

# High methane combustion activity of PdO/CeO<sub>2</sub>–ZrO<sub>2</sub>–NiO/γ-Al<sub>2</sub>O<sub>3</sub> catalysts



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## ABSTRACT

PdO/CeO<sub>2</sub>–ZrO<sub>2</sub>–NiO/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared for the combustion of methane at moderate temperatures. The introduction of a small amount of NiO within the cubic fluorite CeO<sub>2</sub>–ZrO<sub>2</sub> structure as a promoter effectively enhanced the oxygen release and storage abilities of the catalysts, thereby achieving the complete oxidation of methane. The catalyst with the highest activity for methane combustion was 11.3 mass% PdO/20 mass% Ce<sub>0.64</sub>Zr<sub>0.16</sub>Ni<sub>0.2</sub>O<sub>1.9</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, and efficient combustion was realized at a temperature as low as 300 °C.

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## 1. Introduction

Methane (CH<sub>4</sub>) is the main component of natural gas, which is a significant fuel resource. Natural gas engines are environmentally advantageous due to their relatively low emissions of nitrogen oxides and particulate matter compared to diesel and gasoline engines [1]. However, the major disadvantage associated with methane utilization is unburned methane emissions from natural gas engines. Since methane is a highly potent greenhouse gas, and its global warming effect is approximately 20 times higher than that of CO<sub>2</sub>, it is important to minimize methane emissions into the atmosphere. One effective method to reduce methane emission is the employment of catalytic exhaust converters, in which methane is eliminated by catalytic oxidation at low temperatures. However, among all alkanes, methane is the most difficult to oxidize completely over a catalyst because methane oxidation requires a much higher temperature than the oxidation of other alkanes. Although methane has been catalytically converted into carbon dioxide and steam over noble metal [2–8] and metal oxide catalysts [2,3,9–14], reaction temperatures of over 350 °C were necessary for complete oxidation using these catalysts.

Ceria-based solids exhibit high activities for the catalytic combustion of methane. Ceria (CeO<sub>2</sub>), with a cubic fluorite structure, can

release and uptake oxygen in non-stoichiometric amounts because cerium ion exist in both the trivalent (Ce<sup>3+</sup>) and tetravalent (Ce<sup>4+</sup>) oxidation states. The partial substitution of Ce<sup>4+</sup> with Zr<sup>4+</sup> in the lattice of CeO<sub>2</sub> enhances the oxygen storage capacity, resulting in improved redox properties and increased thermal resistance. These improvements are connected to the abilities to transport oxygen and to cycle easily between the reduced and oxidized states. Taking advantage of this ability to remove and supply oxygen molecules easily to adjust the air/fuel ratio, the binary CeO<sub>2</sub>–ZrO<sub>2</sub> system has been practically used as a promoter in automotive exhaust catalysts to optimize catalyst performance. However, the operating temperature for these systems is relatively high, and lower temperatures are required for methane cleaning.

In our previous studies, we found that the introduction of bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) into the CeO<sub>2</sub>–ZrO<sub>2</sub> lattice effectively enhanced the oxygen release and storage properties of CeO<sub>2</sub>–ZrO<sub>2</sub> [15–17] because the oxide ion vacancy formed by the introduction of low-valent Bi<sup>3+</sup> ions (compared to Ce<sup>4+</sup> and Zr<sup>4+</sup>) facilitated the supply of oxide ions. Furthermore, cubic fluorite-type Ce<sub>0.64</sub>Zr<sub>0.16</sub>Bi<sub>0.20</sub>O<sub>1.8</sub> (CZB) was loaded on a high-surface-area γ-Al<sub>2</sub>O<sub>3</sub> support, and the Ce<sub>0.64</sub>Zr<sub>0.16</sub>Bi<sub>0.20</sub>O<sub>1.8</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (CZB/Al<sub>2</sub>O<sub>3</sub>) solid exhibited remarkable low-temperature reduction behavior below 100 °C [18,19]. To develop novel catalysts that can completely oxidize methane at moderate temperatures, palladium-supported Ce<sub>0.64</sub>Zr<sub>0.16</sub>Bi<sub>0.20</sub>O<sub>1.8</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (PdO/CZB/Al<sub>2</sub>O<sub>3</sub>) catalysts were prepared. Consequently, we demonstrated that the PdO/CZB/Al<sub>2</sub>O<sub>3</sub> catalysts can completely oxidize methane at temperatures as low as 320 °C, which is ca. 30 °C lower than the temperature required for methane oxidation with the PdO/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

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(PdO/CZ/Al<sub>2</sub>O<sub>3</sub>) catalyst (350 °C) [20]. Note that Zhou et al. also reported the methane activities of catalysts formed by the introduction of rare earths (La, Pr, Nd, Sm, and Y) [21,22], transition metals (Cr, Mn, Fe, Co, and Ni) [23], Mg, and alkaline earth metals (Ca, Sr, and Ba) [24,25] into PdO/CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. However, their ceria-based promoters were not single-phase but mixtures of cubic and tetragonal phases due to the excess Zr concentrations (Zr/Ce = 4); therefore, the temperatures required for complete methane oxidation were over 400 °C [23].

