaction test without catalyst was performed, and the curve of CO₂ yield was added to Fig. 1(a). After the oxidation treatment (Fig. 1(a)), the propene oxidation reaction was initiated at 200 °C over all Pd/CZ, and the ignition temperature was ca. 250 °C over CZ support. In the case of the catalysts with Pd loadings of 0.2, 1.0, and 5.0 wt.%, the total oxidation of propene was achieved under 500 °C. On the other hand, the propene conversion over 0.04Pd/CZ was 70% even at 600 °C, whereas the light off temperature was 200 °C and its activity was higher than that of CZ. The order of catalytic performance (5.0 > 1.0 > 0.2 > 0.04Pd/CZ > CZ) after the oxidation treatment was same with the order after the reduction, as can be seen in Fig. 1(b). The activities of 0.04, 0.2 and 1.0Pd/CZ, however, were improved by the reduction treatment, and the total oxidation of propene was achieved at 450 °C over 0.04Pd/CZ reduced in hydrogen. This result indicated that the chemical state of palladium species should be significant, as discussed in Section 3.5.

Fig. 2 shows the results of propene oxidation tests under insufficient oxygen condition (O₂: 0.4%). After the oxidation at 600 °C (Fig. 2(a)), the ignition temperatures on Pd/CZ catalysts were around 200 °C, and the light off curves below the conversion of 20% were similar with the curves of Pd/CZ under stoichiometric condition (Fig. 1(a)). In the conversion over 20%, however, the catalytic performances under insufficient oxygen conditions were inferior to the performances of Pd/CZ under stoichiometric condition. The improvements of catalytic activities by the reduction

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