To develop advanced catalysts, we focused on nickel oxide (NiO) as a dopant of CeO<sub>2</sub>-ZrO<sub>2</sub> promoter to facilitate methane oxidation. We chose NiO because the introduction of divalent Ni<sup>2+</sup> ions into tetravalent Ce<sup>4+</sup> and Zr<sup>4+</sup> sites is expected to form oxide anion vacancies for oxide ion migration. Furthermore, the valence change of Ni<sup>2+</sup>, which is possibility to change to Ni<sup>3+</sup>, should improve the redox properties. Herein, we introduced a small amount of NiO as a substitute for Bi<sub>2</sub>O<sub>3</sub> into Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and investigated the catalytic activity for methane oxidation of 11.3 mass% PdO/20 mass% Ce<sub>0.8(1-x)</sub>Zr<sub>0.2(1-x)</sub>Ni<sub>x</sub>O<sub>2.0</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, denoted by PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub>.

## 2. Experimental

The Ce<sub>0.8(1-x)</sub>Zr<sub>0.2(1-x)</sub>Ni<sub>x</sub>O<sub>2.0</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (CZNi(x)/Al<sub>2</sub>O<sub>3</sub>) samples were synthesized using the conventional wet coprecipitation method. Before preparation, commercial γ-Al<sub>2</sub>O<sub>3</sub> (AA-300, DK Fine) powder was ground in an agate mortar and then mechanically pulverized by a ball-milling apparatus (Pulverisette 7, FRITSCHE GmbH) at a rotation speed of 300 rpm for 2 h. Aqueous solutions of 1.0 mol L<sup>-1</sup> Ce(NO<sub>3</sub>)<sub>3</sub>, 0.1 mol L<sup>-1</sup> Zr(NO<sub>3</sub>)<sub>2</sub>, and 0.1 mol L<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub> were mixed with 15 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub> in stoichiometric amounts. The solution was then impregnated on the γ-Al<sub>2</sub>O<sub>3</sub> powder, with the CZNi(x)/Al<sub>2</sub>O<sub>3</sub> content adjusted to 20 mass%. The mixture was stirred at room temperature for 30 min. The pH of the aqueous mixture was adjusted to 11 by the dropwise addition of aqueous ammonia (6%). After stirring for 12 h at room temperature, the resulting precipitate was collected by filtration, washed several times with deionized water, and then dried at 80 °C for 6 h. Subsequently, these samples were heated at 500 °C for 1 h under ambient air atmosphere. Supported palladium catalysts (PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub>) were prepared by the impregnation of Pd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> solution (Tanaka Precious Metals) into the CZNi(x)/Al<sub>2</sub>O<sub>3</sub> samples. Subsequently, the catalysts were dried at 80 °C for 12 h and then calcined at 400 °C for 4 h. The amounts of PdO and CZNi(0.2) were adjusted in the range of 8.0–13.6 and 16–25 mass%, respectively.

X-ray fluorescence (XRF; ZSX100e, Rigaku) was used to determine the compositions of the catalysts. X-ray powder diffraction (XRD; SmartLab, Rigaku) patterns were measured with Cu Kα radiation (40 kV, 30 mA) in the 2θ range from 10° to 70°. Brunauer, Emmett, and Teller (BET) specific surface area was measured by nitrogen adsorption at -196 °C (TriStar 3000, Shimadzu). Temperature programmed reduction (TPR) measurement was carried out under a flow of 5 vol% H<sub>2</sub>-Ar (50 mL min<sup>-1</sup>) at a heating rate of 5 °C min<sup>-1</sup> (BELCAT-B, BEL JAPAN). Following the TPR experiment, the oxygen storage capacity (OSC) was measured using the pulse-injection method at 427 °C.

The methane oxidation activity was tested in a conventional fixed-bed flow reactor consisting of a quartz glass tube (diameter = 10 mm) with a feed gas mixture of CH<sub>4</sub> (1.0 vol%) and air (balance) fed at a rate of 33.4 mL min<sup>-1</sup> over 0.1 g of catalyst. The space velocity was 20,000 h<sup>-1</sup>. The catalysts were pre-treated at 200 °C for 2 h under Ar flow (20 mL min<sup>-1</sup>) prior to the catalytic activity tests. The catalytic activity was evaluated in terms of methane conversion. The gas composition after the reaction was analyzed using gas chromatography with thermal conductivity detection (GC-8AIT, Shimadzu).

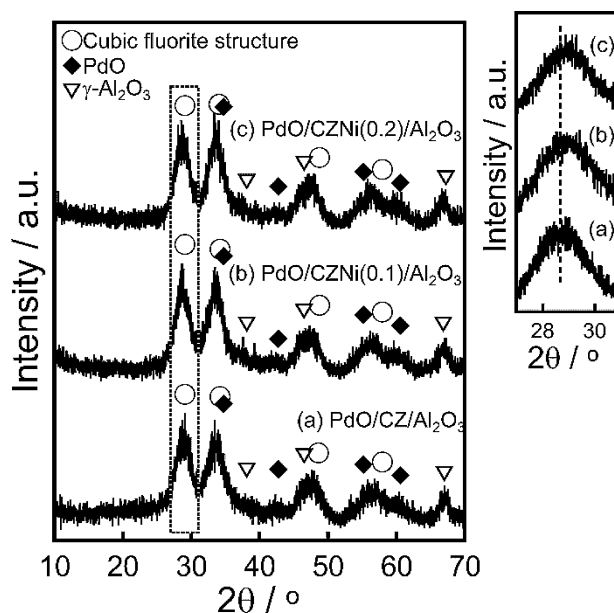


Fig. 1. XRD patterns of the PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub> catalysts.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was performed with an in situ FTIR spectrophotometer (FT/IR-6100, JASCO). An environmental DRIFTS chamber was equipped with CaF<sub>2</sub> windows, allowing thermal and water resistance. All spectra were obtained after averaging 100 scans with a resolution of 4 cm<sup>-1</sup>. The flowing gas was changed according to the following sequence: air, N<sub>2</sub>, 10 vol% CH<sub>4</sub>-N<sub>2</sub>, 10 vol% CH<sub>4</sub>-air, and air with 33.4 mL min<sup>-1</sup>. As a reference, KBr was measured in air at 400 °C.

## 3. Results and discussion

The XRD patterns of the PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Fig. 1. The patterns clearly indicated the formation of a crystalline phase indexed by a cubic fluorite single phase (PdO) and a γ-Al<sub>2</sub>O<sub>3</sub> phase; no crystalline impurities or metallic palladium was observed. The inset shows an enlarged view of the pattern in the 2θ range from 26° to 32°. The diffraction peaks assigned to the cubic fluorite phase shifted slightly to higher angles with increasing Ni<sup>2+</sup> content (x), suggesting that the Ce<sup>4+</sup> (ionic radius = 0.097 nm) [26] and Zr<sup>4+</sup> (ionic radius = 0.084 nm) [26] in CeO<sub>2</sub>-ZrO<sub>2</sub> were partially substituted with Ni<sup>2+</sup> (ionic radius = 0.069 nm) [26] to form a solid solution.

The compositions and BET specific surface areas of the PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub> catalysts are presented in Table 1. The compositions determined by XRF analysis were in good agreement with the stoichiometric values within the experimental error. The BET specific surface areas of the PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub> (x = 0.1, 0.2) catalysts were smaller than that of PdO/CZ/Al<sub>2</sub>O<sub>3</sub> and decreased with increasing Ni content, likely due to the lower melting point of NiO

Table 1  
Measured composition and BET surface areas of the PdO/CZNi(x)/Al<sub>2</sub>O<sub>3</sub> catalysts.

Catalyst	Measured composition	BET surface area/m <sup>2</sup> g <sup>-1</sup>
PdO/CZNi(0.2)/Al <sub>2</sub> O <sub>3</sub>	10.7 mass% PdO/19 mass% Ce <sub>0.66</sub> Zr <sub>0.16</sub> Ni <sub>0.18</sub> O <sub>1.91</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	175.3
PdO/CZNi(0.1)/Al <sub>2</sub> O <sub>3</sub>	11.6 mass% PdO/20 mass% Ce <sub>0.72</sub> Zr <sub>0.19</sub> Ni <sub>0.09</sub> O <sub>1.95</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	184.8
PdO/CZ/Al <sub>2</sub> O <sub>3</sub>	11.5 mass% PdO/20 mass% Ce <sub>0.79</sub> Zr <sub>0.21</sub> O <sub>2.0</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	219.4

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